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**Charge Density Studies of 3-[(*p*-Nitrophenoxy)methyl]-3-chlorodiazirine
and Monochloropentaaziridinocyclotriphosphazene and
Hydrogen Bonding in π -Arene Systems.**

by

Pradip Kumar Bakshi

Submitted in partial fulfilment of the requirements for the
degree of Doctor of Philosophy

at

Dalhousie University

Halifax, Nova Scotia,

July, 1995

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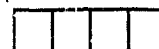
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To my teachers

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Abstract

This report deals with two aspects of x-ray crystallography, (i) structural and electron density determination and (ii) classification and geometry of hydrogen bonding to aromatic π systems.

(i) Structural and electron density determination:

The compound, 3-[(*p*-nitrophenoxy)methyl]-3-chlorodiazirine, $C_8H_6N_3O_3Cl$, was chosen because of its stability in x-ray radiation. The nature of bonding in diazirine ring is also a long standing question. The compound is triclinic, PT, with $a = 6.034(1)$ Å, $b = 8.429(3)$ Å, $c = 9.805(2)$ Å, $\alpha = 107.51(2)^\circ$, $\beta = 96.58(2)^\circ$, $\gamma = 91.21(1)^\circ$, $V = 471(1)$ Å³, $Z = 2$. The diazirine ring skeleton is normal with N = N distance of 1.222(5) Å and N - C - N angle of 49.8(3)°. The deformation density studies show that the diazirine ring in this compound possesses some degree of π -complex character.

Aziridinocyclotriphosphazene compounds are of interest because of their effectiveness as anticancer drugs. Monochloropentaaziridinocyclotriphosphazene, $N_3P_3(az)_5Cl$ is one of the promising examples. The compound $N_3P_3(az)_5Cl$ is triclinic, PT, $a = 8.665(1)$ Å, $b = 14.013(2)$ Å, $c = 7.965(1)$ Å, $\alpha = 90.49(1)^\circ$, $\beta = 113.62(1)^\circ$, $\gamma = 89.92(1)^\circ$, $V = 886.1(2)$ Å³, $Z = 2$. The phosphazene ring is slightly puckered. The P - N bond lengths related to P which has Cl bonded to it, are shorter than the others. Both bow tie I and bow tie II conformational az rings are present in this compound. The electron density studies show that the nature of bonding in the tricy-clophosphazene ring is consistent with the Dewar Island model.

(ii) Classification and geometry of hydrogen bonding to aromatic π system:

To understand the nature and significance of hydrogen bonds of the type $X - H \dots \pi(\text{aromatic})$ ($X = N, O$), crystal structures of nineteen tetraphenylborate (TB) salts of organoammonium cation and $[Li(H_2O)_4]^+$ have been determined. These structures plus a few literature structures of TB salts provide a large variety of $H(X) \dots \pi$ bonds which has been classified as normal, bifurcated (interion, intracation, homodesmic and heterodesmic) and trifurcated. The cation orientation in the TB compound where the H-bond is claimed with respect to that in non-hydrogen bonded compounds is opposite. This demonstrates that the $H(X) \dots \pi$ interaction in TB compounds is a positive tendency rather a passive response to overall packing requirements in the crystal.

Abbreviations and Symbols

$\rho(\mathbf{r})$	Electron density in molecule
$\Delta\rho(\mathbf{r})$	Difference electron density
$\mathbf{r}$	Vector to a point in real space
K	Scale factor
$\mathbf{H}(h_1, h_2, h_3)$	Vector to a point in reciprocal space
$ F_o(\mathbf{H}) $	Observed structure factor amplitude
$ F_c(\mathbf{H}) $	Calculated structure factor amplitude
ρ_c	Core atomic density
ρ_v	Valence density
$Y_{lm}(\theta, \phi)$	Multipolar spherical harmonic functions in real form
κ', κ''	Expansion-contraction parameters
P_c	Core population parameters
P_v	Valence population parameters
P_{lm}	Multipole population parameters
R_1	Slater-type radial functions
N_1	Normalization factor
$\delta\rho(\mathbf{r})$	Deformation electron density
MW	Formula weight
Z	Number of molecules in the unit cell
a, b, c	Unit cell dimensions
α, β, γ	Angles between crystal axes
V	Volume of unit cell

μ	Linear absorption coefficient
d_c	Calculated density
θ	Bragg angle
h,k,l	Miller indices of the reflecting plane
$MoK\alpha, CuK\alpha$	Radiation used
λ	Wavelength of x-radiation
$x/a, y/b, z/c$	Fractional coordinates
U_{iso}	Isotropic temperature factor
U_{eq}	Equivalent temperature factor
U_{ij} 's	Anisotropic temperature factors
$F(000)$	Number of electrons in the unit cell
F_o, F_{obs}	Observed structure amplitude
F_c, F_{calc}	Calculated structure factor
N_{me}	Total number of measured reflections
N_{un}	Number of unique reflections after merging
N_{ob}, d	Number of reflections considered observed
N_v, p	Number of parameters refined
R	R -factor
R_w	Weighted R -value
R_m	Merging R -value for equivalent reflections
GOF	Goodness of fit parameter
w	Weight in minimised function
t	Temperature ($^{\circ}C$) of measurement
lt	Low temperature

rt	Room temperature
HO	High order
TLS	Translation/Libration/Screw
L ₁ , L ₂ , L ₃	Three principal librational axes
rms	Root mean square
ν	Vibrational frequency (stretching)
δ	Vibrational frequency (bending)
az	Aziridinyl= -N(CH ₂) ₂
Me	Methyl= -CH ₃
Et	Ethyl= -CH ₂ CH ₃
Pr	Propyl
Im	Iminium
TB	Tetraphenylborate anion

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1. Introduction

1.1. General Introduction

The contribution of single-crystal x-ray diffraction in structural studies is immense. Much of our knowledge of the details of molecular structure, structure-activity relationships, intermolecular interactions, hydrogen bonding and even the nature of chemical bonding has been drawn from the many structures that have been determined by x-ray diffraction. Since x-rays are scattered by electrons, an experimental electron density distribution can be calculated using high quality x-ray intensity data. This property is used to solve some of the fundamental problems of chemical bonding¹⁻³. Information about net atomic charges, dipole moments, electric field gradients, electrostatic potentials, intermolecular interaction energies, etc. can also be obtained from x-ray diffraction results^{4,5}.

The goal of my project was to acquire a thorough competence in x-ray crystallography. However, in this report, I deal with two main areas of interest, (i) electron density studies and (ii) classification and geometry of hydrogen bonding to aromatic π systems.

i) Electron density studies:

The structure and electron density of a rare crystalline diazine compound, 3-[(*p*-nitrophenoxy)methyl]-3-chlorodiazirine, $C_8H_5N_3O_3Cl$, have been determined. Diazirine compounds are highly temperature and light sensitive, and easily lose nitrogen by thermal and photochemical activation. These properties make this compound difficult to handle and to study by x-ray crystallography even at low temperature. This is evident

in the literature. Besides the structural and electron density studies of $C_8H_6N_3O_3Cl^{6,7}$, only two structural reports of "all light elements" diazirine compounds^{8,9} have been found. The studied compound, $C_8H_6N_3O_3Cl$, was stable in the x-ray beam at $-65^\circ C$ and decayed only 7.2%, during the data collection up to $\theta = 45^\circ$. The bond lengths and angles inside the ring are in good agreement with the previously reported values. The electron density calculations by both $X - X_{BO}$ and multiple refinement programs, indicate that the diazirine ring consists of bent bonds with somewhat π -complex character (Fig. 1). The drainage of electron density occurs from $N = N$ and $N - C$ bonds to the apical C atom which is bonded to chlorine.

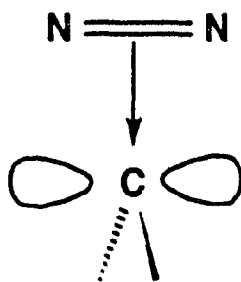


Fig. 1. Possible π -complex interaction between $N = N$ and the apical C atom of the diazirine ring.

The significant contribution of aziridinotricyclophosphazene compounds as drugs in treatment of many animal diseases is now well known^{10,11}. Monochloropentaaziridinotricyclophosphazene, $P_3N_3(az)_5Cl$, is one of the most promising compounds. In order to establish the relation between its structure and its pharmacological activity, the structure of $P_3N_3(az)_5Cl$ has been determined. Structural investigation indicates that this compound has both conformations "bow tie I" and "bow tie II" aziridinyl rings which is

the pre-requirement for its biological activity¹². The phosphazene ring is slightly puckered and the P - N bonds, related to the phosphorus which is bonded to chlorine, are significantly shorter. The deformation density studies of the phosphazene ring support the Dewar island model (Fig. 2) and indicate that conjugation beyond the three-centre islands is of minor importance. The electron density distribution inside the

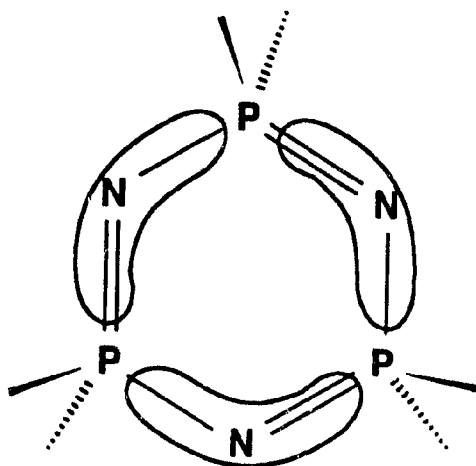


Fig. 2. Dewar island model of the cyclotriphosphazene ring.

P_3N_3 ring of this compound is less than that of hexaaziridinocyclotriphosphazene benzene clathrate¹³. The general appearance of the electron density maps of the five aziridinyl rings are similar. The fact that the electron density contours are outside the internuclear axes reveals the characteristics of a strain bent bonds framework for the three-membered aziridinyl rings.

ii) Hydrogen bonding to aromatic π system:

The first demonstration of the existence of an X - H... π (aromatic) bond in a crystal appeared in the literature in 1957¹⁴. It was a combined calorimetric and x-ray

study of NH_4BPh_4 . The very weak $\text{N} - \text{H} \cdots \pi$ bond in this crystal is associated with an estimated activation energy for NH_4^+ reorientation of only about 0.5 kcal/mole. Since then the reports on this field appearing in the literature are few and unsystematic. That has given us the opportunity to shed light on the nature of $\text{X} - \text{H} \cdots \pi$ interactions.

In order to investigate $\text{X} - \text{H} \cdots \pi$ ($\text{X} = \text{N}, \text{O}$) bonds, 18 organoammonium tetraphenylborate (TB) compounds have been prepared and structurally characterised by x-ray crystallography. The chosen cations are $\text{MeRC}=\text{N}^+\text{HR}^+$, quinuclidinium, dabcoH(1+), N-triphenylboro-N'-Me-piperazinium, dimethylammonium, diisopropylammonium, azoniacycloheptane, 2,2'-bipyridinium, 1,10-phenanthroline, 1-adamantammonium, 1,3-adamantanediammonium, Ph_2I^+ and 1-azoniapropellane. The cations containing H(N) atom(s) form hydrogen bonds with aromatic π systems. These bonds can be normal, branched (bifurcated or trifurcated, homodesmic or heterodesmic), intracation or interion.

An example of an $\text{O} - \text{H} \cdots \pi$ system, of particular interest to the coordination chemist, is $[\text{Li}(\text{H}_2\text{O})_4]\text{BPh}_4$ which has also been reported. In this compound the Li cation is coordinated by no fewer than eight $\text{O} - \text{H} \cdots \text{phenyl}$ bonds and appear to be the first reported case of such an exhaustive $\text{O} - \text{H} \cdots \pi(\text{aromatic})$ coordination.

In an ordinary $\text{X} - \text{H} \cdots \text{Y}$ hydrogen bond to an atom acceptor, Y, the hydrogen bond geometry can be described properly in terms of three internuclear distances, $\text{X} - \text{H}$, $\text{H} \cdots \text{Y}$ and $\text{X} \cdots \text{Y}$. On the other hand, in the case of an $\text{X} - \text{H} \cdots \pi$ hydrogen bond to an aromatic π system (specifically, to a phenyl group) there is no termination point, and therefore, the distances corresponding to $\text{H} \cdots \text{Y}$ and $\text{X} \cdots \text{Y}$ are ill-defined. Thus, only a qualitative estimation of $\text{X} - \text{H} \cdots \pi$ geometry can be achieved, either by considering the centre of the phenyl ring as the reference point or with respect to the shortest

H...C(phenyl) distance. The same argument has been applied in this study. The distances and angles found for normal and branched X - H... π bonds in organoammonium TB salts are:

	normal	branched
d(H...C) (Å)	2.6(1) - 3.5(8)	3.0(3) - 4.3(5)
d(H... π_c) (Å)	2.1 - 3.3	2.3 - 4.1
d(X...C) (Å)	3.3(1) - 4.1(9)	3.4(1) - 4.5(7)
d(X... π_c) (Å)	3.0 - 4.0	3.1 - 4.4
(X - H... π_c)(°)	124 - 177	80 - 164

A comparison of the orientation of a cation containing H(N), with respect to a similar cation orientation where H(N) has been replaced by either an alkyl group or a lone pair(s), demonstrates that the formation of an X - H... π interaction is a positive tendency (reinforced by ion charge interaction) rather than a passive response to overall packing requirements in the crystal. The X...B distance(s) in the compounds where X - H... π bonding is claimed is significantly shorter than that in non-hydrogen bonded compounds.

The ir spectra of several samples have been recorded; in some cases, with a view to identifying those compounds (e.g. iminium salts) and in others, to clarify the X - H... π geometry present.

Electron density maps of [DabcoH]TB have also been calculated. The maps show that the N - H vector points towards the electron cloud of the C - C - C region of the phenyl ring closest to the B atom as shown schematically in Fig. 3. This is not

unexpected, since -BPh_3^- is a powerful σ -electron releasing group¹⁵.

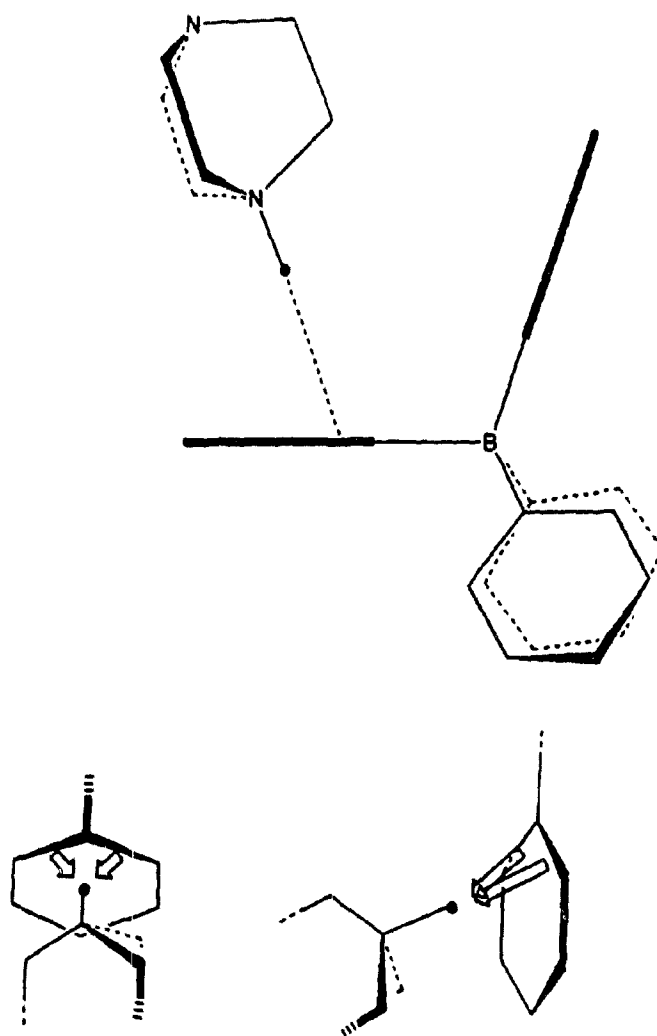


Fig. 3. A schematic representation of the interior $\text{H(N)}\dots\pi$ interaction in DaHTB.

1.2. X-ray Analysis in a Nutshell

When x-rays pass through the matter they are scattered by their interaction with extra-nuclear electrons. The scattering can occur in two ways: (1) the coherent scattering - if the electrons radiate x-rays of the same frequency as the incident beam and, (2) the incoherent scattering - if the electrons scatter x-rays of longer wavelength than the incident beam. Since both the coherent and incoherent scattering occur simultaneously and then according to the Thomson formula,

$$I_e = I_{coh} + I_{incoh} \quad (1)$$

where I_e = the total intensity scattered by the electron, I_{coh} = the intensity scattered by the coherent process and I_{incoh} = the intensity scattered by the incoherent process. If f is the coherent scattering factor of the electron, then,

$$I_{coh} = I_e f^2 \quad (2)$$

$$\text{therefore, } I_{incoh} = I_e(1 - f^2) \quad (3)$$

The scattering factor f is always equal to unity for $\theta = 0$; it decreases with an increase in θ , the decrease being more rapid if the electron cloud is more extended. Inversely, incoherent scattering is always zero for $\theta = 0$. It increases with θ and, for small angles, is proportional to $\sin^2\theta$. In most x-ray diffraction studies of crystals incoherent scattering is not taken into account explicitly because it simply contributes to the background intensity.

The intensity of coherent scattering is determined by summing the scattering amplitudes of all the electrons and then squaring the sum. Thus, for an atom of Z electrons,

$$I_{coe} = \left(\sum_{i=1}^Z f_i \right)^2 I_e \quad (4)$$

where f_i , the scattering factor for the i electron. Again, if the number of electrons per unit volume in a small element of volume (dv) at r is $\rho(r)$ and its phase with respect to origin is $2\pi\mathbf{H}\cdot\mathbf{r}$, then the total scattering,

$$f_i = \int \rho_i(r) \exp(-2\pi i \mathbf{H} \cdot \mathbf{r}) dv \quad (5)$$

The quantity f is called the atomic scattering factor. Its maximum value for a given atom i is Z_i , the atomic number of the i th atomic species, and decreases with increasing $\sin\theta/\lambda$. Radiation scattered at high values of $\sin\theta/\lambda$ is mainly due to electrons of inner shells of the electron cloud (core) whereas scattering of valence electrons is efficient only at low $\sin\theta/\lambda$ values. Thus, f is the sum of core and valence electron scattering:

$$f = f_{\text{core}} + f_{\text{valence}} \quad (6)$$

The atomic scattering factor depends upon the nature as well as the thermal vibrations of the atom. The effect of thermal vibration on f can be expressed by the following equation:

$$f = f_0 e^{-B(\sin^2\theta)/\lambda^2} \quad (7)$$

where B is related to the mean-square amplitude ($\bar{u}^2$) of atomic vibration by

$$B = 8\pi^2 \bar{u}^2 \quad (8)$$

For a group of atoms in the unit cell, the equation (5) becomes

$$F(\mathbf{H}) = \sum f_i(\mathbf{H}) \exp(-2\pi i \mathbf{H} \cdot \mathbf{r}_i) \quad (9)$$

$F(\mathbf{H})$ is called the structure factor - the combined scattering of x-rays for all atoms in the unit cell. The structure factor can also be expressed as an ordinary complex quantity,

$$F(\mathbf{H}) = A(\mathbf{H}) + iB(\mathbf{H}) \quad (10)$$

where,

$$A(\mathbf{H}) = \sum f_i(\mathbf{H}) \cos 2\pi \mathbf{H} \cdot \mathbf{r}_i$$

$$B(\mathbf{H}) = \sum f_i(\mathbf{H}) \sin 2\pi \mathbf{H} \cdot \mathbf{r}_i$$

The structure factor can also be considered as the sum of the wavelets scattered from all the infinitesimal elements of the electron density in a unit cell. Since the wavelet scattered by each element is

$$\rho(\mathbf{r})\exp[2\pi i(\mathbf{H}.\mathbf{r})]dv \quad (11)$$

then
$$F(\mathbf{H}) = \int_V \rho(\mathbf{r})\exp[2\pi i(\mathbf{H}.\mathbf{r})]dv \quad (12)$$

The expression for the electron density in direct space in terms of the structure factors in reciprocal space is

$$\rho(\mathbf{r}) = (1/V)\sum_{\mathbf{H}} F(\mathbf{H})\exp[2\pi i(\mathbf{H}.\mathbf{r})] \quad (13)$$

Comparison of the expression for the electron density, equation (13), with that for the structure factor, equation (12), indicates that the electron density is the Fourier transform of the structure factors, while the structure factors are in turn the Fourier transform of the electron density.

The electron density in the crystal is periodic. Therefore, it can be represented as a three dimensional Fourier series,

$$\rho(\mathbf{r}) = (1/V)\sum_{\mathbf{H}} |F(\mathbf{H})| \exp[2\pi i(\mathbf{H}.\mathbf{r}) - i\alpha(\mathbf{H})] \quad (14)$$

where V is the volume of the unit cell, $|F(\mathbf{H})|$ is the amplitude of the diffracted beam in the directions of the scattering vectors $\mathbf{H}(h_1, h_2, h_3)$, and $\alpha(\mathbf{H})$ is the corresponding phase angle. To construct the electron density, both the amplitude as well as the phase angle of all the diffraction beams are necessary. However, x-ray diffraction provides only the amplitude,

$$|F(\mathbf{H})| = (K I(\mathbf{H})/L_p)^{1/2} \quad (15)$$

where, K is a constant, depends on crystal size, beam intensity, and a number of fundamental constants; $I(\mathbf{H})$, the diffracted intensity in the direction of scattering vectors;

L, the Lorentz factor; and, p, the polarization factor.

For the corresponding phase angle, we need to know whether each Fourier wave starts at the origin with a maximum ($\alpha = 0$) or a minimum ($\alpha = \pi$) or some intermediate value. The absence of this phase information is called the phase problem and can be solved by using either the Patterson method or the "Direct" method^{16,17}. Once the amplitude and the phase angle of the diffraction wave are known, the electron-density $\rho(\mathbf{r})$ at each point $\mathbf{r}(r_1, r_2, r_3)$ of the unit cell can be calculated by the summation of the Fourier series in equation (14). Since the nuclear positions are located at the highest electron-density peaks, the atomic arrangement can be read off directly from $\rho(\mathbf{r})$. Once the approximate positions and identities of all the atoms in the asymmetric unit are known, the amplitude and phases of the structure factors can readily be calculated. These calculated amplitudes $|F_c|$, may be compared with the observed amplitude $|F_o|$. A good agreement between the $|F_c|$ and $|F_o|$ indicates a correct model. The most common parameter used to express this agreement is the R index (also called agreement index or residual)

$$R = \sum[|F_o| - K|F_c|] / \sum|F_o| = \sum|\Delta F| / \sum|F_o| \quad (16)$$

where K is a scale factor bringing $|F_c|$ on the same scale of $|F_o|$, obtained as

$K = \sum \Delta F_o / \sum |F_o|$. This is the basic way that the crystal structures are determined.

To solve the fundamental problem of the nature of the chemical bond, the accurate determination of charge density distribution in the compound is very important. As we know, the changes in electron density distribution due to the formation of molecules are small in magnitude compared with the total electron density. Thus a more sensitive function must be introduced to obtain chemical information from the observed electron density. This function can be obtained by subtracting all the unperturbed

spherical atom density from the total density,

$$\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \sum \rho_{i, \text{sph}}(\mathbf{r}-\mathbf{r}_i) \quad (17)$$

where $\rho(\mathbf{r})$ is the total electron density at a point $\mathbf{r}$ in space, and $\rho_{i, \text{sph}}$ is the unperturbed, spherically averaged atom densities located at the same position, $\mathbf{r}_i$ in space. The sum in equation (5) gives an imaginary electron density constructed by superposition of free atoms placed at their molecular geometry and called pro-molecule density. Thus the difference $\Delta\rho(\mathbf{r})$ between the actual density and the pro-molecule density is known as the "deformation density", which represents the deformation density from spherical atom density upon the formation of a molecule.

The deformation density $\Delta\rho$ can be conveniently calculated from a function of observed and calculated structure amplitudes:

$$\Delta\rho(\mathbf{r}) = (1/V) \sum_{\mathbf{H}} [|F_o(\mathbf{H})|/k - |F_c(\mathbf{H})|] \exp(2\pi i \mathbf{H} \cdot \mathbf{r}) \quad (18)$$

where, $\mathbf{r}$ is the vector determining the point in the unit cell, V is the volume of the unit cell, k is the scale factor, $|F_o(\mathbf{H})|$ is the amplitude of the diffracted beam in the direction of the scattering vector $\mathbf{H}(h_1, h_2, h_3)$ and $|F_c(\mathbf{H})|$ is the calculated structure amplitude.

The deformation density, therefore, corresponds to a point by point subtraction of an F_o Fourier map from an F_o map calculated with the same phases. This map shows peaks everywhere where the F_o model fails to provide the electron density implied by the F_o data and holes (negative electron density) where it provides too much. Hence, through the direct observation of the difference electron density maps, the bonds and their chemical significance in molecules can be studied.

Since $\Delta\rho(\mathbf{r})$ is only a very small fraction (about 3-6%) of $\rho(\mathbf{r})$ in the region of the

atoms, it is very susceptible to experimental error in the x-ray measurements and to inadequacies in the model. Experimental error may be divided into statistical and systematic errors.

One of the important statistical errors is the errors of observed structure amplitude $\sigma(\rho_{\text{obs}})$, caused when the measurement of symmetry related reflections are not considered. These errors are generally estimated based on the discrepancies among the symmetry-related reflections as follows:

$$\rho^2(|F|) = \rho_{\text{count, statistics}}^2 + (\alpha \cdot |F|)^2 \quad (19)$$

where the first term represents the error due to counting statistics. The discrepancy parameter of α varies from 0.010-0.015 in accurate diffraction measurements.

Other statistical errors are related to the accuracy of the least-squares refinement, and estimated from the errors of scale and atomic parameters calculated in the refinement. These errors in the positional and thermal parameters employed to obtain ρ_{calc} and the scale factor have a serious influence within about 0.3 Å of the nuclear positions¹⁸.

Deformation density also suffers from the systematic errors in the positions of the atoms. A conventional least-squares refinement rarely gives the true atomic parameters because the valence electron densities around the atomic nuclei are generally deformed upon molecular formation, and therefore refinement of this aspherical density within a spherical atom model gives errors in positions and thermal parameters. Unbiased parameters can be obtained from a single crystal neutron diffraction experiment^{19,20} or with the high-order refinement based on high angle x-ray data only^{20,21}, making the reasonable approximation that valence electron density is diffused and contributes to the low-angle reflection data only. Other crystallographic

sources of systematic errors are absorption of x-rays in the crystal, extinction effect, multiple reflections, and thermal diffuse scattering²².

Absorption irregularly reduces the observed intensities of diffraction, but in all but a special crystal by different factors for different reflections. The effect is greatest at low Bragg angle, so that there is a systematic error even for a spherical crystal. Uncorrected significant absorption causes variations in thermal parameters, in an attempt to compensate for the effect.

Extinction also attenuates the observed intensities, and it is most severe for low-angle, strong reflections. It reduces overall precision and systematically affects thermal parameters.

Multiple reflections occur when a single crystal is so oriented that two or more reciprocal-lattice points lie on the sphere of reflection at the same time. This error changes the intensities of the diffracted beam significantly.

Thermal diffuse scattering, produced as a result of cooperative lattice vibrations, has the effect of increasing observed intensities. The effect, however, increases with $\sin^2\theta$, so the net effect is to reduce thermal parameters from their true values.

All these errors can be avoided by applying appropriate corrections and experimental techniques e.g. low temperature measurement and measurement of symmetry-related reflections²³. In particular, low temperature measurements are essential for the following reasons:

- 1) a reduction in temperature will reduce the anharmonicity of the external molecular vibrations so that introduction of a complex model in the refinement can be avoided.

- 2) the effect of thermal diffuse scattering decreases relative to the intensity of

the Bragg reflections when the temperature is lowered, thus another source of error in the temperature parameters is reduced.

3) reduction of the thermal vibration at the lower temperature greatly increases the intensity of the high order reflections, which improves the atomic resolution.

Using x-ray diffraction data, the experimental deformation density maps can be computed in two ways:

The $X - X_{\text{HO}}$ method^{24,25}, an empirical method of separating the diffraction effects of the core and valence electrons. The data set is divided into 'high-order' and 'low-order' sets on the basis of a selected $\sin\theta/\lambda$ value. Usually $\sin\theta/\lambda > 0.7 \text{ \AA}^{-1}$ for high

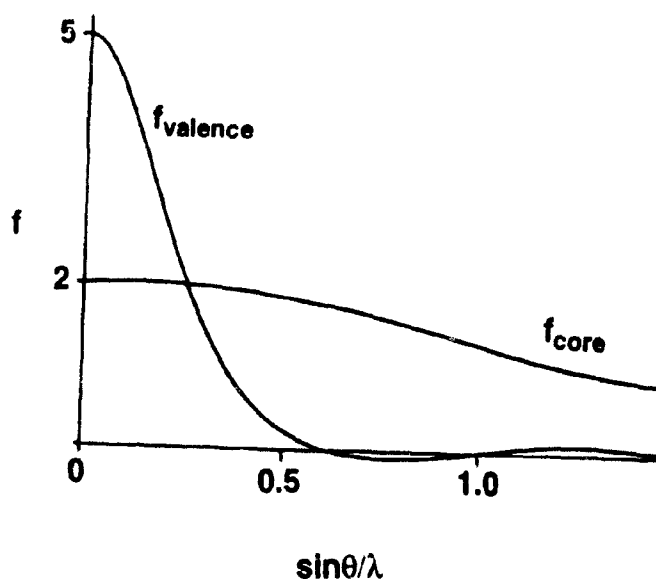


Fig. 4. Variation of the core and valence scattering factors of N atom with $\sin\theta/\lambda$.

order data. The high order data are relatively unbiased by the valence electrons and are derived essentially from the diffraction by the core electrons of the atoms (Fig. 4). Thus the positional and thermal parameters obtained from the high order refinement

give accurate positions of the atomic nuclei and are insensitive to chemical bonding. The difference Fourier map calculated using the high-order positional and thermal parameters with low-angle data represents the difference between the experimental (F_o) and high-order calculated structure factors (F_c).

However, the deformation density calculated by X - X_{HO} method usually contains random noise, partly because of some statistical and systematic errors and partly because of using the scattering factors of neutral, spherical atoms (the model used in conventional refinement of x-ray data). In order to include parameters that describe the distortions of the atomic electron distribution as a result of chemical bonding and the crystalline environment, an expanded refinement program has been developed. This is based on the concept of rigid pseudoatom model^{26,27}. In this model, the molecular charge density $\rho(r)$ in the crystal is described by a sum of rigid pseudoatom densities, where each pseudoatom is centred on an atomic nucleus. Each pseudoatom has an invariant core, usually consisting of a neutral spherical Hartree-Fock atomic density, just as in conventional structure analysis. In addition, it has a series of nuclear-centred electron density terms, 'electron population parameters', each with an adjustable weight. These terms are intended to model the effect of the molecular and crystal environment, whereby the pseudoatom may become aspherical and carry a net charge.

The idea of pseudoatom model was further improved by Hansen and Copens²⁸, by introducing the description of the distorted atom (pseudoatom) density in terms of atom-centred multipole expansions, in the form:

$$\rho_{\text{pseudoatom}}(r) = \rho_{\text{core}}(r) + \sum_{lm} P_{lm} R_l y_{lm}(\theta, \phi) \quad (20)$$

where the P_{lm} are refinable parameters, the R_l are radial functions, and the $y_{lm}(\theta, \phi)$ are

the spherical harmonic angular functions in real form. They incorporated the expansion-contraction parameter kappa which modifies the isolated-atom valence shell density and allows for the contraction of positively and expansion of negatively charged atoms in agreement with theoretical concepts. In a multipolar atomic density model used in MOLLY²⁹, electron densities at each atom are described by

$$\rho(r) = P_c \rho_c(r) + \kappa' P_v \rho_v(\kappa' r) + \sum_{l=0}^3 \sum_{m=-l}^{+l} \{ \kappa''^3 P_{lm} R_l(\kappa'' r) y_{lm}(\theta, \phi) \} \quad (21)$$

where ρ_c and ρ_v are the spherically-averaged Hartree-Fock atomic core and valence densities, with the ρ_v normalized to one electron; the $y_{lm}(\theta, \phi)$ are the multipolar spherical harmonic angular functions in real form; κ' and κ'' are expansion-contraction parameters, which can be refined together with the population parameters P_v and P_{lm} . Slater-type radial functions $R_l = N_l r^n \exp(-\kappa'' \zeta r)$ are used, in which N_l is a normalization factor, $n = n(l)$ and ζ are parameters. The refinable parameters, in this method, are the population parameters P_c , P_v and expansion-contraction coefficients κ' , κ'' together with the coordinates and temperature factors. In the multipole refinements, the expansion was truncated at the hexadecapole level ($l_{\max} = 4$) for 2nd row atoms, the octapole level ($l_{\max} = 3$) for the 1st row atoms, and at the dipole level ($l_{\max} = 1$) for the hydrogen atoms. Thus the electron density distribution in this model, is described in terms of a small number of analytical functions rather than a large grid of points. As a result, the deformation density maps obtained from multiple refinement program are effectively free from the random noise of the experiment. Obviously, this procedure is relatively model dependent compared with a spherical least-square refinement. The success of the fitting procedure is usually checked by the residual map, which contains all features not

accounted for in the multipole model. For a correct model and good data it should be a flat and featureless map.

The parameters obtain from multiple refinement can also be used to calculate d-orbital populations, the electrostatic potential, atomic charges and dipole moments etc. In addition to these, this method retains the radial nodes of the atomic shells, allows for full treatment of extinction and can be used for joint x-ray and neutron diffraction data, if neutron data are available.

Thus, using x-ray diffraction techniques the following deformation electron density maps can be calculated using least-squares refinement (spherical and multipole).

Electron Density Maps

Direct Fourier Map

$$\rho(\mathbf{r}) = (1/V) \sum_{\mathbf{H}} F(\mathbf{H}) \exp(-2\pi i \mathbf{H} \cdot \mathbf{r})$$

Difference Fourier Maps

general expression:

$$\Delta\rho(\mathbf{r}) = (1/V) \sum_{\mathbf{H}} [F_1(\mathbf{H}) - F_2(\mathbf{H})] \exp(-2\pi i \mathbf{H} \cdot \mathbf{r})$$

(a) difference map

$$F_1(\mathbf{H}) = F_o(\mathbf{H})$$

$$F_2(\mathbf{H}) = F_c(\mathbf{H}) \text{ (conventional refinement)}$$

(b) $X-X_{\text{HO}}$ deformation map

$$F_1(\mathbf{H}) = F_o(\mathbf{H})$$

$$F_2(\mathbf{H}) = F_{c, \text{sph}}(\mathbf{H}) \text{ (parameters from HO refinement)}$$

(c) experimental deformation map

$$F_1(\mathbf{H}) = F_o(\mathbf{H})$$

$$F_2(\mathbf{H}) = F_{c, \text{sph}}(\mathbf{H}) \text{ (multipole refinement)}$$

(d) dynamic deformation map

$$F_1(\mathbf{H}) = F_{c, \text{mul}}(\mathbf{H})$$

$$F_2(\mathbf{H}) = F_{c, \text{sph}}(\mathbf{H}) \text{ (multipole refinement)}$$

(e) static deformation map

$$\delta\rho(\mathbf{r}) = \rho_{\text{mul}} - \rho_{\text{sph}}$$

(f) residual map

$$F_1(\mathbf{H}) = F_o(\mathbf{H})$$

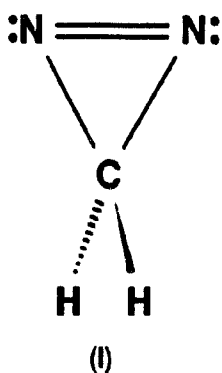
$$F_2(\mathbf{H}) = F_{c, \text{mult}}(\mathbf{H}) \text{ (multipole refinement)}$$

2. Structure Determination and Electron Density Analysis by X-ray Diffraction Methods.

2.1. 3-[(*p*-Nitrophenoxy)methyl]-3-chlorodiazirine

2.1.1. Introduction

A diazirine compound was first prepared by Paulsen³⁰, and Schmitz and Ohme³¹ independently in 1960. Since then, a high level of activity in the study of the chemistry of the diazirines³²⁻³⁵ has been observed because they are important source for the generation of carbenes. Diazirine is a three membered ring compound containing two equivalent nitrogen nuclei. It is a cyclic diazomethane, belonging to a C_{2v} symmetry group. Its structure was first elucidated in 1962 by Pierce and Dobyns³⁶ using the high resolution microwave spectroscopy. Experimentally, the geometric structure for diazirine is in accord with its Lewis diagram (I):



Thermolysis or photolysis of diazirines results in the extrusion of dinitrogen and production of the carbene. The ease of formation of molecular nitrogen makes these compounds highly light and temperature sensitive. They are, in general, either liquids or gases at room temperature and therefore, reports on their isolation and structural

characterization in the solid state even at low temperature are scanty. Apart from the structure of heteromatal complexes, until 1994, there are only three reports on structural studies of all light atom diazirine compounds: 3-(1-naphthylmethyl)-3-chlorodiazirine⁸, 3-[(*p*-nitrophenoxy)methyl]-3-chlorodiazirine^{6, 7} and 3-(trifluoromethyl)-3-phenyldiazirine⁹. The 3-[(*p*-nitrophenoxy)methyl]-3-chlorodiazirine (Fig. 5) is a relatively stable compound and it was available in such a good crystalline form that it was possible to collect the low-temperature (-65°C) x-ray data of a quality suitable for deformation electron density studies.

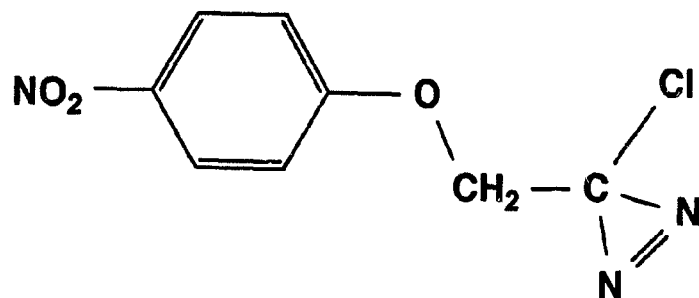


Fig. 5. 3-[(*p*-Nitrophenoxy)methyl]-3-chlorodiazirine molecule.

2.1.2. Bonding in the Diazirine

The nature of bonding in small ring systems has been a topic of major interest for many years. Much of the discussion centres around the cyclopropane ring as it appears in various environments and guises. The replacement of one or two of the -CH_2 groups by heteroatoms produces a wide variety of molecules. Many models have been proposed to discuss the nature of bonding in such three-membered ring compounds, the proper description of which is still the subject of some debate.

Baeyer³⁷ first explains the relative stabilities of cycloalkanes in the light of the concept of molecular strain. This view has been challenged recently by various authors³⁸⁻⁴¹ who have pointed out that the structure and stability properties of cyclopropane and possibly other three-membered rings evade classical strain theory. From the analyses of the physical and chemical properties of small cycloalkanes they came to a conclusion that the delocalisation of σ electrons provides the extra stability to cyclopropane.

The π -complex model, probably the most studied model for compounds of general formula A_2X , developed by Dewar et al.⁴², indicated that two kinds of interactions must be considered in three membered rings. The first interaction is an electron donation from the π orbital of the basal group to a vacant orbital of the apical group. The second interaction is a back donation of electrons from a filled p orbital of X into an antibonding π^* orbital of the basal groups. Three situations are possible depending which interaction is stronger: 1) when donation and back-donation are of comparable magnitude, a stable three membered ring is formed; 2) if donation prevails over back donation, a three-membered ring results which possesses partial π -complex character; and 3) if there is just donation to the apical group, a π -complex is formed.

They also suggested that a change in the electronegativity difference between the apical and basal groups leads to a continuous transition from the classical ring structure (small electronegativity difference) to a π -complex (large electronegativity difference).

Later, Cremer and Kraka⁴³ have approached the problem of distinguishing between a three-membered ring and a π -complex by analyzing electron density distribution. They showed that strong back-donation leads to outwardly curved (convex) bond paths, while relatively weak back-donation yields inwardly curved (concave) bond paths (Fig. 6). Thus, the extent of curvature is a property of each individual bond in a molecule and provides an effective basis for characterizing strained bonds.

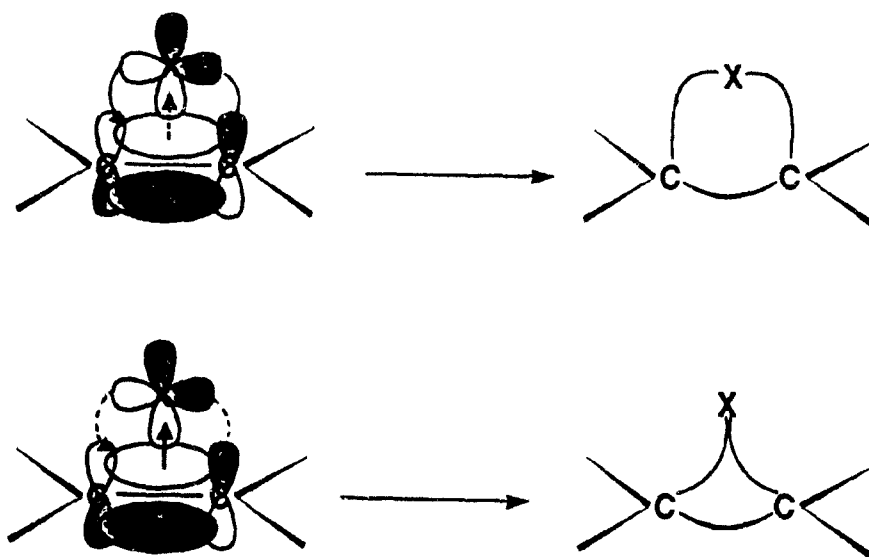


Fig. 6. Donor-acceptor interactions between A_2 and X . The direction of charge transfer is indicated by arrows (dashed arrows indicate reduced charge transfer).

In the context of diazirine compounds, the observations of two authors are noteworthy:

1) From the results of various quantum chemical calculations, N.C. Baird⁴⁴ pointed out

that the σ molecular orbitals of diazine are rather complicated in that they do not correspond closely to the localized picture of normal chemical bonding nor to the Walsh orbitals for cyclopropane-like molecules. Baird himself also performed *ab initio* calculations for various monosubstituted diazirines N_2CHX and compared his result with that of unsubstituted diazine. He noticed that replacement of hydrogen of simple diazine by an electronegative substituent drains electron density from the carbon $2p_\pi$ orbital, which can regain it in part by combining with the bonding $\pi(N = N)$ orbital.

2) Yamabe *et al.*⁴⁵ who analyzed diazine from the viewpoint of transition-metal complex of molecular nitrogen, pointed out that the $N = N$ double bond in diazine is largely weakened in comparison with that of diazomethane. He explained it in terms of back donation and charge transfer interaction between the π and π^* orbital of N_2 unit and the orbitals of the CH_2 group which are of π symmetry. These charge transfer interactions are also contribute to the formation of the C - N bond of diazine.

For a better understanding of the bonding of the diazine ring skeleton it is useful to calculate the deformation electron density maps of both unsubstituted and substituted diazine compounds. So far, only one report on total electron density study of diazine has been found in the literature, where Kochanski and Lehn⁴⁶ used an *ab initio* SCF-LCAO-MO method for their calculation. The electron densities are bent outside the carbon-nitrogen triangle; the angle of bending is 5° for the C - N bonds but is smaller for the $N = N$ double bond (approx. $2 - 3^\circ$). The ring N atoms are σ -acceptors (0.21 e each) and very weak π donors (0.03 e each) and C is π -acceptor but retains its σ -population of the separated atom.

Under these circumstances, since 3-(*p*-nitrophenoxy)methyl-3-chlorodiazirine is stable in x-rays, it was decided to examine the deformation density of this compound.

2.1.3. Structure Determination

2.1.3.1. Experimental and Low Temperature Refinement

A colourless needle crystal having approximate dimensions of 0.20 X 0.20 X 0.35 mm was mounted in a Mark-Rohrchen glass capillary. All measurements were made on a CAD4 diffractometer with graphite monochromator and cooling device. Unit cell dimensions were obtained from a least-squares fit to the setting angles of 25 carefully centred reflections in the range $24.28 < 2\theta < 35.32^\circ$. The space group was determined on the statistical analysis of intensity distribution, and the successful solution and refinement of the structure.

The data were collected at a temperature of -65°C , the temperature at which the crystal was found to be reasonably stable in the x-ray beam. The acquisition of the entire data was done in three different shells; each shell had a 5° overlap with the other. Within the shells, besides the periodic measurement of the intensity of three standard reflections, there were also frequent measurements of sections of the data where a well over-determined data set was obtained. Plotting of the intensities of three standard reflections (1 -3 5, -3 -3 0, and -1 5 1) showed a number of sections where the equipment was not in good thermal equilibrium. A total of 400 reflections were removed from those sections.

The intensity of the three representative reflections which were monitored after every 150 reflections revealed a deterioration of 7.2% during the entire data collection. The data were processed using the routine procedure. The data were corrected for Lorentz and polarization effects. Decay, and absorption corrections were not applied.

The structure was solved by direct methods⁴⁷ followed by the difference electron

density syntheses and was refined by full-matrix least-squares using the observed reflections [$I > 3\sigma(I)$] up to $\theta = 25^\circ$. The non-hydrogen atoms were refined first with isotropic and then with anisotropic temperature factors. All of the hydrogen atoms were placed in their geometrically calculated positions with a C - H distance of 1.08 Å. Their positions were kept fixed and assigned fixed isotropic temperature factors with a value of $1.2 \times B_{eq}$ of the atom to which each was bonded. During refinement, the unit weighting scheme was used and the function minimised was $\sum w(|F_o| - |F_c|)^2$, where w is the weight. Neutral atom scattering factors for nonhydrogen atoms were taken from Cromer and Waber⁴⁸ and scattering factors for hydrogen atoms were taken from Stewart, Davidson and Simpson⁴⁹. Anomalous dispersion effects were included in F_{calc} ⁵⁰; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer⁵¹.

All calculations for structure solution and refinement were performed using TEXSAN⁵². The crystallographic data and the information concerning data collection and the refinement procedure are given in Table 1. The diagrams were drawn using the programme ORTEP⁵³.

2.1.3.2. Results and Discussion

The structure of the compound is shown in Fig. 7 and the atomic positions, bond lengths and bond angles are given in Tables 2 - 4. This compound is essentially a substituted derivative of methylchlorodiazirine. The structural parameters of diazine ring are in excellent agreement with those of the simple substituted diazirines, listed in Table 5. The diazine ring is as usual with N = N bond length of 1.222(5) Å, C - N distances of 1.453(5) and 1.448(5) Å, and N - C - N bond angle of 49.8(3)°. The geometry of the C(1) atom has a distorted tetrahedral configuration with the angles

Cl(1) - C(1) - C(2), Cl(1) - C(1) - N(1), Cl(1) - C(1) - N(2) and N(1) - C(1) - N(2) 117.1(3), 116.2(3), 116.1(3) and 49.8(3)°, respectively. The N(1) - C(1) - N(2) plane forms an angle 88.9° with the Cl(1) - C(1) - C(2) plane. This is consistent with the angles between related planes in other diazirine compounds. The Cl(1) - C(1) - C(2) bond angle is 117.1(3)°, also consistent with the value of the corresponding Cl - C - C bond angle (113.9(7)°, observed in 3-(1-naphthylmethyl)-3-chlorodiazirine⁸.

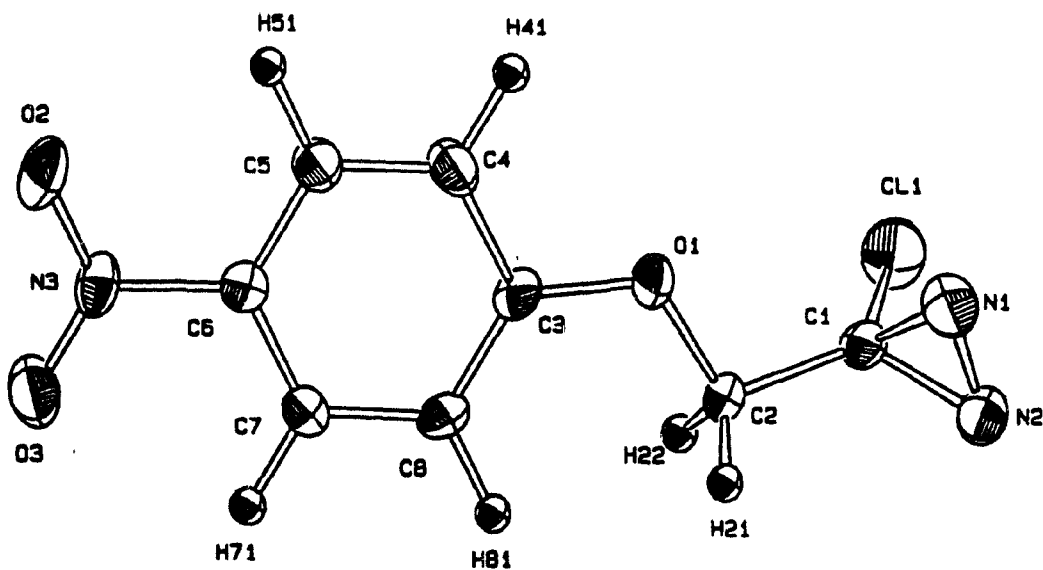


Fig. 7. Molecular structure of 3-[(*p*-nitrophenoxy)methyl]-3-chlorodiazirine. Vibrational ellipsoids are at the 50% probability level.

Table 1. Physical properties and parameters for data collection and refinement of 3-[(*p*-nitrophenoxy)-methyl]-3-chlorodiazirine (It).

Formula	C ₈ H ₆ N ₃ O ₃ Cl
Formula weight	227.61
Crystal System	triclinic
<i>a</i> (Å)	6.034(1)
<i>b</i> (Å)	8.429(3)
<i>c</i> (Å)	9.805(2)
α (°)	107.51(2)
β (°)	96.58(2)
γ (°)	91.21(1)
<i>V</i> (Å ³)	471(1)
Space Group	PT (No. 2)
<i>Z</i>	2
<i>d</i> _{calc} (g/cm ³)	1.602(3)
<i>F</i> ₀₀₀ (e)	232
μ (MoK α) (cm ⁻¹)	3.91
Radiation	MoK α (λ = 0.70926 Å)
Scan Type	ω - 2 θ
2 θ _{max} (°)	90.0°
Reflections:	
total measured	10,414
unique total	7742 (100 <i>R</i> _m = 2.63)
Total observed	2104
Conventional refinement: (unit weighting scheme, θ = 25°)	
unique used ($I > 3\sigma(I)$)	1286
Parameters refined; d/p	136; 9.5
Agreement factors:	
100 <i>R</i>	5.00
100 <i>R</i> _w	5.64
G.O.F.	3.96
Residual e.d. (min, max) (e/Å ³)	-0.30, 0.37
Multipole refinement: (σ weighting scheme, θ = 25°)	
unique used ($I > 2\sigma(I)$)	1454
Agreement factors:	
100 <i>R</i>	3.11
100 <i>R</i> _w	3.30
G.O.F.	2.84
Residual e.d. (min, max) (e/Å ³)	-0.22, 0.23

The benzene ring is para substituted with electron withdrawing groups at both positions. The mean C - C bond distance and C - C - C bond angles are 1.385(8) Å and 120(1)° respectively. The phenyl ring is essentially planar; the maximum deviation from the plane is 0.013(5) Å (C(4)). The plane of the -NO₂ group is inclined at an angle 2.7° to the plane of the phenyl ring. The mean N - O bond length is 1.222(1)Å.

Table 2. Positional parameters and equivalent isotropic temperature factors (Å²) of nonhydrogen atoms in C₈H₆N₃O₃Cl (lt) (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	U _{eq}
Cl(1)	0.0300(2)	0.2859(2)	0.4430(1)	0.0509
N(1)	0.1461(6)	-0.0334(5)	0.3501(4)	0.0422
N(2)	0.2650(6)	0.0239(5)	0.4653(4)	0.0400
C(1)	0.2228(7)	0.1402(5)	0.3839(5)	0.0338
C(2)	0.3971(7)	0.1859(6)	0.3028(5)	0.0367
O(1)	0.2926(5)	0.1511(4)	0.1589(3)	0.0403
C(3)	0.4004(7)	0.2055(5)	0.0645(4)	0.0336
C(4)	0.2749(7)	0.1872(6)	-0.0679(5)	0.0382
C(5)	0.3632(7)	0.2449(6)	-0.1679(4)	0.0379
C(6)	0.5796(7)	0.3159(5)	-0.1356(4)	0.0321
C(7)	0.7080(7)	0.3314(5)	-0.0059(5)	0.0342
C(8)	0.6187(7)	0.2758(5)	0.0969(5)	0.0348
N(3)	0.6721(7)	0.3823(4)	-0.2409(4)	0.0386
O(2)	0.5569(6)	0.3667(5)	-0.3556(4)	0.0546
O(3)	0.8601(6)	0.4501(4)	-0.2089(4)	0.0524

Table 3. Interatomic distances (Å) for C₈H₆N₃O₃Cl (lt) (with e.s.d.'s in parentheses).

Cl(1) - C(1)	1.727(4)	C(3) - C(8)	1.395(6)
N(1) - N(2)	1.222(5)	C(4) - C(5)	1.371(6)
N(1) - C(1)	1.453(5)	C(5) - C(6)	1.386(6)
N(2) - C(1)	1.448(5)	C(6) - C(7)	1.380(6)
C(1) - C(2)	1.499(6)	C(7) - C(8)	1.388(6)
C(2) - O(1)	1.419(5)	C(6) - N(3)	1.468(5)
O(1) - C(3)	1.367(5)	N(3) - O(2)	1.221(5)
C(3) - C(4)	1.390(6)	N(3) - O(3)	1.223(5)

Table 4. Interbond Angles (°) for C₈H₆N₃O₃Cl (It) (with e.s.d.'s in parentheses).

N(2) -N(1) -C(1)	64.9(3)	C(4) -C(3) -C(8)	121.7(4)
N(1) -N(2) -C(1)	65.3(3)	C(3) -C(4) -C(5)	119.7(4)
Cl(1) -C(1) -N(1)	116.2(3)	C(4) -C(5) -C(6)	118.7(4)
Cl(1) -C(1) -N(2)	116.1(3)	C(5) -C(6) -C(7)	122.2(4)
Cl(1) -C(1) -C(2)	117.1(3)	C(6) -C(7) -C(8)	119.5(4)
N(1) -C(1) -N(2)	49.8(3)	C(3) -C(8) -C(7)	118.2(4)
N(1) -C(1) -C(2)	119.3(4)	C(5) -C(6) -N(3)	118.8(4)
N(2) -C(1) -C(2)	121.2(4)	C(7) -C(6) -N(3)	119.0(4)
C(1) -C(2) -O(1)	105.4(3)	C(6) -N(3) -O(2)	118.2(4)
C(2) -O(1) -C(3)	118.4(3)	C(6) -N(3) -O(3)	118.1(4)
O(1) -C(3) -C(4)	114.9(4)	O(2) -N(3) -O(3)	123.7(4)
O(1) -C(3) -C(8)	123.4(4)		

Table 5. Comparison of bond lengths and bond angles for diazirines (e.s.d.'s are in parentheses)⁶.

Compounds (°)	bond lengths (Å)		bond angles N - C - N
	N = N	C - N	
(C ₁₀ H ₇ CH ₂)ClCN ₂	1.244(10)	1.465(10)	50.3(5) ^a
(C ₇ H ₇ O ₂ S)(CF ₃)CN ₂	1.228(9)	1.490(7)	48.5(4) ^a
this work	1.222(5)	1.451(3)	49.8(3) ^a
MeClCN ₂	1.241(5)	1.462	50.2(5)
MeBrCN ₂	1.240(5)	1.462	50.2
(Me) ₂ CN ₂	1.235(5)	1.490(10)	48.9
MeHCN ₂	1.235(5)	1.481(10)	49.3(3)
H ₂ CN ₂	1.228(3)	1.482(3)	48.9
F ₂ CN ₂	1.293(9)	1.426(4)	53.9(4)

^aDimensions derived from single-crystal x-ray diffraction. Other dimensions derived from rotational spectra.

The unit cell contains two molecules which lie approximately on the (100) plane, forming molecular sheets. These sheets are stacked along the *b* axis.

2.1.4. Electron Density Studies

2.1.4.1. X - X_{HO} Deformation Density Studies

Once the refinement had converged, the structure was re-refined using the high-order reflections ($\theta > 25^\circ$). At these angles the diffractions from the bonding and lone pair electrons are negligible, and the refinement is responding only to the intensities obtained from the core electrons of each atom. The hydrogen atoms were placed geometrically with $C_{\text{aliphatic}} - H = 1.06 \text{ \AA}$ and $C_{\text{aromatic}} - H = 1.08 \text{ \AA}$, the distances derived from neutron structures of similar compounds^{54,55}. The parameters from the high order refinement were then used with the low angle data ($3^\circ \leq \theta \leq 25^\circ$) to refine the scale factor and calculate the F_o for all the reflections. Only the reflections ($I > 3\sigma(I)$) were used for all calculations. All calculation and refinement were performed by TEXSAN⁵² using unit weights.

The low order data are more susceptible to bonding effects concentrated in the valence electrons. Thus, when the structure factors (F_o) calculated with high angle parameters are subtracted from the low angle F_o data, a significant portion of the difference remains. This difference represents the bonding and lone pair electron density. The difference map obtained using this method is called X - X_{HO} map.

The X - X_{HO} maps was calculated by the oblique plane Fourier procedure in TEXSAN⁵².

2.1.4.2. Multipole Deformation Density Studies^a

Molly refinements were done using all the reflections having $I > 2\sigma$ in the

^a The author is highly indebted to Dr. Witold Kwiatkowski for his sincere help and cooperation during refinement of the structure using the Molly program.

following way: first x , y , z , u_{ij} of all the non hydrogen atoms were refined with high angle data ($\theta > 25^\circ$). The hydrogen atoms were then placed in their geometrically calculated positions with distances of 1.06 and 1.08 Å for the aliphatic C - H and the aromatic C - H bonds respectively. These parameters were then kept fixed. The scale factor, the population and expansion parameters (p_v , k' , p_{lm} , and k'') were then refined individually using the low angle data ($\theta < 25^\circ$). However, refinement of the scale factor with other multipole parameters showed a high correlation. Therefore, the multipole parameters were refined separately from the scale factor. In each case, refinement was continued until the shift was found considerably lower than the shift error. The chlorine atom was refined to hexadecapolar ($l = 4$), the nitrogen and the carbon atoms to octapolar ($l = 3$) and the hydrogen atoms to dipolar ($l = 1$) parameters. After refinement of all the multipole and extinction parameters, the dynamic deformation maps of both rings were computed and it was seen that a mirror symmetry could be imposed on the diazirine ring. A mirror constraint was applied to the diazirine ring^b. In this ring the mirror plane was perpendicular to the plane of the ring, contained the carbon atom and bisected the N = N bond. Thus by C_s symmetry, the multipole parameters of N(1) are equivalent to N(2). Appropriate constraints were also applied on the multipole parameters of C(1) to maintain C_s symmetry. Some details of the refinement are given in Table 1 and the multipole population parameters are listed in Tables 68-69 (Appendix 1). Fig. 8 shows the numbering scheme and the local co-ordinate systems used for the Molly refinement. The dynamic deformation, residual maps, were calculated using the NF(locally modified NIELSAV) program⁵⁶.

^b Applications of mirror symmetry on the diazirine ring improves the d/p ratio, and removes some bad correlation.

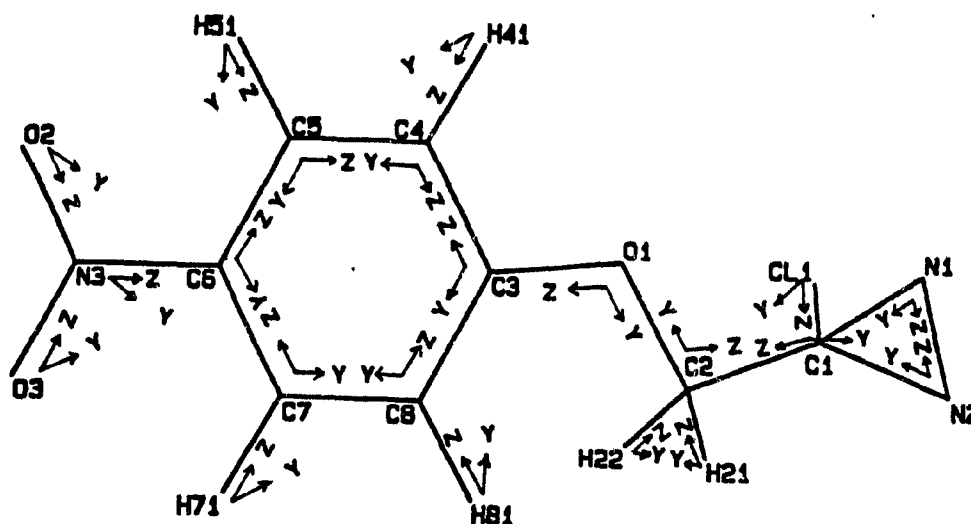


Fig. 8. Directions of local orthogonal reference axes for the atom-centered multipole functions.

2.1.4.3. Results and Discussion

The deformation density of the aromatic portion of the ring is almost as expected. Fig. 9 shows the $X - X_{HO}$ map of *p*-nitrophenoxy fragment of the molecule, which was calculated in the plane of the atoms N(3), C(7) and C(4) with the data cut-off at $\sin/\lambda = 0.60 \text{ \AA}^{-1}$. This map contains a certain amount of noise in the form of minor peaks and troughs, however the main features clearly resemble those reported for *p*-nitropyridine-N-oxide⁵⁷.

The main characteristic features of this map are as follows: i) the bonding density is at or near the midpoint of the bonds, ii) the electron density on the C - C bond is cylindrical, which indicates the presence of σ and π bonding in the aromatic

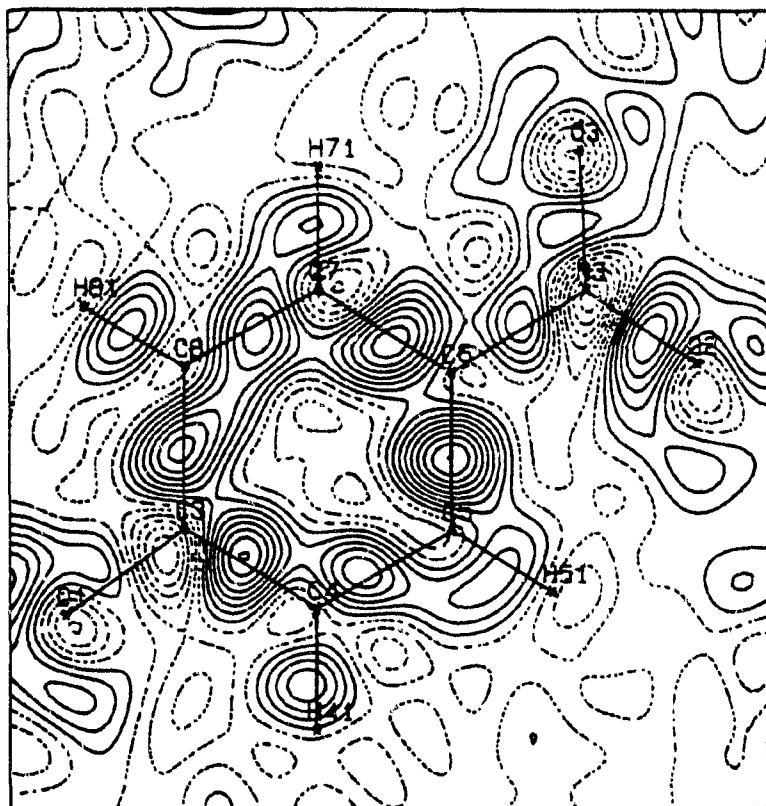


Fig. 9. $X - X_{BO}$ map on a plane through the atoms N(3), C(7) and C(4). Contours are at $0.08 \text{ e}/\text{\AA}^3$.

ring, and iii) the density features around the oxygen atom are compatible with the presence of a lone pair on the oxygen atoms.

The dynamic deformation density map of the same fragment is shown in Fig. 10. Like the $X - X_{BO}$ map, this map also shows more electron densities in the ring C - C bond at C(3) and C(6) which are attached to the electron withdrawing group. A clear reduction of the electron densities on C(4) - C(5) and C(7) - C(8) is also observed.

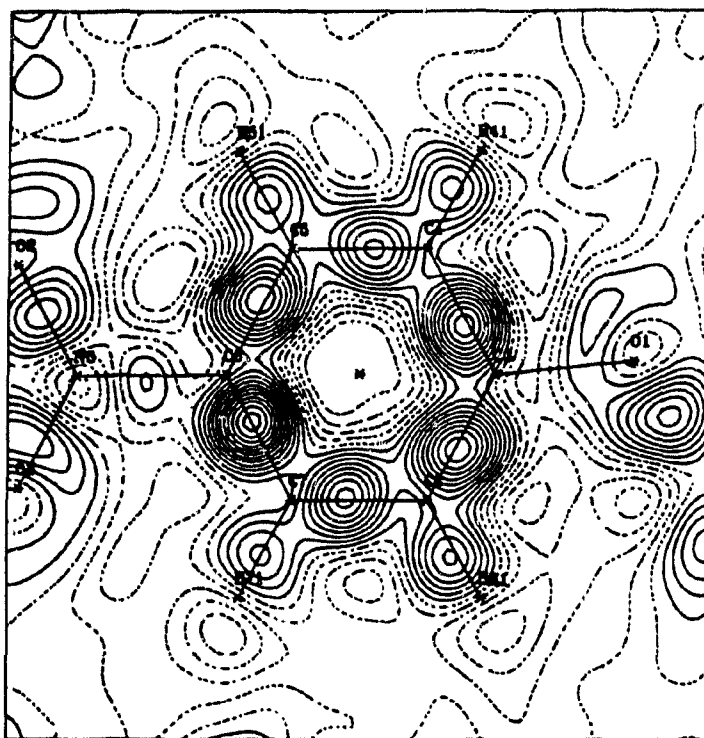


Fig. 10. Dynamic deformation density map in the plane of the phenyl ring. Contours are at $0.05 \text{ e}/\text{\AA}^3$.

Thus, the bond peaks C(4) - C(3), C(8) - C(3) and C(5) - C(6), C(7) - C(6) are polarised toward C(3) and C(6), respectively, indicating that C(3) and C(6) are more electronegative than the other ring carbon atoms. The electron density in the C - N bond is lower and the density of the C - O bond is even lower than that of the C - N bond. Such a result is not unexpected. Dunitz et al.⁵⁸ rioted from their study of

tetrafluoroterephthalodinitrile that the C - X (X = N, O and F) single bond deformation densities are less than those for the C - C bond and decrease in the order C - N > C - O > C - F. This is because spherically averaged atomic density is used for the reference and subtracted for the deformation densities. A spherically averaged N atom has 5/4 electrons per L-shell orbital, while an sp-, sp²-, or sp³-hybridized N atom has one electron in each of three bonding orbitals and one pair of electrons in a nonbonding orbital. Similarly spherically averaged O and F atoms with, respectively, 6/4 and 7/4 electrons per L-shell orbital. On the other hand, a C atom has one electron per L-shell orbital, whether spherically averaged or s and p hybridized. Thus the effect of subtraction of spherically averaged N, O and F atoms, leading to apparently deficient bond-pair densities, and by corollary, excessive lone-pair densities.

The N - O bonding electron density contours are not equivalent, 0.25 e/Å³ on N(3) - O(2) and 0.20 e/Å³ on N(3) - O(3) bond (Fig. 11). The chemical environments of

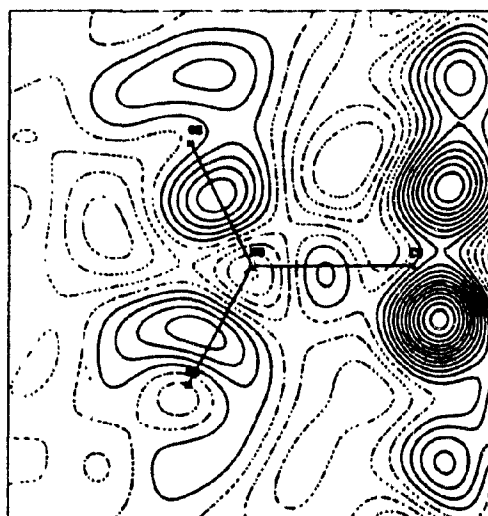


Fig. 11. Dynamic deformation map on the plane of the nitro group. Contours are at 0.05 e/Å³. Zero and negative contour lines are broken.

these two oxygen atoms are also different. O(2) has a close contacts of 3.155(6) Å to C(1), 3.249(6) Å to N(2) in the adjacent diazirine ring and 2.808 Å to H(22) beneath it whereas the shortest contact to O(3) is 3.410(5) Å to O(1) beneath it and 3.084 Å to H(51) in adjacent phenyl group. Thus, different levels of lone pair electron density appeared, 0.15 e/Å³ at O(2) and 0.05 e/Å³ at O(3), at roughly 90° from the N - O bond axis, which is an indication of the highly unhybridized s and p lone pairs on the oxygen.

The electron density map calculated through the plane bisecting two opposite C - C bonds of the aromatic ring is shown in Fig. 12. The peaks are extended in the direction normal to the molecular plane, reflecting a combination of σ - and π - covalent interaction. The electron density is also slightly squashed on the inside by repulsion and elongated on the outside of the ring.

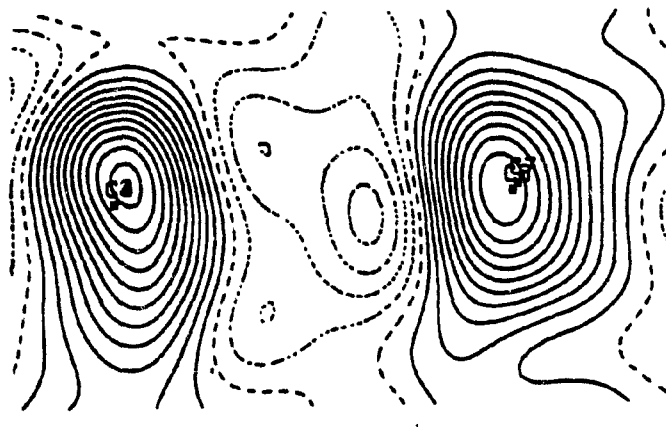


Fig. 12. $X - X_{B0}$ map on a plane bisecting two opposite C - C bonds in the aromatic ring. Contours are at 0.05 e/Å³.

The $X - X_{B0}$ map calculated through the plane bisecting the vector between atoms C(2) and C(3) is shown in Fig. 13. It clearly displays the lone pair moiety around the etherial

oxygen atom where the two lone pair electron density maxima coalesce into a broad full-moon. The peaks are above and below the oxygen atom and at an angle of about 120° with the C - O bond.

The residual electron density map through the plane of this fragment is essentially featureless (Fig. 14). It shows a density range that seldom exceeds $\pm 0.1 \text{ e}/\text{\AA}^3$ and is never more than $\pm 0.2 \text{ e}/\text{\AA}^3$.

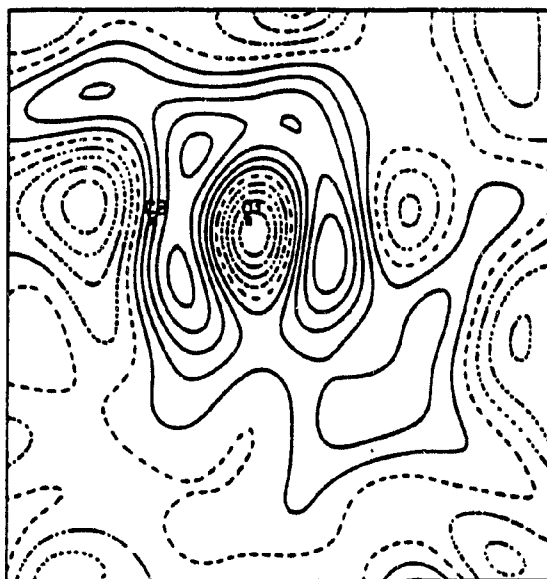


Fig. 13. $X - X_{\text{BO}}$ map on a plane bisecting the vector between atoms C(2) and C(3). Contours are at $0.04 \text{ e}/\text{\AA}^3$.

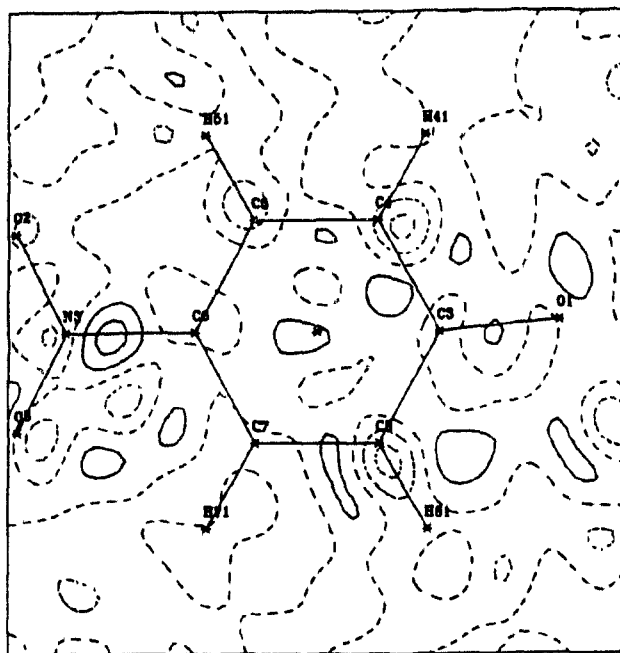


Fig. 14. The residual electron density map in the region of the *p*-nitrophenoxy fragment. Contours are at 0.1 e/Å³.

The $X - X_{HO}$ and dynamic deformation maps through the plane of diazirine ring are presented in Fig. 15. Both maps clearly present a high level of electron density in the region of the N - N bond which comes inside the framework of the ring. The two lower electron density peaks of the C - N bonds are clearly outside the carbon-nitrogen axis and displaced towards the C(1) atom. The appearance of these electron density distributions can be explained by the fact that in addition to the bent bonds usually observed in such three-membered rings, a significant donation of π electrons also

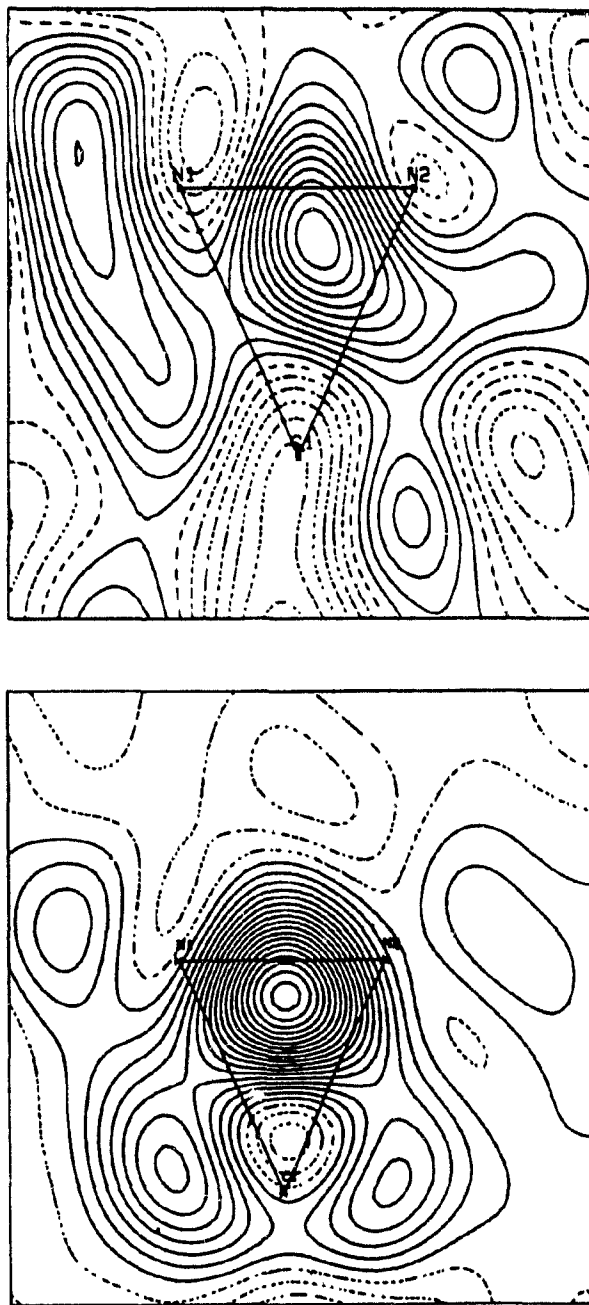


Fig. 15. Deformation electron density maps through the plane of the diazirine ring. Upper: $X - X_{HO}$, contour interval $0.04 \text{ e}^-/\text{\AA}^3$; lower: dynamic (multipole), contour interval $0.03 \text{ e}^-/\text{\AA}^3$; positive contours solid, zero and negative contours dashed.

occurs from N - N bond to the carbon atom in a manner analogous to a metal π -complex. However, the deformation density map of an unsubstituted diazine ring obtained by the theoretical calculation also provides confirmation for the concept of bent bonds in the diazine ring but shows little π -complex character⁷. This discrepancy arises due to the presence of an electronegative chlorine atom which pulls the electrons and increases the electropositivity of C(1). Accordingly, more electron density is moved from the N = N and C - N bonds towards the C(1) and thereby form a convex shaped N - C and concave shaped N = N maximum electron density path. The pulling effect of chlorine can also be seen if we compare the N = N bond distance in this chloro derivative (1.222(5) Å) with that of unsubstituted diazine compound (1.194 Å³⁵, *ab-initio*, 6-31*). Two peaks, about 0.8 Å apart from each nitrogen atom, represent the lone pair electron density, the intensity of which is significantly less than the bonding electron density. Similar observation was made by Baert *et al.*⁵⁹. The difference in lone pair electron densities is also noticeable. This can be explained by the fact that the axis of the lone pair on N(2) is directed toward the plane of the phenyl ring resulting in an interaction between the lone pair on N(2) and the π electron cloud of the aromatic system which ultimately reduces the lone pair density on N(2).

The residual electron density map of the diazine ring (Fig. 16) is almost featureless. The maximum residual density is 0.2 e/Å³, some of which is certainly due to the chemical and symmetry constraints.

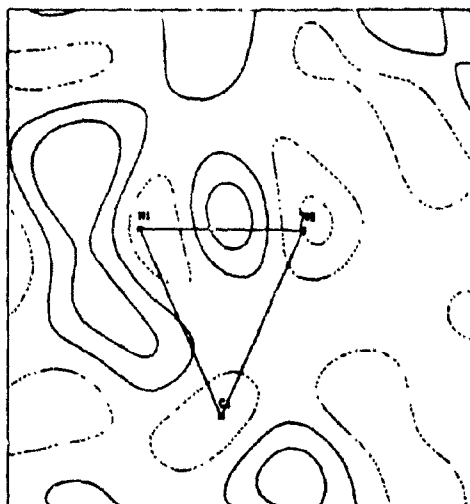


Fig. 16. The residual electron density map through the plane of the ring. Contours are at $0.1 \text{ e}^-/\text{\AA}^3$. Zero and negative contours are broken.

2.1.4.4. Summary

A careful deformation density study of the diazine compound at -65°C has been made from x-ray diffraction measurements. So far as we know, this is the first experimental electron density report for this system. This compound contains a well known *p*-nitrophenoxy fragment, the deformation density of which is comparable with the reported *p*-nitropyridine-N-oxide molecule⁵⁷. This resemblance adds credence to our electron density results for the diazine ring. It is clear from the appearance of both X_{B0} and dynamic deformation maps of the diazine ring that the classical strain theory is not adequate to explain its bonding arrangement properly. Rather, its bonding can be explained in a better way using the π complex model.

2.2. Monochloropentaaziridinocyclotriphosphazene

2.2.1. Introduction

Aziridinocyclotriphosphazene and its chloro derivatives are well known as antitumour active agents against many animal leucomas, melanomas, sarcomas etc.^{10,11}. However, no significant metabolization was observed when these compounds were injected to animals and/or patients⁶⁰ and therefore, there might be a relationship between the in vitro geometric structure of the molecules and their in vivo antitumour actions. It was found that the spatial distribution of aziridinal wings (az) are more important for their biological activity than the number of aziridinyl wings. The antitumour effectiveness occurs when both conformations "bow tie I" and "bow tie II" aziridinyl wings exist in the same molecule of the drug¹². In the "bow tie I" conformation, the aziridinyl ring is perpendicular to the phosphazene ring plane; on the other hand, in the "bow tie II" the aziridinyl ring is parallel to the phosphazene ring plane⁶¹. Structural study of this class of compounds by x-ray diffraction technique is thus very important to determine the conformations of the az wings, and thus their biological activity.

Monochloropentaaziridinocyclotriphosphazene, $N_3P_3(az)_5Cl$, is one of the most promising examples because it has both conformations of the aziridinyl rings. Similar conformational arrangements of az rings have been found in pentaziridinocyclodiphosphathiazene (crystallizes in the orthorhombic system, space group $P2_12_12_1$, $Z = 4$), which has already shown its significant effectiveness on all the tumours it was tested on¹⁰. The structural and electron density studies on $N_3P_3(az)_5Cl$ (Fig. 17) are presented below.

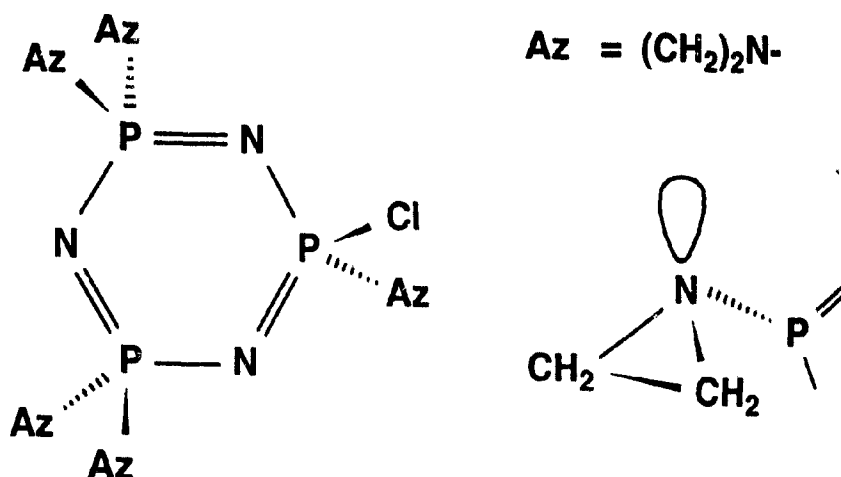


Fig. 17. Monochloropentaaziridinocyclotriphosphazene molecule.

2.2.2. Bonding in the Cyclophosphazene

Cyclophosphazenes consist of $[-N=PX_2-]$ repeating units in a valence unsaturated skeleton. The ring size can vary from three to seventeen $[-N=PX_2-]$ units. The substituent, X, can be halogen, pseudohalogen, amino, azido, or a wide variety of organic groups such as alkoxy, aryloxy, alkylamino, arylamino, alkyl, aryl, etc. Whatever the ring size and substituents, some important structural features of cyclophosphazenes are essentially the same⁶². They are as follows:

- 1) They are very stable and chemically inert compounds with almost equal P - N distances around the ring unless there are differing substituents at the various P atoms. The P - N distances in phosphazenes (1.47 - 1.62 Å) are shorter than expected for pure covalent σ bonds (1.77 Å).
- 2) The ring bond angle at phosphorus is remarkably constant, ranging between 115° and 127° and usually close to 120°, while those at nitrogen vary from 120° to 148.6°.

3) Some cyclic phosphazenes are planar and some are puckered, but the presence or absence of puckering appears to have little influence on molecular stability.

From the structural and other evidence, it is clear that the skeletal bonds of this ring are essentially covalent having both σ and π character. The σ -framework of the ring system is constituted from sp^3 hybrid orbitals of phosphorus and nitrogen hybrid orbitals preferably sp^2 . Two of the three sp^2 nitrogen orbitals in the P - N - P plane form σ bonds to neighbouring phosphorus atoms and the third, projecting out of the ring, is occupied by a lone pair. This leaves nitrogen with singly occupied p_z orbital (if the ring skeleton is assumed to be in the xy plane), perpendicular to the local ring plane. The four σ bonds formed by phosphorus involving all of sp^3 orbitals leave it too with an unpaired electron, the location of which is not clear. The current hypothesis is that overlapping of a singly occupied p_z orbital with an appropriate d orbital of phosphorus produces π molecular orbital, antisymmetric in the P - N - P plane. The use of phosphorus d_{xz} orbital leads to a delocalized bonding with alternate signs around the ring (heteromorphic) whereas, d_{yz} orbital leads to constant signs of interaction (homomorphic) (Fig. 18). In a homomorphic π system, the Huckel aromaticity

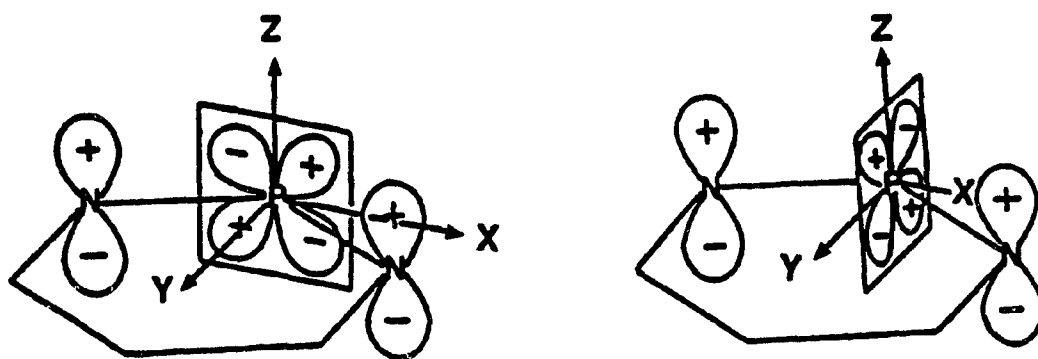


Fig. 18. π -bonding in the phosphazene.

theory would hold and the electron density distribution should be comparable to the $p_\pi - p_\pi$ aromatic system. On the other hand, in a heteromorphic π system, a broadly delocalised "pseudoaromatic" π orbital could be formed. Finally, if both heteromorphic and homomorphic π systems contribute equally, the delocalised system would break up into three-centre P - N - P bonds (usually called Dewar Islands) and broad delocalisation effects would not be expected⁶³⁻⁶⁴.

In addition, the sp^2 lone pair on each N can be involved in coordinate bonding to vacant $d_{x^2-y^2}$ and d_{xy} orbitals on the P in the xy plane and forms another type of π bond (symmetric in the P - N - P plane), usually designated by π' . This system too could be homomorphic and/or heteromorphic depending on the phosphorus d orbitals used (Fig. 19).

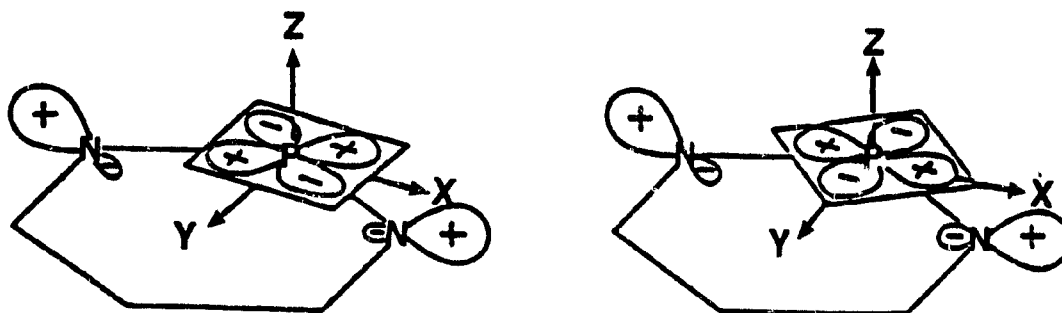


Fig. 19. π' bonding in the phosphazene.

The effect of substitutions on bonding in the phosphazenes has also been studied⁶⁵⁻⁶⁷. The presence of a highly electro-negative group will contract the phosphorus d orbitals and facilitate the donation of the nitrogen sp^2 lone pair electron to the π' system. Conversely, the electron donating substituents can participate in the

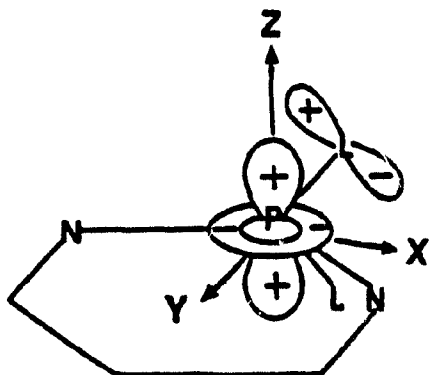


Fig. 20. Exocyclic π -bonding in the phosphazene.

exocyclic π bonding (Fig. 20) by means of the d_z^2 orbital on phosphorus which localize the nitrogen lone pair and disrupts the π' system. Hence, the nature of the exocyclic groups may be expected to influence the balance of π and π' bonding and this will in turn influence the ring conformation in a particular compound.

Some amount of transannular bonding interaction between endocyclic phosphorus atoms has also been suggested⁶⁸ (Fig. 21). In $(NPX_2)_3$ trimers, the energy of such interaction is about 10% of the P - N bond energy.

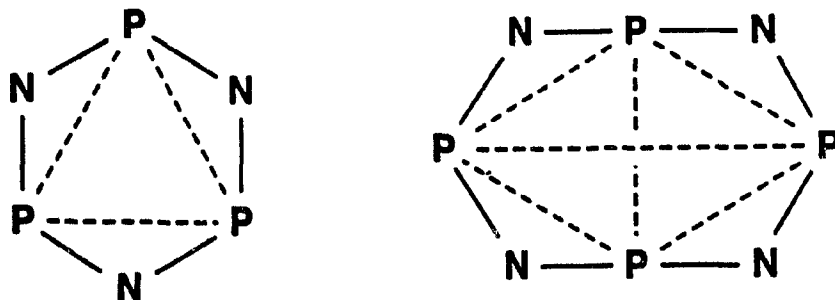


Fig. 21. Transannular bonding in the cyclophosphazene.

Thus, different models can be anticipated from the above discussion. To date, no unambiguous evidence has appeared to favour one model or another, even though theoretical calculations and some experimental evidence suggest that the π bonding is predominantly antisymmetric of the three-centre Dewar Island type⁶⁹. In light of these controversial proposals, our group has started to calculate electron density maps of various substituted phosphazenes through low temperature x-ray crystallographic work in order to gain some insight about the electron density distribution on nitrogen and phosphorus atoms, which could help to understand the π bonding arrangement in phosphazene rings.

2.2.3. Bonding in Aziridine

Like in other three-membered ring compounds, the bonding arrangement in the aziridine ring is not completely understood. In nearly all modern textbooks, Baeyer's strain concept is used to rationalize the stability of small cycloalkanes and other strained compounds. Recently this view has been challenged by many authors³⁸⁻⁴¹. According to them, the bonding system of A_2X type three-membered ring compounds can be explained using the π -complex model. Thus the bonding in aziridine can be regarded as being constructed from the interaction of π and π^* orbitals of an ethylene fragment with empty and filled orbitals on the heteroatom N. The first type of interaction involves the transfer of electron density to the electronegative N atom; the second type involves back donation of electron density to the olefinic fragment. The electron distribution in the bonding systems of these rings is determined by the relative strengths of the two types of interactions. Aziridines have short C - C bonds (1.498 Å, on average) compared with the sp^3 hybrid C - C single bond (1.54 Å) suggesting that they

have much more s character than normal. This, combined with the enhanced π type characteristics of the ring bonds, permits the transmission of conjugation through the ring systems⁷⁰. Under these circumstances, we calculate its deformation electron density map for comparison with the theoretical models.

2.2.4. Structure Determination

2.2.4.1. Experimental and Conventional Refinement

A colourless needle crystal of $N_3P_3(az)_5Cl$ having approximate dimensions of 0.20 X 0.30 X 0.40 mm was mounted on a glass fibre. All measurements were made on a Rigaku AFC5 diffractometer with graphite monochromated $MoK\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) at room temperature using the $\omega - 2\theta$ scan technique to a maximum 2θ value of 60.0° .

Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centred reflections in the range $22.34 < 2\theta < 29.79^\circ$. The space group was determined on statistical analysis of intensity distribution, and the successful solution and refinement of the structure.

The data were scaled and corrected for Lorentz and polarization effects using routine procedures. No decay and absorption correction were applied.

The structure was solved by direct methods⁴⁷. The non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were placed in their idealized positions with a C - H distance of 1.08 $\text{\AA}$. Their positions were kept fixed during refinement and assigned fixed isotropic temperature factors with a value of $1.2 \times B_{eq}$ of the atom to

which each was bonded. Full-matrix least-squares refinement was continued until the shift error was 0.01. The weighting scheme was based on counting statistics and included a factor ($p = 0.01$) to downweight the intense reflections. The crystallographic data and the refinement procedure are given in Table 6.

All calculations were performed using the TEXSAN⁵² crystallographic software package of Molecular Structure Corporation. The programme ORTEP⁵³ was used for drawing the diagram.

Table 6. Physical properties and parameters for data collection and refinement of $N_3P_3(az)_5Cl$ (rt).

Formula	$C_{10}H_{20}N_8P_3Cl$
Formula Weight	380.7
Crystal System	triclinic
a (Å)	8.665(1)
b (Å)	14.013(2)
c (Å)	7.965(1)
α (°)	90.49(1)
β (°)	113.62(1)
γ (°)	89.92(1)
V (Å ³)	886.1(2)
Space Group	PT (No. 2)
Z	2
d_{calc} (g/cm ³)	1.427(2)
$F(000)$ (e)	396
μ (cm ⁻¹)	4.89
$2\theta_{max}$ (°)	60
Reflections:	
Total measured	5,499
Unique total	5,174 ($100R_m = 4.58$)
Unique used ($I > 3\sigma(I)$)	2,323
Parameters used; d/p	200; 11.6
Agreement Factors:	
$100R$	3.94
$100R_w$	4.10
GOF	1.75
Residual e.d. (min, max) (e/Å ³)	-0.36, 0.33

2.2.4.2 Results and Discussion

The final atomic positions, bond lengths and bond angles are gathered in Tables 7-9 and the structure of the compound is shown in Fig. 22. The N_3P_3 ring has very slight crown conformation, with N(1), N(2), and N(3) being 0.082, -0.003 and -0.163 Å respectively from the plane through the three phosphorus atoms. Within the ring, the P - N bond lengths are not uniform, ranging from 1.571(3) to 1.604(3) Å. Two P - N

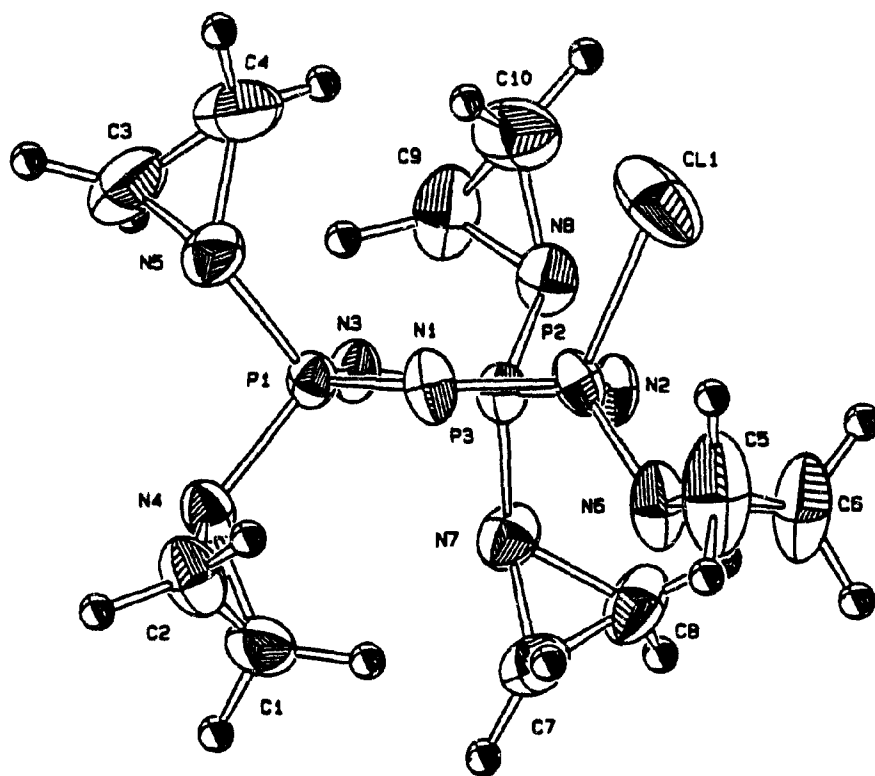


Fig. 22. Molecular structure of $N_3P_3(az)_5Cl$. Vibrational ellipsoids are at the 50% probability level.

Table 7. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for $\text{N}_3\text{P}_3(\text{az})_5\text{Cl}$ (rt) (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	U_{eq}
Cl(1)	0.7151(2)	0.0548(1)	0.0948(2)	0.0789
P(1)	0.8054(1)	0.3453(1)	0.1415(1)	0.0290
P(2)	0.8107(1)	0.1655(1)	-0.0045(1)	0.0324
P(3)	1.1109(1)	0.2474(1)	0.2301(1)	0.0288
N(1)	0.7129(3)	0.2584(2)	0.0067(4)	0.0363
N(2)	1.0074(3)	0.1608(2)	0.1014(4)	0.0333
N(3)	1.0016(3)	0.3318(2)	0.2619(4)	0.0308
N(4)	0.7802(4)	0.4483(2)	0.0307(4)	0.0352
N(5)	0.6933(4)	0.3698(2)	0.2646(5)	0.0451
N(6)	0.7627(4)	0.1398(2)	-0.2224(5)	0.0500
N(7)	1.2489(4)	0.2940(2)	0.1554(5)	0.0411
N(8)	1.2435(4)	0.1994(2)	0.4264(4)	0.0411
C(1)	0.7947(6)	0.4489(3)	-0.1445(5)	0.0503
C(2)	0.6288(5)	0.4618(3)	-0.1396(6)	0.0516
C(3)	0.7707(6)	0.4175(4)	0.4425(6)	0.0644
C(4)	0.7155(6)	0.3175(4)	0.4297(7)	0.0665
C(5)	0.6166(6)	0.0836(4)	-0.3404(7)	0.0839
C(6)	0.7870(6)	0.0447(3)	-0.2884(7)	0.0722
C(7)	1.1928(6)	0.3051(3)	-0.0441(6)	0.0535
C(8)	1.3193(5)	0.2318(3)	0.0544(6)	0.0537
C(9)	1.2968(6)	0.2554(4)	0.5951(6)	0.0636
C(10)	1.1806(6)	0.1767(4)	0.5661(6)	0.0653

Table 8. Interatomic distances ($\text{\AA}$) for $\text{N}_3\text{P}_3(\text{az})_5\text{Cl}$ (rt) (with e.s.d.'s in parentheses).

Cl(1)	-P(2)	2.065(2)	N(5)	-C(3)	1.459(5)
P(1)	-N(1)	1.604(3)	N(5)	-C(4)	1.455(5)
P(1)	-N(3)	1.594(3)	N(6)	-C(5)	1.465(5)
P(1)	-N(4)	1.667(3)	N(6)	-C(6)	1.474(5)
P(1)	-N(5)	1.667(3)	N(7)	-C(7)	1.473(5)
P(2)	-N(1)	1.574(3)	N(7)	-C(8)	1.469(5)
P(2)	-N(2)	1.571(3)	N(8)	-C(9)	1.456(5)
P(2)	-N(6)	1.651(4)	N(8)	-C(10)	1.459(5)
P(3)	-N(2)	1.604(3)	C(1)	-C(2)	1.464(6)
P(3)	-N(3)	1.595(3)	C(3)	-C(4)	1.471(7)
P(3)	-N(7)	1.671(3)	C(5)	-C(6)	1.470(7)
P(3)	-N(8)	1.671(3)	C(7)	-C(8)	1.481(6)
N(4)	-C(1)	1.450(5)	C(9)	-C(10)	1.448(7)
N(4)	-C(2)	1.475(5)			

Table 9. Interbond angles ($^{\circ}$) for $\text{N}_3\text{P}_3(\text{az})_5\text{Cl}$ (rt) (with e.s.d.'s in parentheses).

N(1) -P(1) -N(3)	115.9(1)	C(1) -N(4) -C(2)	60.1(3)
N(1) -P(1) -N(4)	112.2(2)	P(1) -N(5) -C(3)	120.8(3)
N(1) -P(1) -N(5)	107.0(2)	P(1) -N(5) -C(4)	122.2(3)
N(3) -P(1) -N(4)	107.9(2)	C(3) -N(5) -C(4)	60.6(3)
N(3) -P(1) -N(5)	113.7(2)	P(2) -N(6) -C(5)	125.1(4)
N(4) -P(1) -N(5)	98.9(2)	P(2) -N(6) -C(6)	123.4(3)
Cl(1) -P(2) -N(1)	107.1(1)	C(5) -N(6) -C(6)	60.0(3)
Cl(1) -P(2) -N(2)	106.0(1)	P(3) -N(7) -C(7)	117.1(3)
Cl(1) -P(2) -N(6)	105.9(1)	P(3) -N(7) -C(8)	118.4(3)
N(1) -P(2) -N(2)	120.0(2)	C(7) -N(7) -C(8)	60.5(3)
N(1) -P(2) -N(6)	108.5(2)	P(3) -N(8) -C(9)	119.4(3)
N(2) -P(2) -N(6)	108.5(2)	P(3) -N(8) -C(10)	118.6(3)
N(2) -P(3) -N(3)	116.2(1)	C(9) -N(8) -C(10)	59.6(3)
N(2) -P(3) -N(7)	111.5(2)	N(4) -C(1) -C(2)	60.8(3)
N(2) -P(3) -N(8)	106.8(2)	N(4) -C(2) -C(1)	59.1(2)
N(3) -P(3) -N(7)	108.7(2)	N(5) -C(3) -C(4)	59.5(3)
N(3) -P(3) -N(8)	112.5(2)	N(5) -C(4) -C(3)	59.8(3)
N(7) -P(3) -N(8)	100.0(2)	N(6) -C(5) -C(6)	60.3(3)
P(1) -N(1) -P(2)	121.7(2)	N(6) -C(6) -C(5)	59.7(3)
P(2) -N(2) -P(3)	121.2(2)	N(7) -C(7) -C(8)	59.6(3)
P(1) -N(3) -P(3)	123.6(2)	N(7) -C(8) -C(7)	59.9(3)
P(1) -N(4) -C(1)	118.5(3)	N(8) -C(9) -C(10)	60.3(3)
P(1) -N(4) -C(2)	118.9(2)	N(8) -C(10) -C(9)	60.1(3)

bonds related to P(2), which has Cl(1) bonded to it, are significantly shorter (mean 1.573(2) Å), resulting from the electron withdrawing effect of the more electronegative chlorine atom. The endocyclic N - P - N angles related to P(1) and P(3) are noticeably squeezed (about 4°) compared with that on P(2). A similar situation has also been observed in earlier reports^{71,72} and explained in terms of the stretching effect on the P_3N_3 ring by the geminal pair of aziridiny groups.

Like other aziridinophosphazene derivatives, the exocyclic P - N distances (mean 1.665(7) Å) in this compound are longer than those observed in aminophosphazene compounds⁷³ (1.652(4) Å in $\text{N}_3\text{P}_3(\text{NMe}_2)_6$, 1.634(5) Å in $[\text{HN}_3^+\text{P}_3(\text{NMe}_2)_6]_2\text{Mo}_6\text{O}_{19}^{2-}$,

1.642(4)Å in $\text{N}_3\text{P}_3(\text{NHPr}^1)_4\text{Cl}_2$, 1.609(5)Å in $\text{N}_3\text{P}_3(\text{NHPr}^1)_4\text{Cl}_2\cdot\text{HCl}$) probably because of the quite pyramidal character of the nitrogen atoms in the aziridinyll group which hinders any $p\pi\text{-}d\pi$ back bonding along these bonds. All aziridinyll rings adopt "bow tie" conformations. According to the VSEPR model of Gillespie⁷⁴, this is the most energetically favourable conformation with the lone pairs of the nitrogen atoms inclined at an angle of 120° to the ring plane. Like $\text{N}_3\text{P}_2\text{S}(\text{az})_5\text{O}^{10}$, this compound also appears to be versatile as regards its aziridinyll groups. Those attached to P(1) and P(3) have the "bow tie I" conformation (i.e. aziridinyll ring planes are almost perpendicular to phosphazene ring plane; dihedral angle, in average 87.9°) whereas the fifth, bonded to P(2), adopts "bow tie II" conformation in which the aziridinyll wing is parallel to the N_3P_3 ring (dihedral angle is 3.73°). The aziridinyll groups are pyramidal. The sums of the interbond angles at the nitrogen atoms in the range 296.0(2) - 308.8(2)° with a mean of 300.7(1)°. The distances of these exocyclic nitrogens from their corresponding PCC planes are 0.677 Å N(4), 0.635 Å N(5), 0.599 Å N(6), 0.692 Å N(7) and 0.675 Å N(8). The actual dimensions of the aziridinyll rings are as expected with mean N - C and C - C distances of 1.464(8) and 1.467(11) Å respectively. The lone pair orbital on the nitrogen atom of each aziridinyll group occupies space within the crystal lattice, so the efficient packing of the molecules in the crystal must take into account both the inter- and intramolecular forces acting on this lone pair.

The P - Cl distance is 2.065(2) Å comparable with the values reported earlier. It was also pointed out that P - Cl bonds vary very little despite changes in valence and coordination number of the phosphorus⁷⁵.

2.2.5. Electron Density Studies

2.2.5.1. Experimental and Low Temperature refinement

The low temperature data were collected for us by Dr. B. Vincent[°] at Molecular Structure Corporation using an R-Axis IIC imaging plate area detector mounted on an RU200 rotating anode x-ray generator equipped with Mo anode. A colourless needle plate crystal (0.20 x 0.10 x 0.07 mm) was used for data collection. The data were collected at a temperature of -65°C. Two different crystal settings were needed for entire data collection.

First, the crystal was mounted in a glass capillary on a traditional xyz goniometer head. Three 4° oscillation frames were taken at 0°, 45° and 90° (in ϕ) respectively. These were used by the indexing software to determine the unit cell and crystal orientation. A total of twenty 9° oscillation frames were collected to give the full 180° rotation range in ϕ , but the software indicated that only 68.1% of the possible data was collected. A total of 12288 reflections were collected in the first setting which produced 7320 unique data- points with a merging *R*-value of 4.44%. With a view to collecting the missing data, the crystal was mounted again on a eucentric goniometer head with the arcs extended out to their extreme positions in both directions to get as different an orientation of the crystal as possible. Again three frames and another twenty 9° oscillation frames were taken; the software then suggested a total of about 90% of the possible data was recorded in both settings. In the second setting, we got 12296 reflections in which 7271 reflections were found unique with a merging *R*-value of

[°] The author is grateful to Dr. Bev Vincent, Molecular Structure Corporation, for collecting the low temperature data of $\text{N}_3\text{P}_3\text{Az}_5\text{Cl}$.

4.46%.

The two data sets were separately processed and used for the refinement of the structure. The positional and thermal parameters of the atoms were taken from room temperature refinement results. During refinement, the unit weighting scheme was used in both cases and the function minimised was $\sum w(|F_o| - |F_c|)^2$, where w is the weight. No absorption nor extinction corrections were applied.

Both data sets were then brought to their absolute scale and combined. Two different crystal settings were used during the data collection, so after sorting all the equivalent reflections it was found that a good number of reflections had been measured more than two times. Then those observations which were weak and significantly different than the others, were removed from the data set. The merging R had then gone down to 3.10%. The structure was then refined using the unique data set. The final R -factor using all the data ($I > 3\sigma(I)$) is 0.0695. Detailed information concerning the data collection and the refinement procedure is compiled in Table 10. The program, SHELX 76⁷⁶, was used for all calculations and refinement.

Table 10. Physical properties and parameters for data collection and refinement of $\text{N}_3\text{P}_3(\text{NC}_2\text{H}_4)_5\text{Cl}$ (It).

Formula	$\text{C}_{10}\text{H}_{20}\text{N}_8\text{P}_3\text{Cl}$
Formula Weight	380.7
Crystal System	triclinic
a (Å)	8.649 (3)
b (Å)	13.975 (5)
c (Å)	7.929 (2)
α (°)	91.02 (1)
β (°)	113.36 (1)
γ (°)	89.71 (1)
V (Å ³)	879.7 (9)
Space Group	PT (No. 2)
Z	2
d_{calc} (g/cm ³)	1.437
F_{000} (e)	396.0
$\mu_{(\text{MoK}\alpha)}$ (cm ⁻¹)	4.98
Radiation	MoK α ($\lambda = 0.71069$ Å)
$2\theta_{\text{max}}$ (°)	82.8
Reflections:	
Total measured	13,292
Unique total	8144 ($100R_m = 3.10$)
Conventional refinement (unit weighting scheme, $\theta = 45^\circ$)	
Unique used ($I > 3\sigma(I)$)	5484
Parameters refined; d/p	280; 19.6
Agreement Factors:	
$100R$	6.95
$100R_w$	7.90
G.O.F.	1.13
Residual e.d. (min, max) (e/Å ³)	-0.67, 0.70
Multipole refinement (σ weighting scheme, $\theta = 45^\circ$)	
Unique used ($I > 2\sigma(I)$)	7756
Agreement Factors:	
$100R$	6.30
$100R_w$	5.50
G.O.F.	2.18
Residual e.d. (min, max) (e/Å ³)	-0.40, 0.36

2.2.5.2. $X - X_{HO}$ Deformation Density Studies

The positional and thermal parameters were re-refined using the high-order reflections ($\theta > 25^\circ$) in order to reduce bias from the aspherical distribution of valence electrons. The parameters from the high order refinement were then used with the low angle data ($3^\circ \leq \theta \leq 25^\circ$), the scale factor was refined and the F_o for all the reflections were calculated. Only the reflections ($I > 3\sigma(I)$) were used for all calculations. All calculation and refinement were performed by TEXSAN using unit weight. The $X - X_{HO}$ map was calculated by the oblique Fourier procedure in TEXSAN⁵².

2.2.5.3. Multipole Deformation Density Studies

In this case, the positional and anisotropic thermal parameters of the non-hydrogen atoms were refined first using the high angle data ($\theta > 25^\circ$). The hydrogen atoms were placed in their geometrically calculated positions with a $C_{\text{aliphatic}} - H = 1.06 \text{ \AA}$, the distance derived from neutron structures of similar compounds. The atomic positions and temperature factors were kept fixed and the multipole parameters were then refined first individually and then in combination, e.g., scale factor(sf), then pv, then (sf + pv), k' , then (sf + k'), (pv + k'), (sf + pv + k'), and so on, using all the data ($I > 2\sigma(I)$). The phosphorus and chlorine atoms were refined to hexadecapolar ($l = 4$), the nitrogen and carbon atoms to octapolar ($l = 3$) and the hydrogen atoms to dipolar ($l = 1$) parameters. To reduce the number of parameters and avoid correlations, mirror symmetry constraints were applied on the phosphazene ring and each of the five aziridiny groups. The environment of P(1) and P(3), both bonded to two az rings, with similar conformations, allow a mirror plane to be placed perpendicular to the plane of the ring passing through N(2) and P(2). Thus, by C_s symmetry, the multipole parameters

of P(1) are equivalent to P(3), N(1) are equivalent to N(2). Appropriate constraints were also applied to N(3) and P(2). In case of aziridiny rings, the mirror plane contained the nitrogen atom and bisected the C - C bond. And again, by the same argument, the multipole parameters of C(1) are equivalent to C(2), C(3) to C(4), C(5) to C(6), C(7) to C(8) and C(9) to C(10). Some details of the refinement are given in Table 10 and the multipole population parameters are listed in Tables 72-73 (Appendix 1). Local pseudoatom co-ordinate systems are defined in Fig. 23.

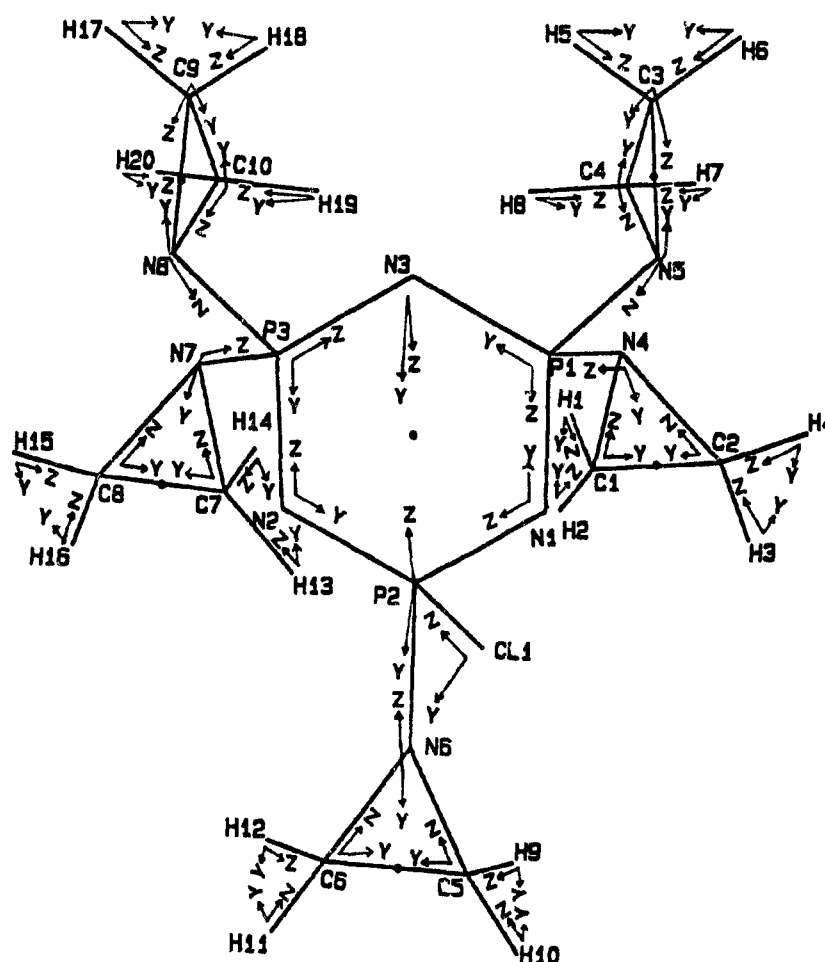


Fig. 23. Direction of local orthogonal reference axes used to define the pseudoatom model.

The dynamic deformation and residual electron density maps obtained using this coordinate system and refinement procedure are shown in Figs. 25-26, 28-29. Many minor changes in refinement parameters, data ranges, etc. were applied in an attempt to improve the quality of the maps, specially for aziridinyl groups, but there was little improvement.

The program Molly²⁹ was used for multipole refinement and the dynamic deformation, residual maps were calculated using the NF (locally modified NIELSAV) program⁵⁷.

2.2.5.4. Results and Discussion

The $X - X_{\text{R0}}$ map of phosphazene ring (Fig. 24) displays a clear reduction in valence electron density at the phosphorus atom, and a clear increase in density at the nitrogen atom which is extended from one endocyclic P - N bond through the nitrogen atom to the second endocyclic P - N bond. This observation is very similar to the restricted delocalisation models for bonding in the cyclotriphosphazene ring. This map also shows how the chlorine atom affects the electron density maxima of N(1) and N(2).

The dynamic deformation density map of the phosphazene ring is shown in Fig. 25. It displays similar features: a node at each phosphorus atom, spreading of the electron density from one P - N bond through the nitrogen to the second N - P bond and higher electron density along the P(2) - N(1) and P(2) - N(2) bonds. With application of C_s symmetry in the phosphazene ring, the electron density distributions on N(1) and N(3) are now equivalent.

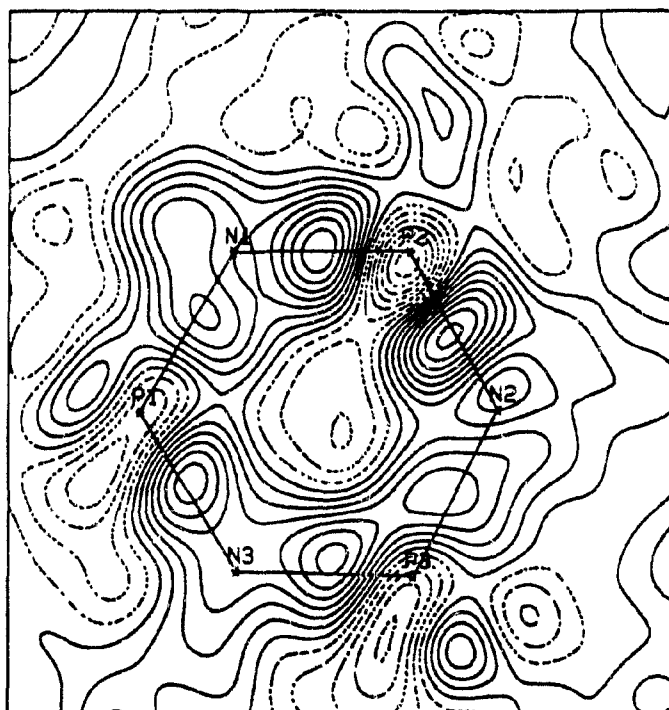


Fig. 24. $X - X_{HO}$ map on a plane through the atoms P(2), N(1) and P(1). Contours are at $0.07 \text{ e}/\text{\AA}^3$.

An interesting feature of the dynamic deformation density map is that the lone pair electron density on N(3) is slightly lower than that of N(1) and N(2). As in $(\text{NPCl}_2)_3$ ⁷⁷, in this compound, a certain degree of exocyclic π bonding interaction between Cl and the skeletal P(2) atom is possible. This favours localization of the lone pair on N(1) and N(2), which is evident when a comparison is made between deformation density maps of the P_3N_3 ring in $\text{N}_3\text{P}_3(\text{az})_6 \cdot \text{C}_6\text{H}_6$ ¹³ and $\text{N}_3\text{P}_3(\text{az})_5\text{Cl}$. In $\text{N}_3\text{P}_3(\text{az})_6 \cdot \text{C}_6\text{H}_6$, Cameron *et al.* observed considerable spreading of the electron density

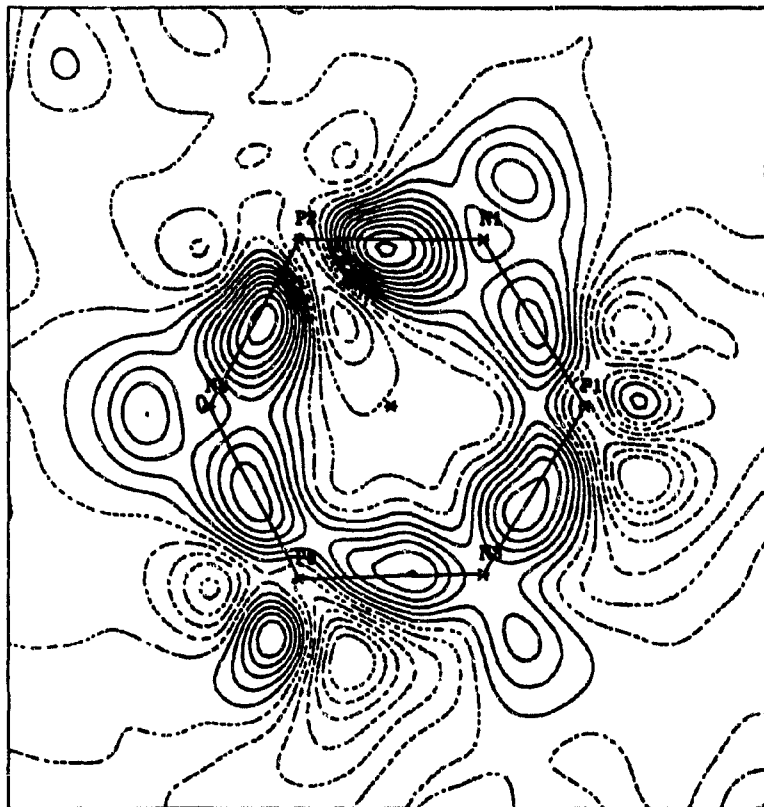


Fig. 25. The dynamic electron density map through the plane of the phosphazene ring. Contours are at $0.05 \text{ e}/\text{\AA}^3$.

inside the phosphazene ring framework and explained it in terms of π' bonding. However, in the compound, $\text{N}_3\text{P}_3(\text{az})_5\text{Cl}$, comparatively lower electron density is observed inside the phosphazene ring. Localization of the nitrogen lone pair by the Cl atom hinders the formation of the π' bonding.

The residual density in the plane containing P(1), P(2) and P(3), calculated after multipole refinement is shown in Fig. 26. The density is apparently well-modelled by the multipole expansion, with the highest residual feature at $0.2 \text{ e}/\text{\AA}^3$.

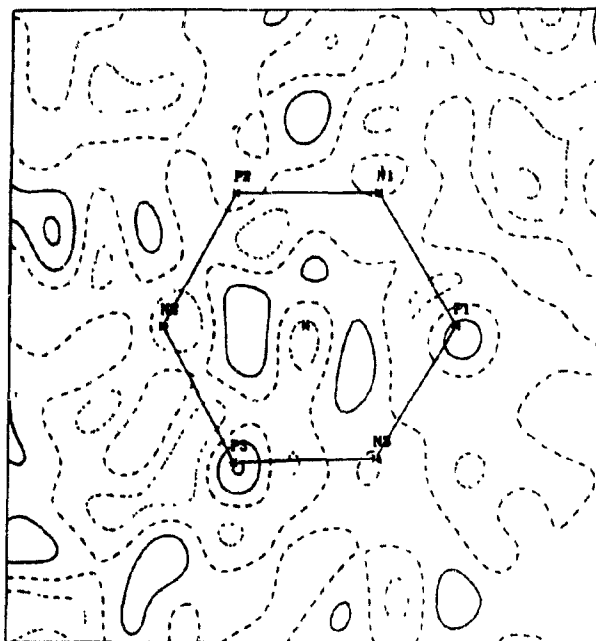


Fig. 26. The residual electron density map on a plane through the phosphazene ring. Contours are at $0.1 \text{ e}/\text{\AA}^3$.

Fig. 27 shows the cross-section through the P(1) - N(3) bond. The electron density is elongated in the direction normal to the plane of the ring suggesting the contribution of the π bonding into the P_3N_3 ring. Another noticeable observation is elongation of the electron density on the inside of the phosphazene ring, which could be explained by the π' bonding contribution.

The compound contains five aziridinyl rings, four of which attached to P(1) and P(3) have bow tie I and the fifth on P(2) has bow tie II conformations. The dynamic deformation density maps of two aziridinyl groups are presented in Fig. 28. The main

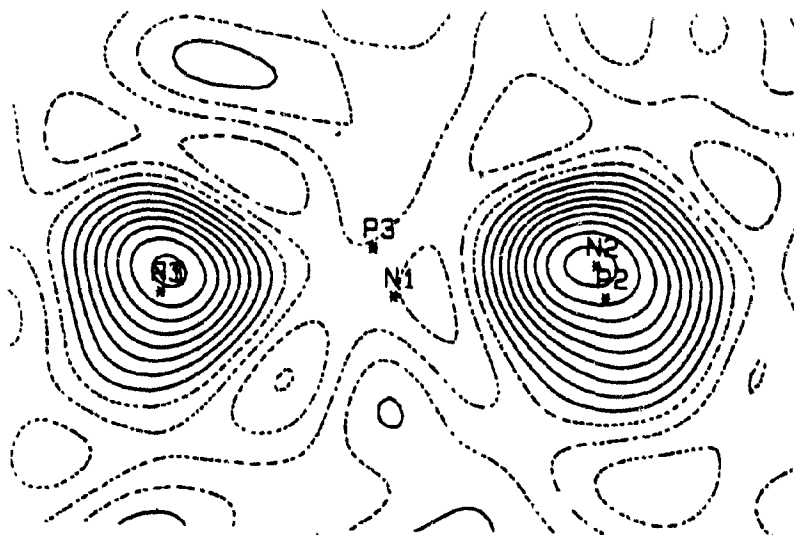


Fig. 27. $X - X_{BO}$ map on a plane bisecting the P - N bonds. Contours are at $0.08 \text{ e}/\text{\AA}^3$.

features of all five rings are similar. The bonding density maxima appear clearly outside the triangle sides, confirming the 'bent bond' concept for such three-membered rings. Similar observation was also made by Cameron *et al.* in aziridinyll compound¹³ and Seiler *et al.* in cyclopropane⁷⁸. The electron density of C - C and C - N bonds displaced slightly from the centre of the bond towards the more electro-negative nitrogen atom indicates that the aziridinyll ring may possess little π complex character. Two unexpected peaks at the carbon atoms are visible. These peaks were also seen by Seiler who quotes theoretical work by Wiberg *et al.*⁷⁹ to explain them. The gross features of the deformation density maps of az rings in both $X - X_{BO}$ (not shown) and multipole deformation density studies are as expected, however the finer details lack quality.

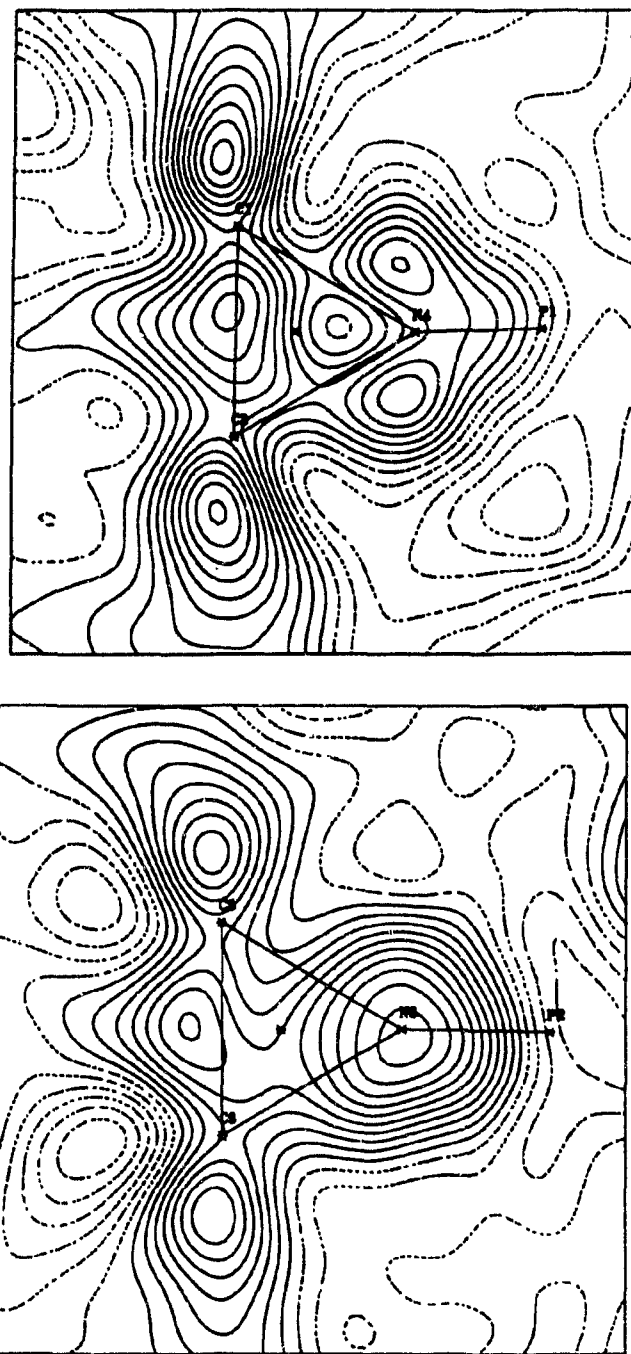


Fig. 28. The dynamic deformation electron density maps on a plane through the aziridinyI rings. upper diagram: - bow tie I conformation; lower diagram - bow tie II conformation. Contour intervals are at 0.02 e/Å³.

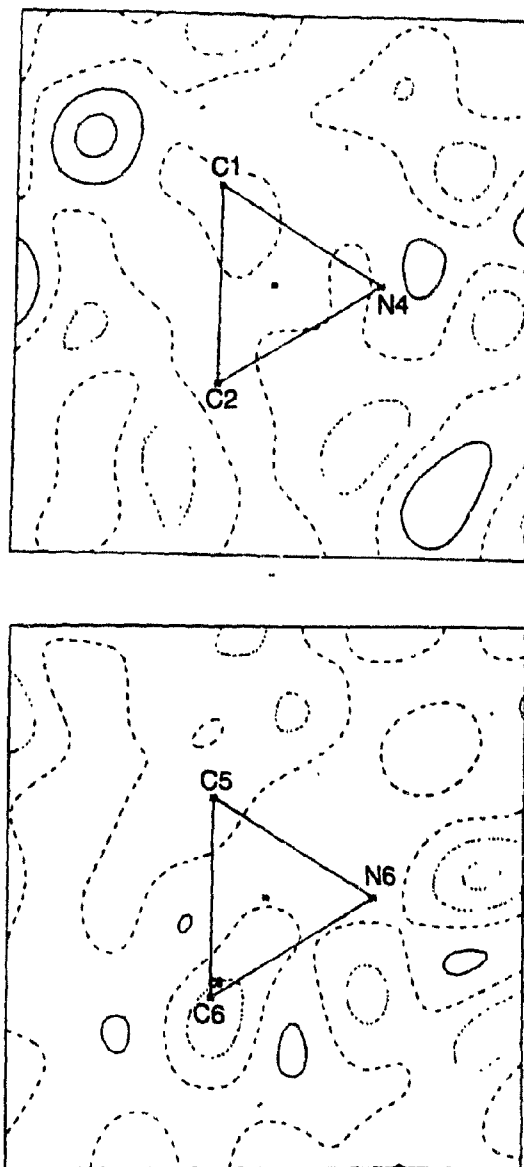


Fig. 29. The residual electron density maps on a plane through the aziridiny rings (the maps of only two az rings are shown), upper diagram - bow tie I conformation; lower diagram - bow tie II conformation. Contours are at $0.1 \text{ e}/\text{\AA}^3$.

This may arise from the large temperature factors of the N and C atoms of the az rings (see in Table 70, Appendix 1). Their residual maps (Fig. 29) are almost featureless.

Fig. 30 shows the electron density maxima in the exocyclic P - N bond and the lone pair electron density of the nitrogen atom. In comparison with the bonding density, the lone pair electron density is significantly low and at about 120° angle to the P - N bond.

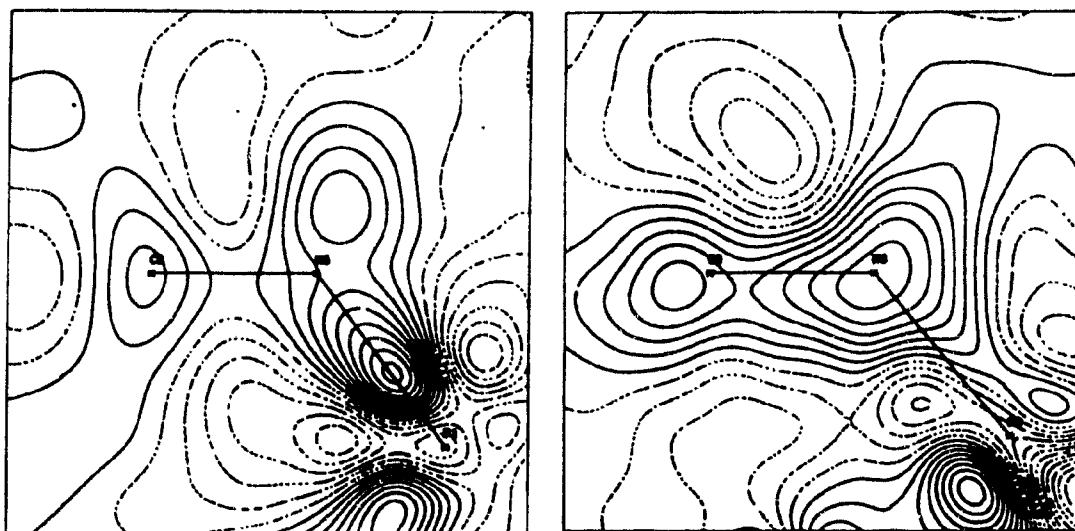


Fig. 30. The maps through the plane perpendicular to the plane of the rings, bisecting the C - N - C angle. Contours are at 0.04 e/Å³.

2.2.6. Summary

Room temperature structural investigation of the $N_3P_3(az)_5Cl$ shows that the bond lengths and angles of both phosphazene and aziridiny ring skeletons are normal.

The deformation density results of the phosphazene skeleton in $P_3N_3(az)_5Cl$ compound supports the Dewar Island model. Each P has a node, and the electron density spreads from one P - N bond through the nitrogen to the second N - P bond. The effect of chlorine on the ring is also noticeable. However, in comparison with the P_3N_3 ring electron density of the $P_3N_3(az)_6.C_6H_6$ ¹³ clathrate, lower electron density is observed inside the phosphazene ring in the compound, $N_3P_3(az)_5Cl$. The best possible explanation is that the atom Cl forms an exocyclic π bond with P atom and disrupts the π' bonding of the ring framework by localizing the lone pair on endocyclic nitrogen atoms. The deformation electron density maps of all aziridinal rings are very similar and comparable with the observation of Cameron *et al.* in compound $P_3N_3(az)_6.C_6H_6$ clathrate.

3. Hydrogen Bonding to Aromatic π Systems in Crystals

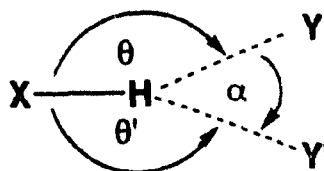
3.1. Introduction

The concept of hydrogen bonding was first introduced to a wider audience by Pauling in the first edition of his book, 'The Nature of the Chemical Bond', in 1939⁸⁰. Subsequently, hydrogen bonding was accepted as an important cohesive force between molecules or ions which contain a proton donor group X - H and a proton acceptor group Y, where X can be any electronegative atom, e.g. O, N, S, F or C, and the acceptor group is a lone electron pair on an electronegative atom or a π -electron orbital of an unsaturated system. Proof of the existence of an X - H...Y hydrogen bond depends on the demonstration that the distance H...Y is less than the sum of $W_H + W_Y$ and that the angle θ lies between 110° and 180° , where W_H and W_Y are the van der Waals radii of the H and acceptor atoms, respectively, and θ is the X - H...Y angle.

Two distinct types of X - H...Y bonds have been observed in the solid state, normal and branched (bifurcated and trifurcated) hydrogen bonds. The most common is the normal hydrogen bond, where the hydrogen atom interacts directly with an acceptor atom. Although in many places this kind of hydrogen bond is described as a linear H-bond, an X - H...Y angle of 180° is seldom observed. Because of the "softness" of the hydrogen bond bending force constants, there is a balance between the ideal value of 180° and the greater probability of bonds making a smaller angle. A typical value of the X - H...Y angle is around 165° .

A bifurcated hydrogen bond (II) is formed as a compromise between the molecular packing and the hydrogen bond configuration requirements and is most common in crystal structures which are proton deficient. It is defined as an interaction between

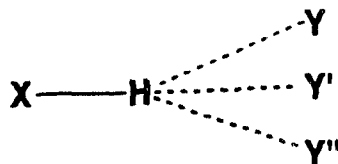
the covalently bonded hydrogen atom of a donor X - H group and two acceptor atoms Y and Y'. The criterion for a bifurcated hydrogen bond is that the hydrogen atom lies in or close to ($< 0.2 \text{ \AA}$) the plane defined by X, Y and Y'. The sum of the angles



(II)

$\theta + \theta' + \alpha$ should also be approximately 360° . In symmetric bifurcated hydrogen bonds, the two H...Y contacts are equal; the two X - H...Y angles are equal and typically in the $125\text{--}140^\circ$ range. An asymmetrically bifurcated bond can be described as one bent hydrogen bond perturbed by an additional long range bent hydrogen bond. In this case, H...Y distances differ by as much as $1.0 \text{ \AA}$ and one X - H...Y angle will be close to 180° whereas the other angle will be close to 90° .

A trifurcated hydrogen bond (III) is defined as one in which the proton interacts with three potential hydrogen bond acceptor atoms, not necessarily all of the same type. The geometrical definition is less rigorous than that for bifurcated hydrogen bonds since it requires only that the X - H...Y, Y', Y'' angles all be greater than 90° . There are only



(III)

few examples of genuine trifurcated hydrogen bonding in the literature; this may be an underestimate caused by the use of arbitrary van der Waals radii cut-offs.

The possibility of hydrogen bonds forming between X - H and π electron donors in solution was recognised in the 1940's. Since then, many spectroscopic⁸¹⁻¹⁰⁵ and theoretical studies¹⁰⁵⁻¹¹⁵ investigating such bonding interactions have been reported. However, prior to our crystallographic investigations of such bonding in solids¹¹⁶⁻¹¹⁹, reports on X - H... π bonds were relatively few and those involving aromatic π systems had been even fewer¹²⁰⁻¹³⁰. In many cases, this feature, although present, went unreported by the authors. This could be because of lack of attention to hydrogen bonding or perhaps it was noticed but not reported because some authors may not have been comfortable with the idea of an X - H... π interaction.

The first demonstration of the existence of an X - H... π (aromatic) bond in a crystal came from a calorimetric-cum-crystallographic study of $[\text{NH}_4][\text{BPh}_4]$ ¹⁴. Later such bonding was confirmed and elaborated on by Knop *et al.*¹²³, who showed from their ir spectroscopic investigation that the H(N)... π interaction is very weak and is associated with an estimated activation energy for the $[\text{NH}_4]^+$ reorientation on the order of only about 0.5 kcal/mole. The sporadic reports on the crystallographic evidence of H(X)... π interaction that have appeared in the literature since then focus mainly on the O - H... π bonds found in peptides or analogous compounds. However, the known examples are too few for a better understanding of this type of bonding interaction, in particular as regards its geometric aspects, and they are too diverse to shed light on the scope of X - H... π (aromatic) interactions.

3.1.1. Location of the Hydrogen Atom

It is difficult to describe the nature of the hydrogen bonding in $X - H \cdots \pi$ systems without at least some knowledge of the location of the hydrogen atoms with respect to their nearest neighbours. In cations which contain $>N^+ - H$ or conjugated $-NH_2$ donor groups, the positions of these hydrogens as well as the orientations of the corresponding $N - H$ vectors, are known with a reasonable degree of certainty from geometrical considerations. However, for groups where there is rotational freedom, such as $-N^+H_3$, the hydrogen positions can be established only by accurate x-ray crystal structure analyses or, better, by neutron diffraction. The exact location of the hydrogen atoms of water molecules is often even more difficult, since these small molecules frequently exhibit both orientational and translational disorder.

It is an unfortunate limitation of crystallography that the position of a hydrogen atom cannot be located accurately by x-ray diffraction. The ability of an atom to scatter or diffract x-rays is proportional to the number of electrons it contains. The hydrogen atom nominally has only one electron and consequently diffracts very little. Its position, therefore, cannot be determined accurately even in compounds where the remaining atoms are the relatively light elements carbon, nitrogen and oxygen. If the quality of the data is very high, then, in the final stages of an x-ray crystal structure analysis, hydrogen positions can be estimated from a Fourier difference map. However, x-ray analysis gives the thermally averaged maxima of the atomic electron density; thus, the accuracy with which hydrogen atoms are located is low even in the best structures (the precision ranges from ~ 0.1 to ~ 0.3 Å, compared with ~ 0.005 Å for nonhydrogen atoms). Low temperature data collection may improve this situation somewhat.

Under these circumstances, the presence of a hydrogen bond is inferred from the

x-ray diffraction results only when an abnormally close approach of donor and acceptor atoms (or groups) is found. The total length, $d(X...Y)$ in $X - H...Y$, is used rather than the actual hydrogen bond length, $d(H...Y)$; when the sum of the van der Waals radii for X and Y is found to be less than $d(X...Y)$, a hydrogen bond is assumed to be present. However, the correct $X...Y$ "cut-off" criteria based on van der Waals radii, are not unambiguously defined. In the literature, there are three commonly used scales of van der Waals radii: i) Pauling¹, ii) Bondi¹³¹ and iii) Allinger¹³².

atoms	van der Waals Radii (Å)		
	Pauling	Bondi	Allinger
H	1.2	1.20	1.50
C	1.2	1.70	1.75
N	1.5	1.55	1.70
O	1.4	1.52	1.65
Cl	1.8	1.75	1.95

The question is, which van der Waals radii values should be used as appropriate for considering an $X...Y$ distance indicative of a hydrogen bond? Many authors believe that criteria based on the Pauling van der Waals radii are too restrictive. The Bondi van der Waals radii or the Allinger van der Waals radii may be more suitable as "cut-off" values for $X...Y$ distances between neighbouring atoms of donor and acceptor groups. Another problem is that the van der Waals surfaces for atoms with oriented lone pairs, such as oxygen and nitrogen, are not spherical¹³³⁻¹³⁴. Commonly reported van der Waals radii may not be directly applicable in this case. The calculated van der Waals radius of H is also ill-defined because of the diffuse and easily polarizable nature of the hydrogen atom electron density¹³².

The position of a hydrogen atom can be established with confidence using neutron diffraction. Neutrons are scattered by the nuclei of the atoms in a crystal. The absolute scattering amplitude of a proton, the hydrogen nucleus, is about one-half of, and that by the deuterium nucleus comparable to, the scattering amplitudes of carbon, nitrogen and oxygen. Hence the position of a H or D atom can in principle be located with a high degree of accuracy by neutron diffraction. Moreover, the nucleus is small compared with the neutron wavelengths (~ 1.0 to 1.5 Å), so the scattering power does not fall off with scattering angle as it does in x-ray diffraction. All this makes neutron diffraction analysis capable of high-precision studies.

There are several problems associated with neutron diffraction study of organoammonium tetraphenylborate compounds. It is difficult to grow the large single crystals necessary for neutron diffraction. The number of hydrogen atoms is comparable to or sometimes exceeds the number of non-hydrogen atoms in the structure which may create a large incoherent background scattering cross-section that can adversely affect the signal-to-noise ratio. For this reason, a completely deuterated sample may be required. The B atom has a high thermal neutron absorption coefficient.

Comparing cases where a crystal structure has been determined accurately by both x-ray and neutron diffraction, the difference between the hydrogen atom positions found by the two methods is about 0.25 Å¹³⁵. The X - H distances obtained by x-ray analysis are always $0.1 - 0.2$ Å shorter than those found in neutron diffraction determinations¹³⁶. For example, C - H distances found in x-ray and neutron diffraction studies are 0.95 Å and 1.08 Å, respectively. In the absence of neutron diffraction results, to describe the hydrogen bonding geometry, it is instructive to normalize the X - H distances to the distances derived from neutron structures of similar compounds (i.e., C - H = 1.08 Å,

N - H = 1.02 Å and O - H = 1.00 Å).

3.1.2. Directionality and Length of the X - H... π Bond

Since the attractive force of the hydrogen bond is primarily electrostatic, the strong directionality associated with covalent bonding is not expected. If it is observed with respect to the acceptor atom, or, more precisely, an electron lone pair localized on an atom, the description of the bond geometry in a normal X - H...acc hydrogen bond is rather simple. The X...acc and H...acc distances ideally are distances between atomic nuclei, although their accuracy will depend primarily on the confidence and accuracy of location of the hydrogen. However, the dimensional properties of the X - H...acc bond are not so simple to describe when the acceptor is a delocalised π system extending over several atoms because the nature and position of the acceptor are ill-defined. In such cases, it may be difficult to identify the acceptor nucleus at which the X - H vector would preferentially point and which would constitute the terminal point of the H...acc segment to define the H...acc bond length.

To appreciate the problems associated with defining the geometry and dimensions of a X - H... π (aromatic) bond, it is instructive to examine the calculated electron-density map of C_6H_6 (Figs. 31-32)^d. The electron density distribution above and below the C_6 ring skeleton is relatively flat. In the plane C, which is perpendicular to the molecular plane δ_h and passes through neighbouring carbon nuclei, the electron density distribution is flat up to 0.4 au = 2.7 e/Å³ (about 1 Å above δ_h), even for the π density. Planes B and D, which are also perpendicular to δ_h and pass through the centre of the

^d The theoretical electron density maps of the benzene molecule were calculated by Prof. R.J. Boyd and Mr. Jian Wang; their contribution is gratefully acknowledged.

ring (π_c), reveal significant zigzag electron density > 0.008 au contours above π_c (at 1 Å above δ_h). The shapes of these higher-density contours are such that the region of low electron density toward the centre is relatively narrow and thus not entirely exclusionary for H-bonding.

High directional selectivity of the X - H... π bond cannot be expected from the density distribution in C_6H_6 (Figs. 30 - 31). *Ab initio* molecular orbital studies of isolated $H_2O-C_6H_6$ ^{103, 105, 108-109, 112-115}, $NH_3-C_6H_6$ ^{108-109, 112-113}, and other such pairs also

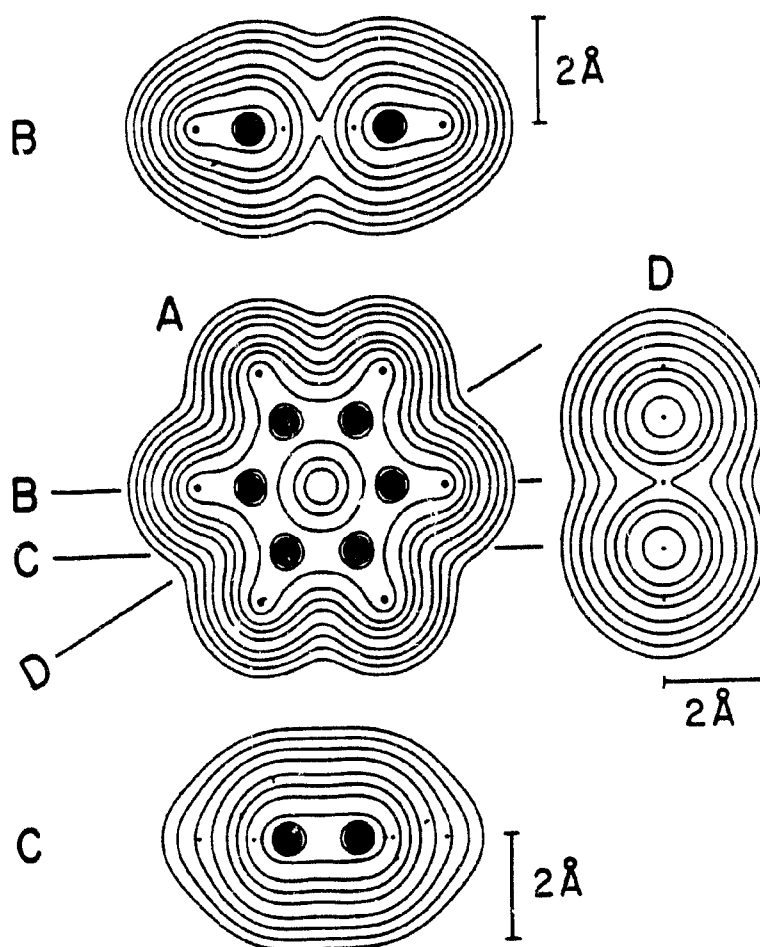


Fig. 31. Total electron density distribution in the benzene molecule, calculated using *ab-initio* 6-31G**. A, distribution in the molecular plane; B-D, distributions in planes perpendicular to the molecular plane. The outermost contour represents 0.002 au and is followed by 0.004, 0.008, 0.02, 0.04, 0.08 au etc. contours are at 1 au ($= 6.749 \text{ e}/\text{\AA}^3$).

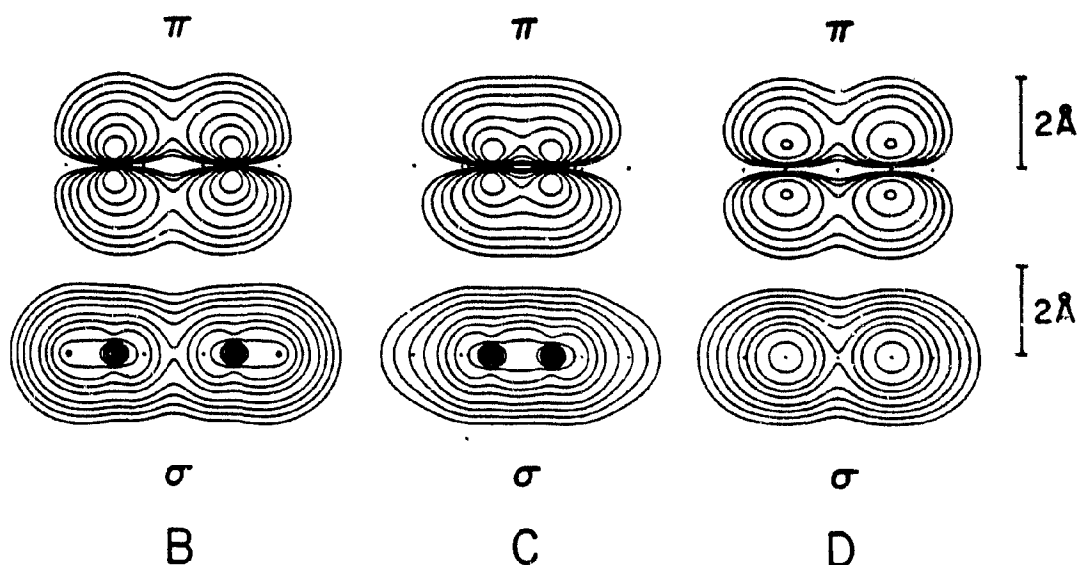


Fig. 32. Electron density distribution in the σ and π systems of the benzene molecule (6-31G**) in planes B-D of Fig. 31.

support this view. Recent calculations using the $\text{H}_2\text{O}-\text{C}_6\text{H}_6$ complex system indicate that the H_2O molecule is situated above the C_6 ring skeleton, with the oxygen atom on or somewhat off (sterically or dynamically) the C_6 axis. The O - H vectors point simultaneously and probably asymmetrically at the annular electron cloud above the ring skeleton. The potential well over the C_6H_6 surface is flat, which makes benzene an excellent target as a hydrogen bond acceptor and also permits free rotation of the H_2O molecule over the C_6H_6 surface with respect to the C_6 axis. These findings are consistent with the expectation from the electron-density distributions shown in Figs. 31 and 32, concerning the lack of a strong directional preference of the H bond. The $\text{O}\cdots\pi_c$ distance in the complex ranges from 3.2 to 3.4 Å, which is in good agreement with the corresponding distances observed in crystals. For the $\text{NH}_3-\text{C}_6\text{H}_6$ complex, the

conclusion is less compelling. The interaction between H(N) and the π electron cloud of the benzene occurs to a lesser extent than it does in the $\text{H}_2\text{O}-\text{C}_6\text{H}_6$ complex. The estimated $\text{N}\dots\pi_c$ distance is longer, about 3.66 Å from the benzene molecular plane.

In the theoretical studies of isolated donor-acceptor pairs described above, there are no external forces acting on the component molecules and thus they can move freely and settle in an orientation that corresponds to the minimum energy of the system. As a result, the direction of the bond is the outcome of the relative orientation of the molecules. On the other hand, in crystals the donor-acceptor pair is not isolated and constraints arise from packing and from multiple choices. The environment and relative orientation in a crystal are largely determined by packing efficiency (and Coulombic energy in ionic crystals) and there may be more than one acceptor available for bond formation to a given X - H. As a result, the H-bonding network formed is a compromise; a wide spread in the distribution of hydrogen bond lengths and branched hydrogen bonds are common in crystals.

As previously discussed, location of hydrogen positions with high accuracy is not possible by x-ray crystallography. Under these circumstances, the distances, $d[\text{H}(\text{X})\dots\text{C}]$ and $d[\text{H}(\text{X})\dots\pi_c]$, are not very reliable although they may be informative. The values which are known with considerable accuracy are the mean distance of the X atom to the ring carbons, $\bar{d}(\text{X}\dots\text{C})$, and the distance from X to the centre π_c of the associated ring, $d(\text{X}\dots\pi_c)$. However, a discussion of X - H... π bonding, based on distances from the ring centre, is artificial if the X - H vector, in reality, points elsewhere in the ring. Viswamitra *et al.*¹³⁷ have recently published a survey of the compounds containing X - H...phenyl bond(s) that have been reported in the Cambridge Structural Database. They observed that in the largest number of cases, the hydrogen atom is directed into

the middle of the aromatic ring system (i.e. centroid type). They also found at least two structural reports^{138,139}, where the X - H group makes a close approach to only two adjacent carbons of a particular phenyl group (i.e. edge type). In this situation, the X - H... π_c bond angle, ω , is not very useful; the angle ϕ which is formed by the N - H vector with the ring plane, also needs to be examined. Furthermore, since the N - H vector can approach the ring from a variety of directions, the angle ψ , formed by the projection of the N - H vector onto the ring plane and the C(α) - C(δ) line, should be examined in conjunction with the angles ω and ϕ , to accurately describe the X - H... π bonding.

Table 11 summarizes the abbreviation used for 16 organoammonium tetraphenylborate compounds that have been studied crystallographically. These compounds, plus a few cited literature structures, provide a sufficient variety of H... π bonding interactions on which to base a classification of bond types and geometries.

Table 11. Crystal structures discussed in this work.

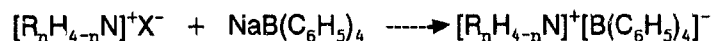
	Compound	Abbreviation	Reference
		This investigation	
1	$[\text{Me}_2\text{C}=\text{NHMe}]^+\text{TB}^-$	ImATB	
2	$[\text{Me}_2\text{C}=\text{NHEt}]^+\text{TB}^-$	ImCTB	
3	$[\text{MeEtC}=\text{NHMe}]^+\text{TB}^-$	ImDTB	
4	$[\text{Me}_2\text{C}=\text{NH}(-\text{CH}_2\text{CH}_2\text{Ph})]^+\text{TB}^- \cdot \text{H}_2\text{O}$	ImETBw	
5	Quinuclidinium TB^-	QTB	
6	Dabco H^+TB^-	DaHTB	
7	$(\text{Ph}_3\text{B})\text{NH}[(\text{CH}_2)_2]_2\text{NHMe}^+\text{TB}^- \cdot \text{Me}_2\text{CO}$	1MPzBTB.Me ₂ CO	
8	2,2'-Bipyridinium TB^-	BPTB	
9	1,10-Phenanthroline TB^-	PTB	
10	$\text{Me}_2\text{NH}_2^+\text{TB}^- \cdot \text{MeCN}$	2MTB.MeCN	
11	$(\text{iso-Pr})_2\text{NH}_2^+\text{TB}^-$	2PiTB	
12	Azoniacycloheptane TB^-	AC7TB	
13	Triamterene TB^-	TMTB	
14	1-Adamantammonium $\text{TB}^- \cdot \text{H}_2\text{O}$	[1-Ad]TBw	
15	1,3-Adamantammonium $2\text{TB}^- \cdot \text{MeCN}$	[1,3-Ad]2TB.MeCN	
16	Tetraaqualithium TB^-	LiTBw	
		Cited from the literature	
17	$\text{Me}_3\text{NH}^+\text{TB}^-$ ($\text{P}2_1$, $Z = 2$)	3MTB	117
18	$\text{Et}_3\text{NH}^+\text{TB}^-$ ($\text{P}2_1$, $Z = 2$)	3ETB	117
19	$n\text{-Bu}_3\text{NH}^+\text{TB}^- \cdot \text{H}_2\text{O}$ ($\text{P}2_1/n$, $Z = 4$)	3BnTBw	122
20	$\text{Me}_2\text{NH}_2^+\text{TB}^- \cdot \text{Et}_2\text{CO}$ ($\text{P}2_1/n$, $Z = 4$)	2MTB.Et ₂ CO	117
21	$\text{Et}_2\text{NH}_2^+\text{TB}^-$ ($\text{P}2_12_12_1$, $Z = 4$)	2ETB	117
22	$[(\text{C}(\text{NH}_2)_3]^+\text{TB}^- \cdot \text{H}_2\text{O}$ ($\text{P}2_1/c$, $Z = 4$)	GTBw	117
23	$\text{MeNH}_3^+\text{TB}^-$ ($\text{Pna}2_1$, $Z = 4$)	1MTB	117
24	$\text{EtNH}_3^+\text{TB}^-$ ($\text{P}2/c$, $Z = 8$)	1ETB	117
25	NH_4^+TB^- ($I42m$, $Z = 2$)	ATB	123

TB^- = tetraphenylborate anion, Im = iminium cation, Q = quinuclidinium cation, DaH⁺ = singly protonated 1-aza-4-azoniabicyclo[2.2.2]octane cation, 1MPzB = N-triphenylboro-N'-Me-piperazinium cation, BP = singly protonated 2,2'-bipyridinium cation, P = singly protonated 1,10-phenanthroline cation, TP = 2,2',2''-tripyrindinium cation, TM = 2,4,7-triamino-6-phenylpteridinium cation, G = guanidinium cation.

3.2. Experimental

3.2.1. Preparation

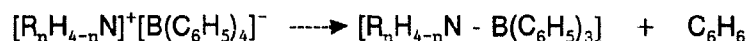
The organoammonium tetraphenylborates were prepared by mixing an aqueous solution of sodium tetraphenylborate with an aqueous solution of an alkylammonium halide salt in the required stoichiometric ratio. The resulting white precipitate was filtered off, washed with water, dried in air at room temperature, and recrystallised from a suitable solvent (ketone/water, acetonitrile/water). The main purpose of the water added during recrystallization was to reduce the rate of evaporation. The proportion of the organic solvent to water was adjusted in the following way. The precipitate was first dissolved in acetone or acetonitrile and then water was added dropwise until precipitation began to occur. Finally, enough organic solvent was added to only just redissolve the solid formed. The resulting solution was then kept at room temperature for slow evaporation, which yielded colourless crystals of the different organoammonium tetraphenylborate salts.



When attempts were made to recrystallise the microcrystalline precipitate of $[MeNH_3]TB$, $[Me_2NH_2]TB$, $[EtNH_3]TB$ and $[(\beta\text{-phenethyl})^+H_3]TB$ salts from ketone/water a series of corresponding iminium salts were produced.



The formation of the compounds DaHTB, 1MPzBTB.Me₂CO, BPTB and PTB deserves some discussion. In all these cases, the intended product was [Cation][TB]₂. An aqueous solution of the organic amine (Dabco, N-Me-piperazine, 2,2'-bipyridyl and 1,10-phenanthroline) was acidified with HCl and then combined with an aqueous solution of NaBPh₄ (organic amine: NaBPh₄ = 1:2). In spite of the stoichiometry the precipitates that formed were all the 1:1 rather than 1:2 salts. The most surprising result was obtained in the case of 1MPzBTB.Me₂CO where elimination of a phenyl ring from a TB anion as benzene had occurred either in the initial precipitation or during recrystallization from an acetone/water solution at room temperature. Abstraction of a phenyl ring from the tetraphenylborate anion usually occurs on heating or on pyrolysis, so it was unexpected to find that this process can occur at room temperature.



A slightly different procedure was adopted for the preparation of LiTBw. It was known that both LiCl and NaBPh₄, but not NaCl, are soluble in acetone. Therefore, acetone was used as the solvent in the first step of the synthesis. LiCl and NaBPh₄ (in the molar ratio 1:1) were dissolved separately in acetone and the two solutions combined. The precipitate of NaCl that formed was filtered off and the filtrate evaporated almost to dryness. The solid was redissolved in acetone and the residue was again removed by filtration; this step was repeated twice to make sure that all of the NaCl have been removed. The final solid was redissolved in water and kept at room temperature for slow evaporation. After a few days, colourless, chunky crystals of LiTBw were obtained.

3.2.2. IR Spectra

The FT-ir spectra of the iminium salts(1-4, 27) and of BPTB, PTB and LITBw have been recorded using fluorolube mulls on CaF_2 plates^o. To eliminate coupling and Fermi resonance effects on the frequency of vibration, the isotopic dilution technique has been employed to study the O - H... π interaction in a LITBw sample with an estimated 3% of the H_2O hydrogens replaced by deuterium.

3.2.3. Structure Refinement

In each case, a good quality crystal was selected for data acquisition. All measurements were made on a Rigaku AFC5R or CAD4 or Picker diffractometer with graphite monochromated $\text{MoK}\alpha/\text{CuK}\alpha$ radiation. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 20 - 25 carefully centred reflections. The space group was confirmed by statistical analysis of intensity distribution and the successful solution and refinement of the structure.

The data were collected using the ω -2 θ scan technique to a maximum 2 θ value of 60.0°. Periodic checks of the intensities of three representative reflections showed no significant variation during the data collections, indicating crystal and electronic stability.

The data were scaled and corrected for Lorentz and polarization effects using routine procedures. An empirical absorption correction was applied using either DIFABS¹⁴⁰ or a ψ -scans.

^o The FT-ir spectra were recorded by Dr. Michael Falk and Mr. Pirig Seto at National Research Council, and their contribution is gratefully acknowledged.

The structures were solved by direct methods⁴⁷. The non-hydrogen atoms were refined first isotropically and then anisotropically. The hydrogens attached to carbon atoms were placed in their geometrically calculated positions ($C - H = 1.08 \text{ \AA}$). In the cations containing nitrogen bonded to one or two hydrogens, the hydrogen(s) was located either from the Fourier difference map or placed geometrically. For compounds in which there were three H atoms on the nitrogen, at least one H(N) was located from the Fourier difference map and the rest were generated geometrically. In all cases, the N - H distances were constrained to $1.02 \text{ \AA}$. The hydrogens of water molecules were located from the Fourier difference map and the O - H distances were then constrained to $1.0 \text{ \AA}$. In ImATB, ImCTB, and 2MTB.MeCN the hydrogens were refined isotropically; in the rest, the hydrogen positions were kept fixed during refinement and assigned fixed isotropic temperature factors of $1.2 \times B_{eq}$ of the atom to which each was bonded. Experimental details are summarised in Table 12 - 19. For atomic coordinates and selected bond lengths and angles of nonhydrogen atoms, see individual structures. Temperature factors and hydrogen atom coordinates are gathered in Appendix 2.

All crystallographic calculations were performed using the TEXSAN⁵² or SHELX76⁷⁶ programs. The programs PLUTO¹⁴¹ and ORTEP⁵³ were used for drawing the diagrams. In an attempt to explain the thermal motion of the atoms of the organoammonium cations, a TLS program¹⁴² was used.

It should be pointed out that, in general, organoammonium tetraphenylborates are weak scatterers. Strong reflections above $\theta = 20^\circ$ (for Mo radiation) are rare. Even after data collection up to $\theta = 30^\circ$, the ratio of the number of reflections used to the number of parameters refined (d/p) rarely exceeded 5. In several cases, attempts were made to collect the data at lower temperatures but this improved the d/p ratio only marginally.

Table 12. Physical properties and crystal data of ImATB and ImCTB.

Formula	BC ₂₈ H ₃₀ N	BC ₂₉ H ₃₂ N
Formula weight	391.4	405.4
Crystal size (mm ³)	0.27 x 0.35 x 0.25	0.40 x 0.50 x 0.20
Crystal system	orthorhombic	monoclinic
Space group	<i>Cmcm</i> (No. 63)	<i>P2₁/n</i> (No. 14)
<i>a</i> (Å)	10.747(2)	12.146(3)
<i>b</i> (Å)	15.641(4)	14.099(2)
<i>c</i> (Å)	13.453(4)	14.177(3)
α (°)	90	90
β (°)	90	96.23(2)
γ (°)	90	90
<i>V</i> (Å ³)	2261(2)	2413(2)
<i>Z</i>	4	4
<i>d</i> _{calc} (g/cm ³)	1.150(1)	1.116(1)
<i>F</i> (000) (<i>e</i>)	840	872
Diffractometer	CAD4	RIGAKU
μ (cm ⁻¹)	0.59	0.60
θ range (°)	3 - 25	2 - 23
Reflections:		
total measured	1474	3725
unique total	1105	3539
unique used	624 (<i>I</i> > 3 σ (<i>I</i>))	1605 (<i>I</i> > 3 σ (<i>I</i>))
Parameters refined; <i>d/p</i>	104; 6.0	180; 5.7
Absorption corrections (min, max)	0.75, 1.21	0.92, 1.04
Weighting scheme	SHELX	σ -weight
100 <i>R</i> , 100 <i>R</i> _w	5.47, 5.78	4.18, 3.83
G.O.F.	2.41	1.67
Residual <i>e. d.</i> (min, max) (<i>e</i> /Å ³)	-0.16, 0.23	-0.18, 0.14

Table 13. Physical properties and crystal data of ImDTB and ImETBw.

Formula	$\text{BC}_{29}\text{H}_{32}\text{N}$	$\text{BC}_{35}\text{H}_{36}\text{NO}$
Formula weight	405.4	497.5
Crystal size (mm^3)	0.27 x 0.20 x 0.40	0.80 x 0.05 x 0.40
Crystal system	orthorhombic	monoclinic
Space group	Cmc2_1 (No. 36)	C2/c (No. 15)
a ($\text{\AA}$)	10.967(5)	30.747(10)
b ($\text{\AA}$)	15.642(5)	9.845(4)
c ($\text{\AA}$)	13.430(4)	19.741(5)
α ($^\circ$)	90	90
β ($^\circ$)	90	97.12(2)
γ ($^\circ$)	90	90
V ($\text{\AA}^3$)	2304(3)	5930(6)
Z	4	8
d_{calc} (g/cm^3)	1.169(2)	1.115(1)
$F(000)$ (e)	872	2128
Diffractometer	RIGAKU	RIGAKU
μ (cm^{-1})	0.60	0.60
θ range ($^\circ$)	2 - 23	2 - 30
Reflections:		
total measured	1871	6117
unique total	1770	5957
unique used	708 ($ I > 3\sigma(I)$)	1378 ($ I > 3\sigma(I)$)
Parameters refined; d/p	175; 4.1	343; 4.0
Absorption corrections (min, max)	0.73, 1.24	0.59, 1.39
Weighting scheme	SHELX	unit
100R, 100R _w	4.79, 5.44	4.99, 5.14
G.O.F.	1.26	2.51
Residual ρ d. (min, max) ($\text{e/\AA}^3$)	-0.20, 0.30	-0.18, 0.19

Table 14. Physical properties and crystal data of QTB and DaHTB.

Formula	BC ₃₁ H ₃₄ N	BC ₃₀ H ₃₃ N ₂
Formula weight	431.4	432.4
Crystal size (mm ³)	0.05 x 0.20 x 0.40	0.20 x 0.20 x 0.15
Crystal system	orthorhombic	orthorhombic
Space group	<i>Pnma</i> (No. 62)	<i>Pnma</i> (No. 62)
<i>a</i> (Å)	18.426(5)	18.208(3)
<i>b</i> (Å)	13.334(1)	13.303(3)
<i>c</i> (Å)	9.994(7)	9.987(2)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
<i>V</i> (Å ³)	2455(3)	2419(1)
<i>Z</i>	4	4
<i>d</i> _{calc} (g/cm ³)	1.167(2)	1.187(1)
<i>F</i> (000) (e)	928	928
Diffractometer	PICKER	RIGAKU
μ (cm ⁻¹)	4.62	0.63
θ range (°)	6 - 60	2 - 25
Reflections:		
total measured	2062	2448
unique total	2062	2448
unique used	799 (<i>I</i> > 3 σ (<i>I</i>))	1061 (<i>I</i> > 3 σ (<i>I</i>))
Parameters refined; <i>d/p</i>	154; 5.2	164; 6.5
Absorption corrections (min, max)	0.59, 1.61	0.95, 1.00
Weighting scheme	unit	unit
100 <i>R</i> , 100 <i>R</i> _w	4.88, 5.05	4.10, 4.20
G.O.F.	2.58	2.03
Residual e. d. (min, max) (e/Å ³)	-0.17, 0.16	-0.16, 0.14

Table 15. Physical properties and crystal data of 1MPzBTB.Me₂CO and BPTB.

Formula	B ₂ C ₅₀ H ₅₄ N ₂ O	BC ₃₄ H ₂₉ N ₂
Formula weight	720.6	476.4
Crystal size (mm ³)	0.25 x 0.15 x 0.10	0.55 x 0.35 x 0.30
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /n (No. 14)	P2 ₁ /n (No. 14)
<i>a</i> (Å)	9.819(3)	9.254(2)
<i>b</i> (Å)	17.779(3)	14.102(9)
<i>c</i> (Å)	24.223(3)	20.304(2)
α (°)	90	90
β (°)	95.46(2)	92.88(1)
γ (°)	90	90
<i>V</i> (Å ³)	4193(3)	2646(2)
<i>Z</i>	4	4
<i>d</i> _{calc} (g/cm ³)	1.142(1)	1.196(1)
<i>F</i> (000) (e)	1544	1008
Diffractometer	RIGAKU	RIGAKU
μ (cm ⁻¹)	0.62	0.62
θ range (°)	2 - 25	2 - 23
Reflections:		
total measured	7505	4145
unique total	7031	3869
unique used	1882 (<i>I</i> > 3 σ (<i>I</i>))	1619 (<i>I</i> > 3 σ (<i>I</i>))
Parameters refined; <i>d/p</i>	496; 3.8	334; 4.9
Absorption corrections (min, max)	0.96, 1.00	-
Weighting scheme	unit	unit
100 <i>R</i> , 100 <i>R</i> _w	4.61, 4.61	3.62, 3.46
G.O.F.	1.76	1.83
Residual <i>e. d.</i> (min, max) (e/Å ³)	-0.17, 0.33	-0.15, 0.09

Table 16. Physical properties and crystal data of PTB and 2MTB.MeCN.

Formula	$\text{BC}_{36}\text{H}_{29}\text{N}_2$	$\text{BC}_{28}\text{H}_{31}\text{N}_2$
Formula weight	500.5	406.4
Crystal size (mm^3)	0.10 x 0.35 x 0.50	0.30 x 0.30 x 0.40
Crystal system	monoclinic	monoclinic
Space group	$\text{P2}_1/\text{n}$ (No. 14)	$\text{P2}_1/\text{a}$ (No. 14)
a ($\text{\AA}$)	11.217(4)	13.481(3)
b ($\text{\AA}$)	13.824(5)	13.478(4)
c ($\text{\AA}$)	18.316(4)	14.428(2)
α ($^\circ$)	90	90
β ($^\circ$)	107.74(2)	109.75(1)
γ ($^\circ$)	90	90
V ($\text{\AA}^3$)	2705(1)	2467(2)
Z	4	4
d_{calc} (g/cm^3)	1.229(1)	1.094(1)
$F(000)$ (e)	1056	872
Diffractometer	RIGAKU	RIGAKU
μ (cm^{-1})	0.59	0.59
θ range ($^\circ$)	2 - 23	2 - 23
Reflections:		
total measured	4200	4225
unique total	3968	3402
unique used	1490 ($I > 2\sigma(I)$)	1655 ($I > 2\sigma(I)$)
Parameters refined; d/p	352; 4.2	320; 5.2
Absorption correction (min, max)	-	0.60, 1.18
Weighting scheme	unit	unit
$100R$, $100R_w$	3.96, 3.95	5.67, 5.67
G.O.F.	2.32	1.16
Residual e. d. (min, max) ($\text{e/\AA}^3$)	-0.16, 0.13	-0.17, 0.14

Table 17. Physical properties and crystal data of 2PITB and AC7TB.

Formula	$\text{BC}_{30}\text{H}_{36}\text{I}$	$\text{BC}_{30}\text{H}_{34}\text{N}$
Formula weight	421.4	419.4
Crystal size (mm^3)	0.30 x 0.40 x 0.40	0.25 x 0.30 x 0.35
Crystal system	monoclinic	monoclinic
Space group	$\text{P2}_1/\text{n}$ (No. 14)	$\text{P2}_1/\text{m}$ (No. 11)
a ($\text{\AA}$)	12.889(6)	9.549(2)
b ($\text{\AA}$)	13.405(5)	13.905(3)
c ($\text{\AA}$)	14.912(8)	10.023(2)
α ($^\circ$)	90	90
β ($^\circ$)	98.81(4)	112.45(2)
γ ($^\circ$)	90	90
V ($\text{\AA}^3$)	2546(4)	1230(1)
Z	4	2
d_{calc} (g/cm^3)	1.099(2)	1.132(1)
$F(000)$ (e)	912	452
Diffractometer	RIGAKU	RIGAKU
μ (cm^{-1})	0.60	0.60
θ range ($^\circ$)	2 - 25	2 - 30
Reflections:		
total measured	4224	3929
unique total	4006	3731
unique used	978 ($I > 3\sigma(I)$)	1261 ($I > 3\sigma(I)$)
Parameters refined; d/p	284; 3.4	172; 7.3
Absorption corrections (min, max)	0.95, 1.00	0.50, 1.24
Weighting scheme	unit	unit
100R, 100R _w	3.91, 4.31	5.69, 6.26
G.O.F.	2.11	3.02
Residual e. d. (min, max) ($\text{e/\AA}^3$)	-0.15, 0.16	-0.16, 0.13

Table 18. Physical properties and crystal data of TMTB and [1-Ad]TBw.

Formula	BC ₃₈ H ₃₅ N ₈	BC ₃₄ H ₄₀ NO
Formula weight	614.6	489.5
Crystal size (mm ³)	0.10 x 0.15 x 0.55	0.80 x 0.65 x 0.50
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /n (No. 14)	P2 ₁ (No. 4)
<i>a</i> (Å)	14.329(4)	13.686(6)
<i>b</i> (Å)	10.544(4)	15.568(6)
<i>c</i> (Å)	22.133(4)	14.177(5)
α (°)	90	90
β (°)	98.75(2)	100.69(3)
γ (°)	90	90
<i>V</i> (Å ³)	3305(1)	2968(4)
<i>Z</i>	4	4
<i>d</i> _{calc} (g/cm ³)	1.235(1)	1.095(1)
<i>F</i> (000) (e)	1296	1056
Diffractometer	RIGAKU	RIGAKU
λ (cm ⁻¹)	0.70	0.60
θ range (°)	2 - 23	2 - 30
Reflections:		
total measured	5124	6735
unique total	4899	6401
unique used	1900 (<i>I</i> > 3 σ (<i>I</i>))	2372 (<i>I</i> > 3 σ (<i>I</i>))
Parameters refined; <i>d/p</i>	424; 4.5	577; 4.1
Absorption corrections (min, max)	-	0.48, 1.40
Weighting scheme	unit	SHELX
100 <i>R</i> , 100 <i>R</i> _w	4.14, 4.81	6.27, 6.95
G.O.F.	2.25	3.28
Residual <i>e. d.</i> (min, max) (e/Å ³)	-0.19, 0.20	-0.21, 0.36

Table 19. Physical properties and crystal data of [1,3-Ad]2TB.MeCN and LITBw.

Formula	$B_2C_{60}H_{63}N_3$	$BC_{24}H_{28}LiO_4$
Formula weight	847.8	398.2
Crystal size (mm ³)	0.20 x 0.15 x 0.40	0.30 x 0.35 x 0.40
Crystal system	monoclinic	tetragonal
Space group	$P2_1/n$ (No. 14)	$I4_1/a$ (No. 88)
<i>a</i> (Å)	13.729(5)	27.566(2)
<i>b</i> (Å)	27.733(2)	27.566(2)
<i>c</i> (Å)	13.936(8)	12.228(2)
α (°)	90	90.00
β (°)	109.77(3)	90.00
γ (°)	90	90.00
<i>V</i> (Å ³)	4993(6)	9291(3)
<i>Z</i>	4	16
<i>d</i> _{calc} (g/cm ³)	1.128(2)	1.139(1)
<i>F</i> (000) (e)	1816	3392
Diffractometer	RIGAKU	RIGAKU
μ (cm ⁻¹)	0.60	0.70
θ range (°)	2 - 23	2 - 23
Reflections:		
total measured	5548	3586
unique total	5211	3422
unique used	1918 ($I > 2\sigma(I)$)	1176 ($I > 3\sigma(I)$)
Parameters refined; <i>d/p</i>	586; 3.3	271; 4.3
Absorption corrections (min, max)	-	0.79, 1.20
Weighting scheme	σ -weight	unit
100 <i>R</i> , 100 <i>R</i> _w	5.94, 6.15	4.70, 5.00
G.O.F.	3.15	3.21
Residual <i>e.d.</i> (min, max) (e/Å ³)	-0.24, 0.22	-0.25, 0.18

3.3. Results and Discussion

3.3.1. Structural Studies

Examples of both interion and intracation hydrogen bonds are observed in the crystal structures of the organoammonium tetraphenylborates (Table 11). All TB compounds contain interion $X - H \cdots \pi$ bonds, either normal or/and branched (bifurcated and trifurcated). The solvated compounds contain also H-bonds between the cation and the solvent molecule(s). Compounds containing intracation hydrogen bonds are rare because their formation requires very specific spatial arrangement of the donor $X - H$ and acceptor groups. However, the compounds BPTB, PTB and TMTB.MeCN contain both intracation ($N - H \cdots N$ in BPTB and PTB; $N - H \cdots \pi$ in TMTB.MeCN) and interion $N - H \cdots \pi$ hydrogen bonds. Figs. 33-34 shows a schematic representation of the various types of H bonding observed in this work. The actual H-bonding situations are presented in Figs. 35-44.

Normal $X - H \cdots \pi$ hydrogen bonds are by far the most common in organoammonium tetraphenylborates. Compounds 2, 5-7, 14, 17-18, 23-24 (type A), 11-13, 20-21 (type B), 13 (type C), 10, 22 (type D), 15 (type E), 15 (type F), 25 (type G), 4, 19 (type H) and 22 (type J) contain normal hydrogen bonds. In normal hydrogen bonds, the $X - H$ ($X = N$ or O) vector points directly towards either the phenyl ring or other donor atoms (O or N) of the solvent molecules. The hydrogen bonding in the H and J type situations is, though normal, more complicated and deserves some comments. In both cases, $N - H$ forms hydrogen bonds to the phenyl ring via intermediary H_2O molecules. In the H type situation, the $N - H$ vector bisects the angle between the two lone pairs of electrons on the water oxygen. However, in the J type situation, two $N - H$ vectors point

toward the O atom and each H(N) engages a lone pair on the oxygen.

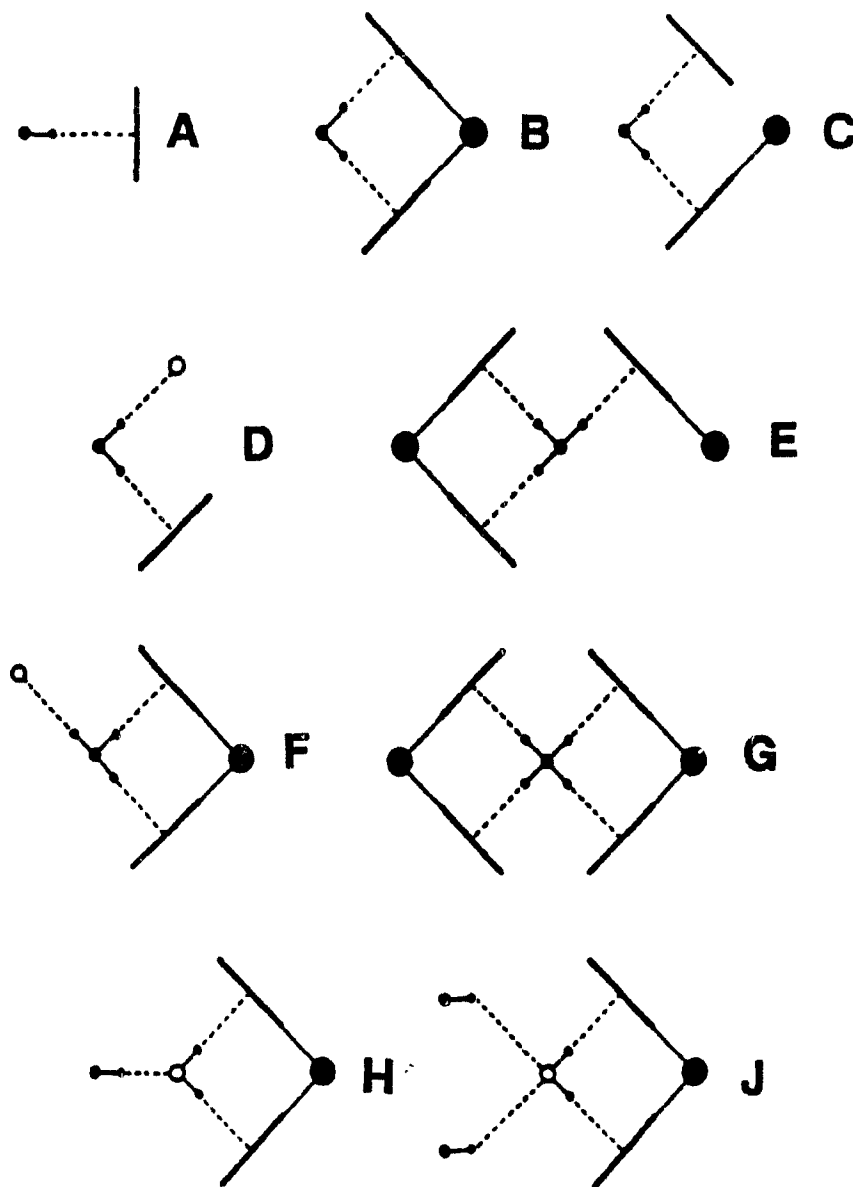


Fig. 33. Schematic representations of normal N - H(N)... π and N - H(N)...O - H(O)... π bonding geometries observed in 25 organoammonium tetraphenylborates presented in this study. Full circles: large, B; medium, N; small, H. Open circles: X = N or O.

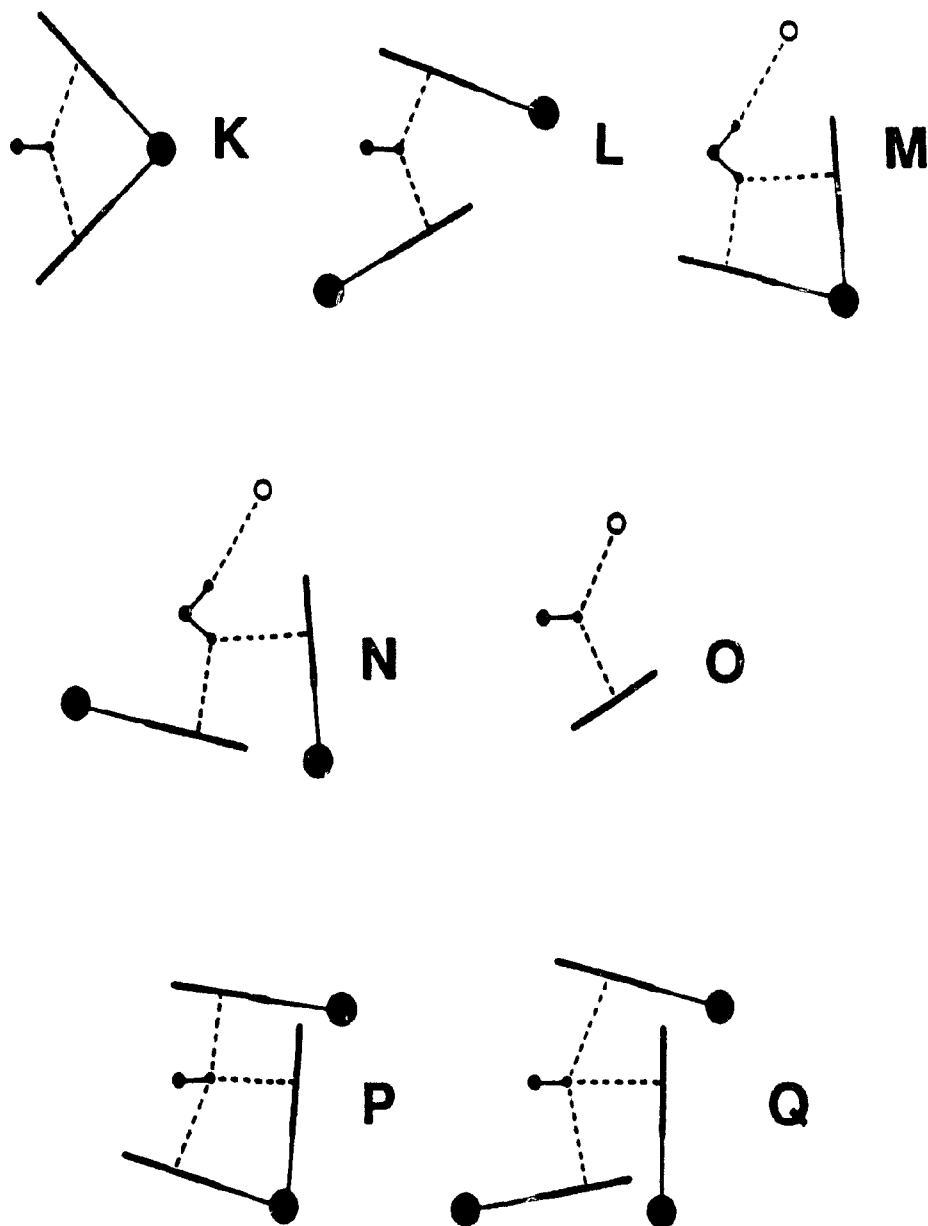


Fig. 34. Schematic representations of branched N - H(N)... π bonding geometries observed in 25 organoammonium tetraphenylborates presented in this study. Full circles: large, B; medium, N; small, H. Open circles: X = N or O.

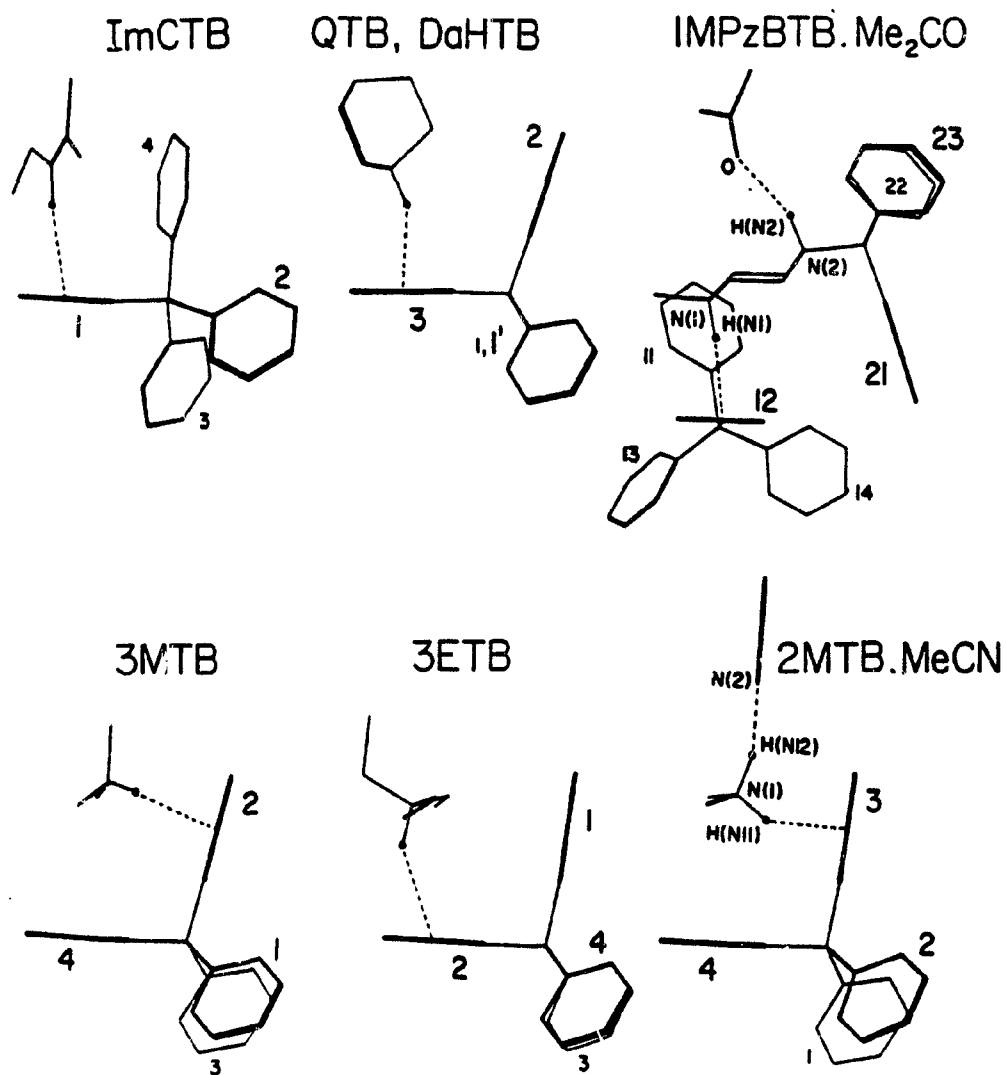


Fig. 35. Normal hydrogen bonds in tetraphenylborates in which the cation is engaged in one N - H(N)⋯π bond. The black dot represents H(N). Broken lines indicate the H(N)⋯π interaction. Ring numbers are labelled in the diagram. Type A; ImCTB, QTB, DaHTB, IMPzBTB.Me₂CO, 3MTB, 3ETB. Type D: 2MTB.MeCN.

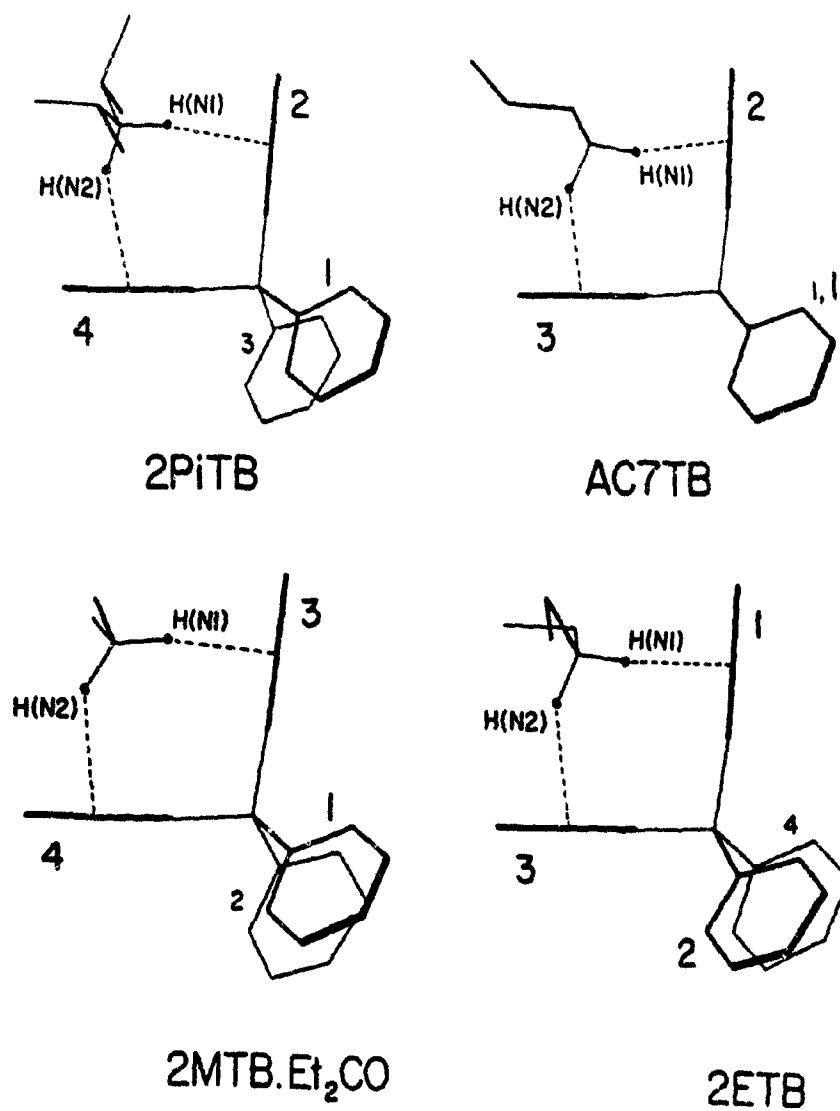


Fig. 36. Normal hydrogen bonds in tetraphenylborates in which the cation nitrogen has two hydrogen atoms both engaged in N - H(N)... π bonds. The black dot represents H(N). Broken lines indicate the H(N)... π interaction. Ring numbers are labelled in the diagram. Type B: 2PiTB, AC7TB, 2MTB.Et₂CO, 2ETB.

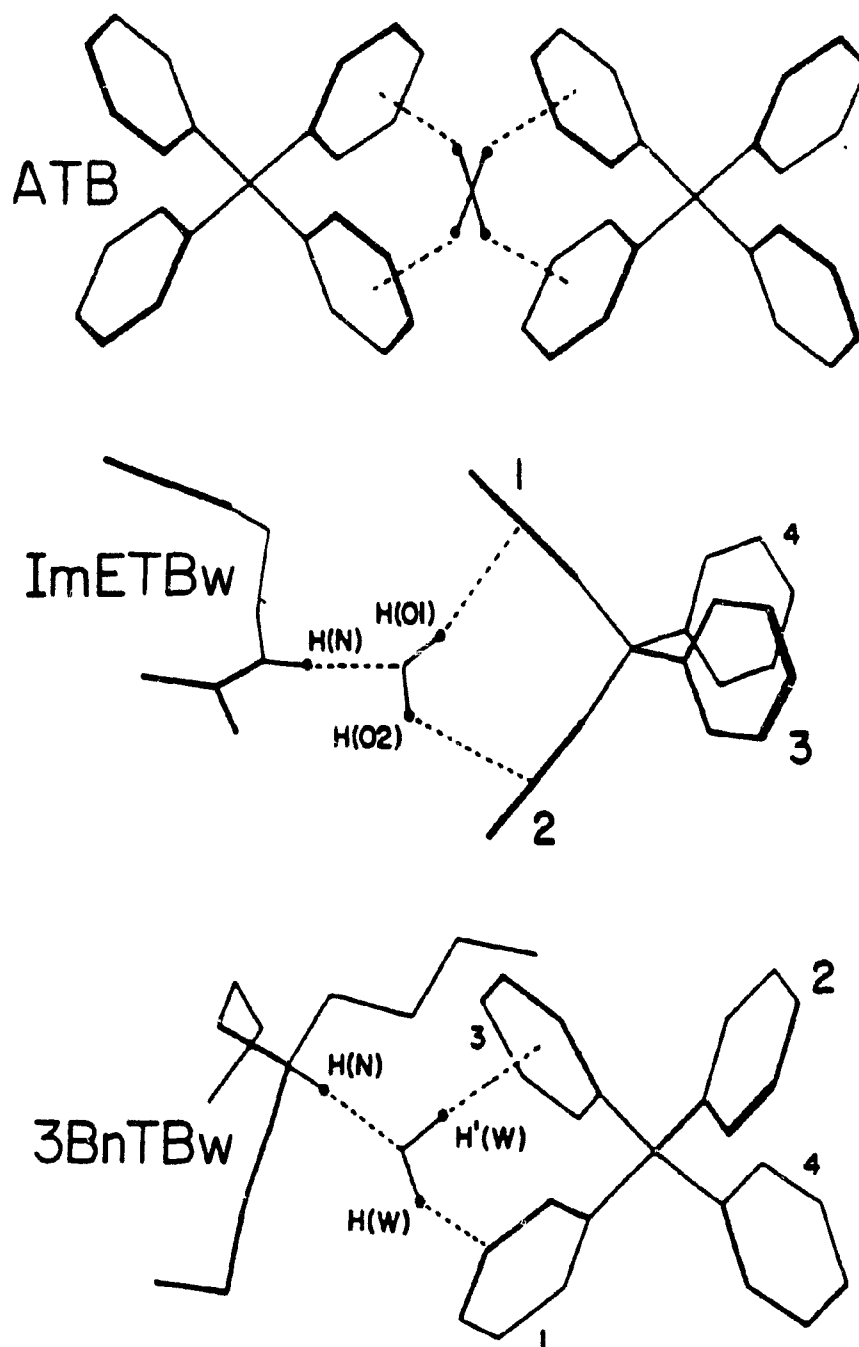


Fig. 37. Hydrogen bonding in ATB (type G). Asymmetric $N \cdots H(N) \cdots O[-H(O) \cdots \pi]_2$ bonds in ImETBw (type H) and 3BnTBw (type H). The black dot represents H(N). Broken lines indicate the $H(N) \cdots \pi$ interaction. Ring numbers are labelled in the diagram.

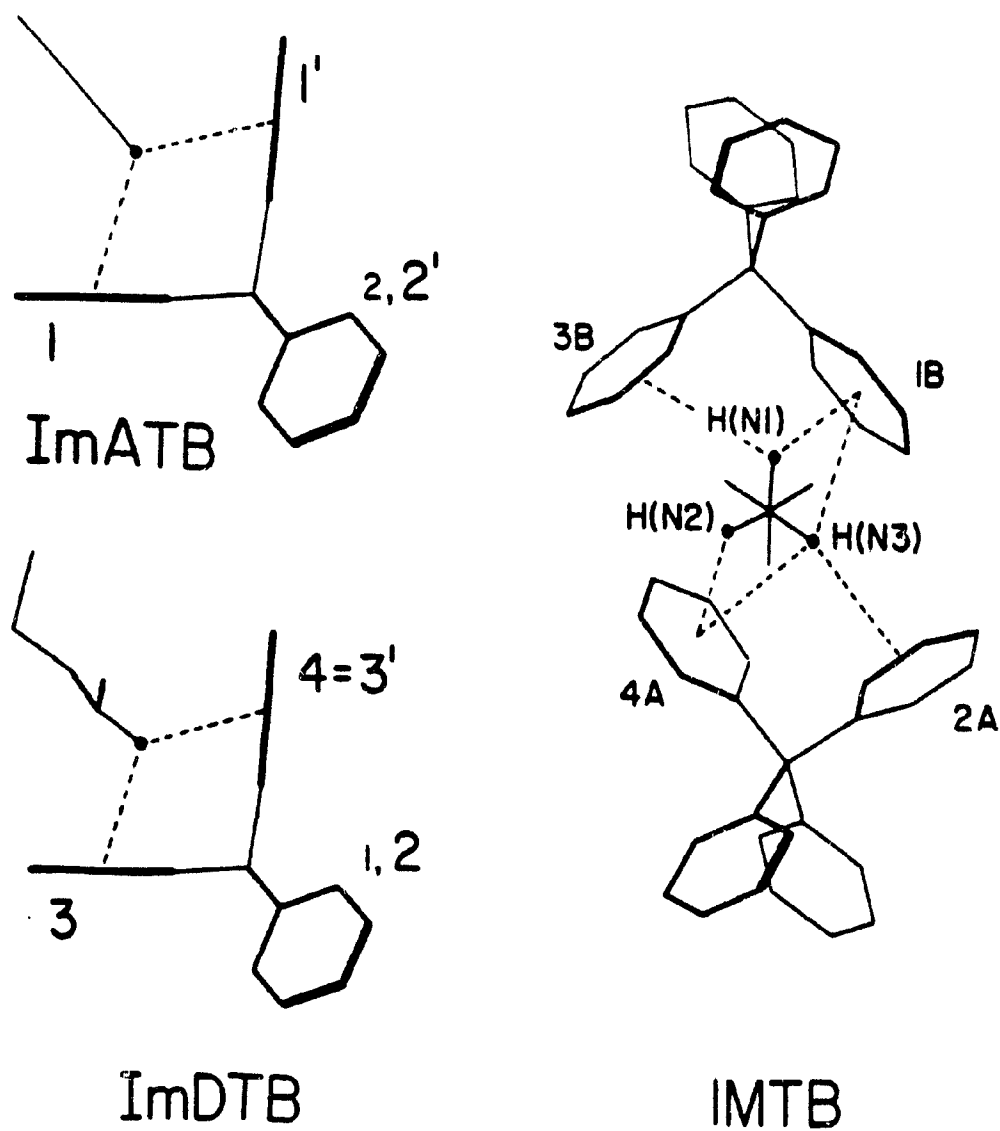


Fig. 38. Bifurcated and Trifurcated H-bonds in ImATB, ImDTB, and IMTB. The black dot represents H(N). Broken lines indicate the H(N)... π interaction. Ring numbers are labelled in the diagram.

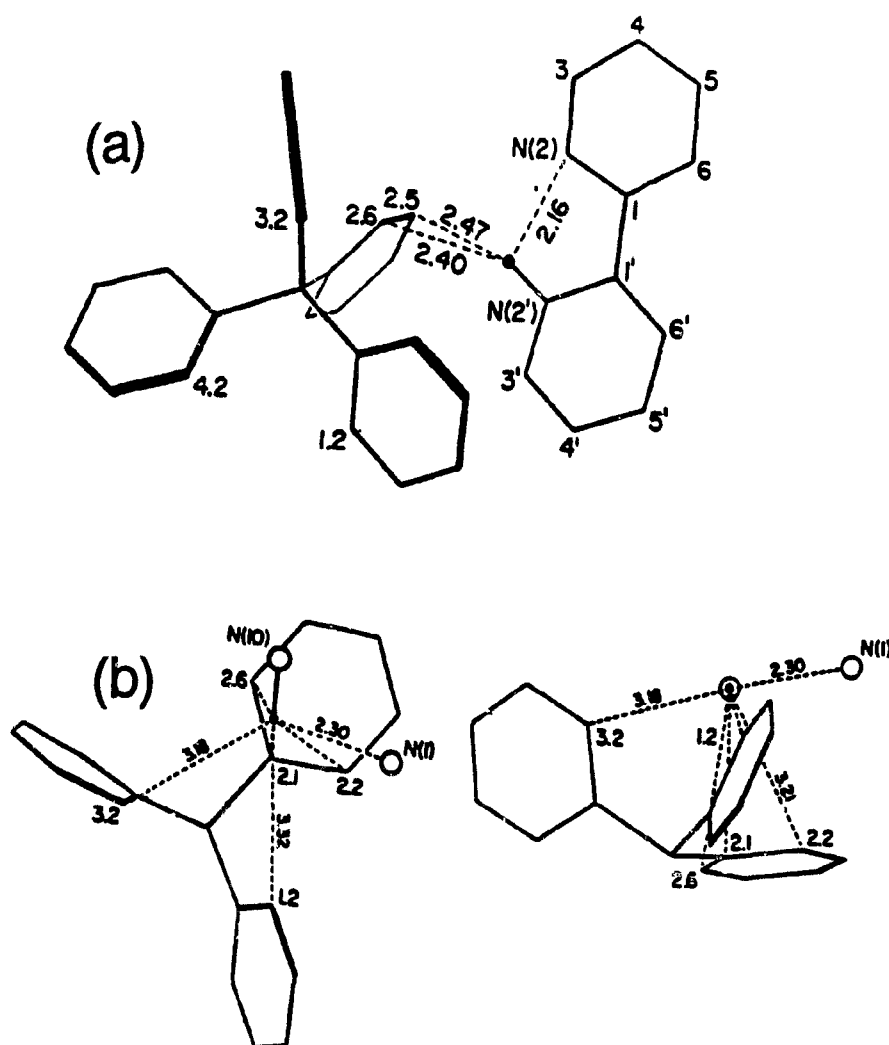


Fig 39. (a) Hydrogen bonding in BTB. H-bonds are indicated by broken lines. Black dot, H(N2'). (b) Proposed hydrogen bonding scheme in PTB. Black dot, H(N10). The fourth phenyl ring of the anion has been omitted for clarity.

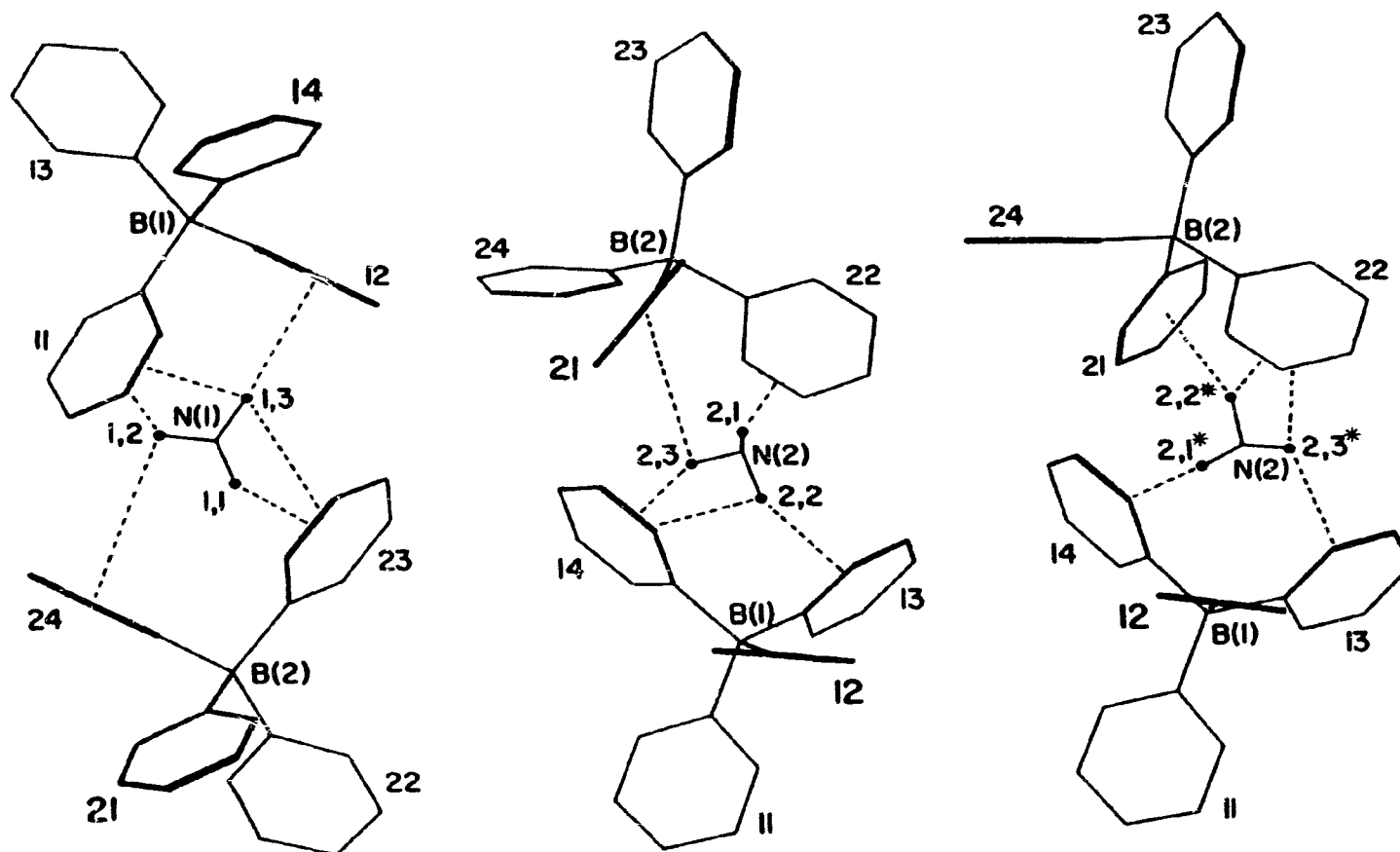


Fig. 40. H-bonding in 1ETB. For clarity the N(1) system and the two orientation of the N(2) system (resolved twofold disorder) are presented separately. Broken lines, H bonds drawn to the centres of the associated rings. Numbering: 1,1 = H(N1,1) etc.; 2,3 = H(N2,3) etc.; 2,3* = H(N2,3*) etc.

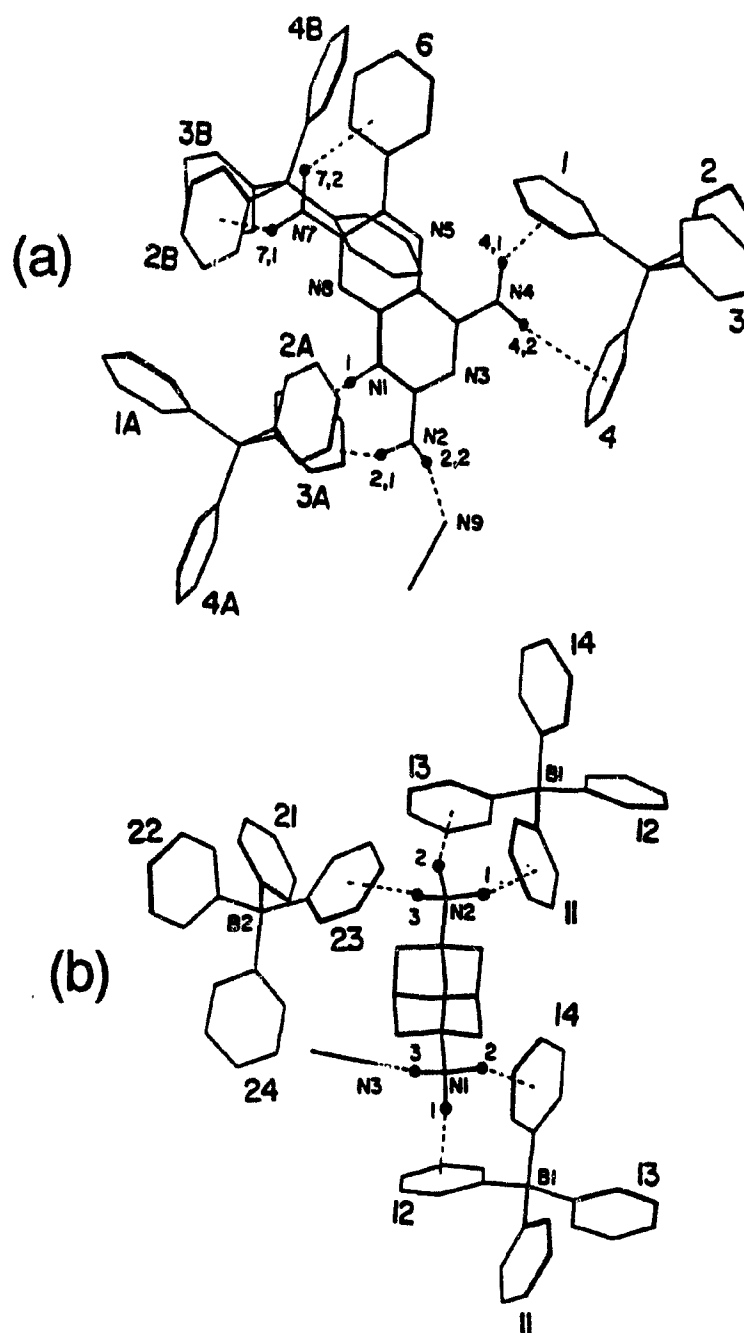


Fig. 41. H-bonding in (a) TMTB.MeCN, and, (b) [1-3Ad]TB.MeCN. The black dot represents H(N). Broken lines indicate the H(N)... π interaction. Numbering: large type, rings; small type, 12 = H(N12) etc. Ring numbers are labelled in the diagram.

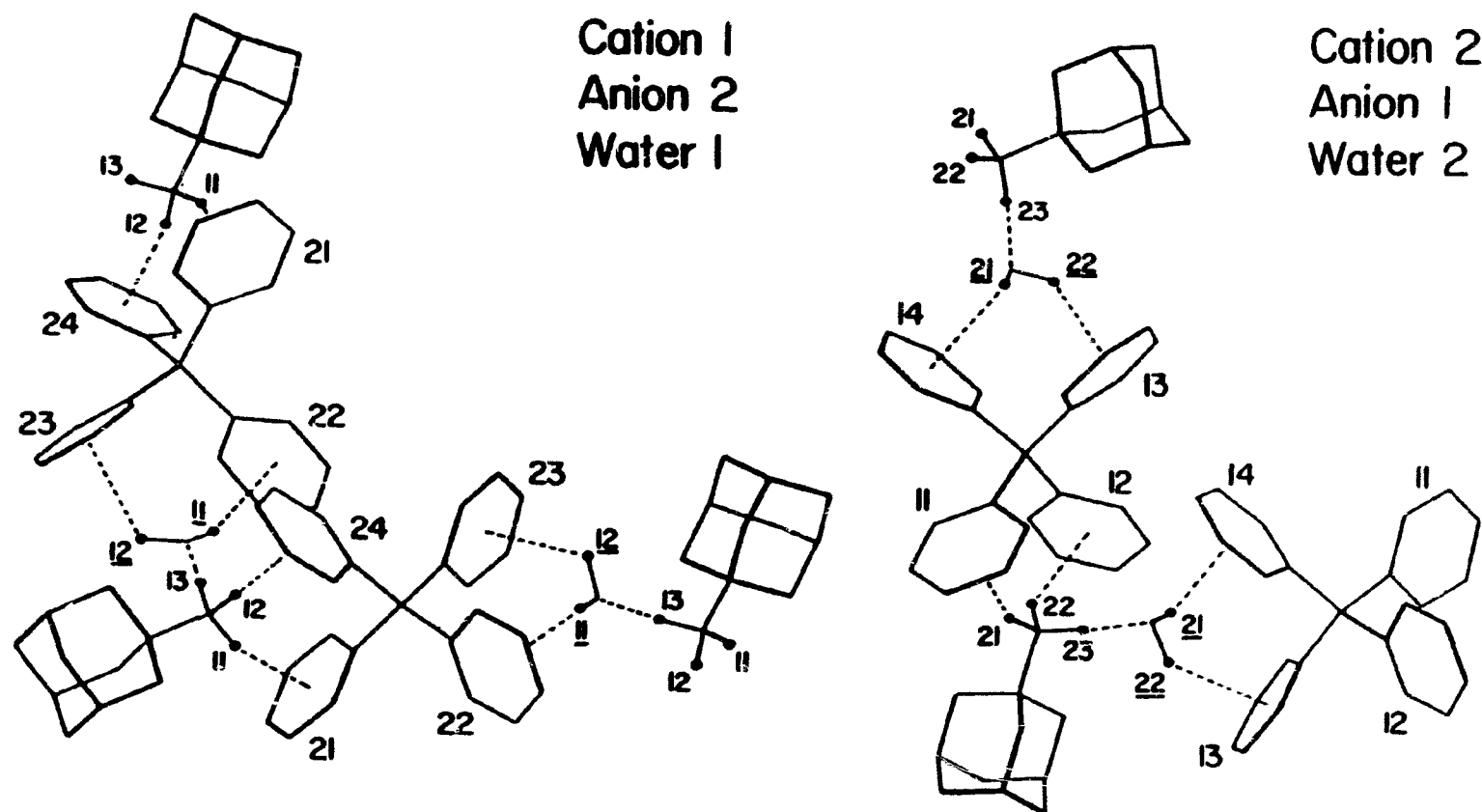


Fig. 42. Hydrogen bonding in 1-AdTBw. The two H-bonding systems are presented separately, for clarity. The black dot represents H(N). Broken lines indicate the H(N)... interaction. Numbering: large type, rings; small type, 12 = H(N12) etc.; small type underlined, 22 = H(O22), etc. Ring numbers are labelled in the diagram.

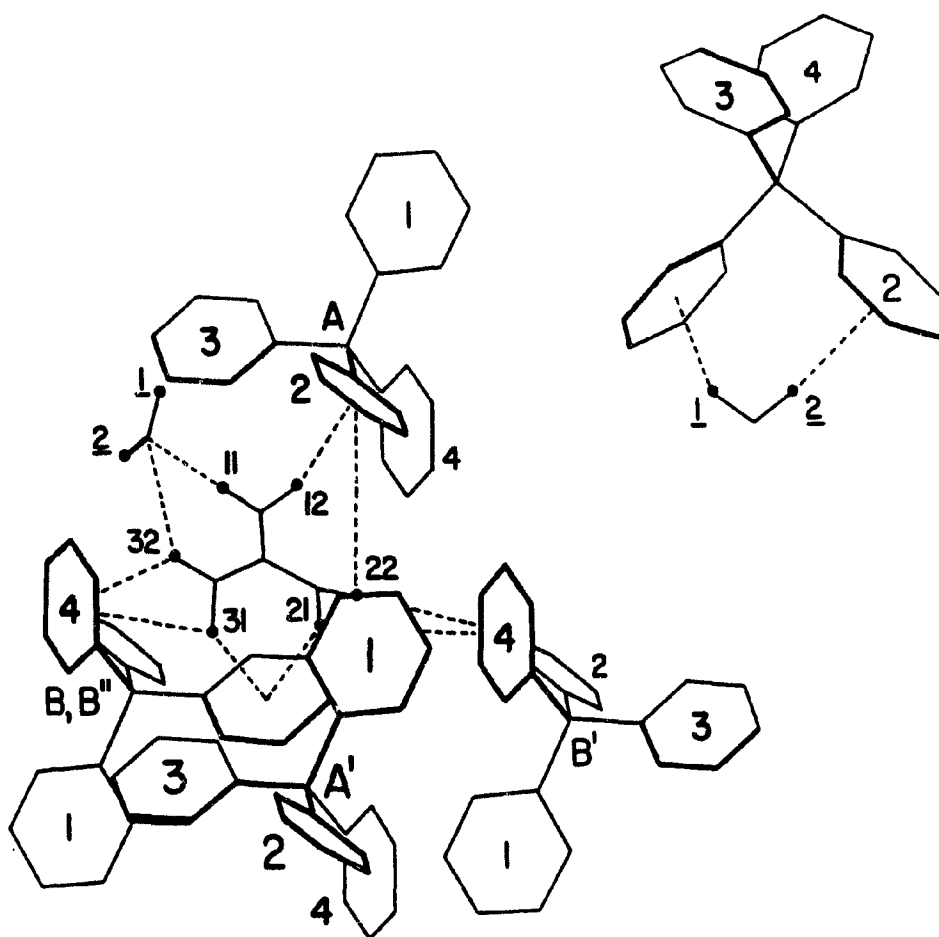


Fig. 43. Hydrogen bonding in GTBw. The black dot represents H(N). Broken lines indicate the H(N)... π interaction. Numbering: 32 = H(N32) etc.; 1, 2 = H(O1), H(O2). Upper right-corner: O(H)... π bonding of the H₂O molecule. Ring numbers are in parentheses. Ring numbers are labelled in the diagram.

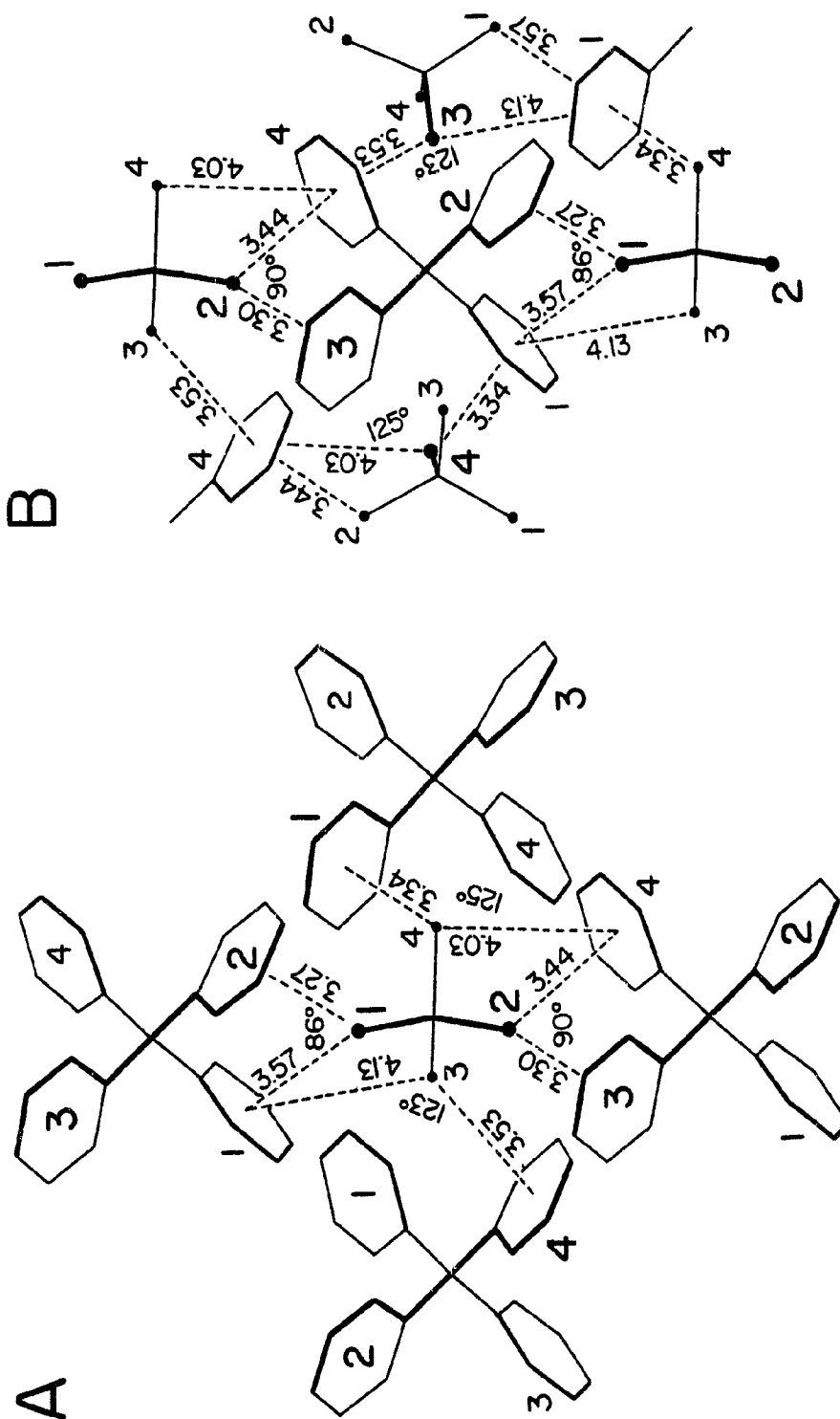


Fig. 44. The H-bonding system in LiTBw as represented by the O... π_c vectors (broken lines; length in Å) (a) cation environment, (b) anion environment. Black circles, oxygen atoms. Ring numbers are labelled in the diagram.

The distribution of normal $H(N)\dots\pi_c$ bond lengths is wide, ranging from 2.13 to 3.27 Å (mean 2.38(25) Å). The $N - H\dots\pi_c$ angles vary from 124° to 177° (mean $152(15)^\circ$)[‡]. This wider $X - H\dots\pi$ bond length distribution, compared with other donor-acceptor combinations, is not unexpected because the large phenyl groups of the tetraphenylborate anion suffer from steric constraints.

Branched hydrogen bonds arise from a compromise in the choice of acceptor in order to satisfy the requirements of molecular packing and hydrogen bond configuration. With the exception of compound 1 (symmetric), all the branched (bifurcated and trifurcated) $N - H\dots\pi$ bonds observed in these TB compounds are asymmetric. In the case of a bifurcated bond, the $N - H$ vector cannot point directly at the electron cloud of a particular phenyl ring of the TB anion, rather it points somewhere in between two phenyl rings or sometimes towards the boron atom (type K). The angle $N - H\dots\pi$ is smaller than that of the normal H-bond and its distribution is considerably broader. The overall mean value for ω is $118(24)^\circ$; the mean for the smaller of the two ω angles in the bifurcated bonds is $98(11)^\circ$ and that for the larger angle is $137(16)^\circ$. The two means for $\bar{d}(N\dots\pi_c)$ ($\bar{d}[H(N)\dots\pi_c]$) in bifurcated bonds are significantly different, indicating that these values depend on the $N - H(N)\dots\pi_c$ angle. Only two examples of trifurcated bonds are available at present, those in 22 and 23. Of the two, the bond in 22 is the more symmetric; the three $N\dots\pi_c$ distances, 4.01, 4.29 and 4.37 Å, are quite similar, as are the $H(N)\dots\pi_c$ distances and the ω angles.

[‡]The only example of intracation $H(N)\dots\pi$ bond in Table 11, that observed in TMTB.MeCN, is normal by definition. However, because of its special geometry, it is not included in the statistics presented here.

The compounds BPTB, PTB and TMTB.MeCN, all have both intracation and inter-ion hydrogen bonds. In BTB and PTB, the N - H group is almost coplanar with the neighbouring heterocycle which favours the formation of intracation hydrogen bonding with the proximal N as the major component of a bifurcated hydrogen bond. The constraint arising from the intracation bonding impacts significantly on the geometry of the other component of the bifurcation, the interior N - H... π interaction. On the other hand, the compound TMTB.MeCN contains a normal intracation N - H... π hydrogen bond (type C). The intracation distances are $H(7,2)... \pi_c = 3.27 \text{ \AA}$ and $N(7)... \pi_c = 3.97 \text{ \AA}$, and the angle $N(7) - H(7,2)... \pi_c$ is 126.6° .

In the absence of a neutron diffraction study, the positions of the hydrogens are not accurately known. For the TB compounds, the two values known with considerable accuracy from the x-ray diffraction results are the $d(X...C)$ and $d(X... \pi_c)$ distances. These two distances and their two less accurate companions, $d[H(X)...C]$ and $d[H(X)... \pi_c]$, are gathered in Table 20. Fig. 45 shows the range and distribution of the $H(N)... \pi_c$ and $N... \pi_c$ distances for the compounds of Table 11. For compounds with one $H(N)$ on the cation nitrogen, forming a normal bond to a phenyl ring of the anion (A type), the ω angle falls between 180° and 120° (mean $\bar{\omega} = 158(11)^\circ$). On the other hand, for type B bonds, where there are two $H(N)$'s on the cation nitrogen and two normal bonds to phenyl rings of the same anion, one bond angle is significantly larger than the other (mean $\bar{\omega}_1 = 170(6)^\circ$, mean $\bar{\omega}_2 = 143(7)^\circ$). This indicates that one N - H vector points at the centre of the associated ring ($\phi \sim 90^\circ$) and makes a better bond, while the other points at the electron cloud in the general vicinity of $C(\delta)$ of its associated ring and interacts poorly. This happens because of the tetrahedral environment at the N atom i.e. from the tendency of the $H(1) - N - H(2)$ angle to be approximately 109° .

The distributions of the points in the plot, $\bar{d}[\text{H}(\text{N})\dots\text{C}]$ vs. $\bar{d}(\text{N}\dots\text{C})$ and $d[\text{H}(\text{N})\dots\pi_c]$ vs. $d(\text{N}\dots\pi_c)$ are similar (Fig. 45), skewed towards the low values. The points cluster about the mean $\bar{d}(\text{N}\dots\text{C})$, $\bar{d}[\text{H}(\text{N})\dots\text{C}]$ distances of 3.57(19), 2.75(20) Å respectively for the normal bonds while the points distribution is much more diffuse for the branched bonds.

Whether the $\text{X}\dots\text{C}$ and $\text{H}(\text{X})\dots\text{C}$ distances will be maximum or minimum will depend on the inclination of the N - H vector with respect to the phenyl ring (ϕ). There are two extreme cases possible. i) The X atom is situated on the C6 axis of the benzene molecule. All the $\text{X}\dots\text{C}$ distances would then be equal and the standard deviation of the $d(\text{X}\dots\text{C})$ would be zero. ii) The X atom is located in the molecular plane and 3.50 Å from π_c . The mean (= the spread) standard deviation of the $d(\text{X}\dots\text{C})$ would then be approximately equal to 1 Å. The observed σ range for $d(\text{N}\dots\text{C})$ is 0.02-0.45 Å for the normal bonds, 0.08-0.91 Å for the bifurcated bonds, and 0.13 - 0.67 Å for the trifurcated bonds. The corresponding σ ranges for $d[\text{H}(\text{N})\dots\text{C}]$ are 0.02-0.50 Å, 0.14-0.96 Å and 0.21-0.59 Å, respectively. For $d(\text{O}\dots\text{C})$ and $d[\text{H}(\text{O})\dots\text{C}]$ the esd ranges are 0.02-0.43 and 0.12-0.39 Å, respectively. The indirect information about ϕ , provided by the σ of $d(\text{X}\dots\text{C})$ and $d[\text{H}(\text{X})\dots\text{C}]$, indicates that the range of ϕ is wide. However, the distributions of the σ values are strongly skewed toward low values, indicating a preference for large ϕ .

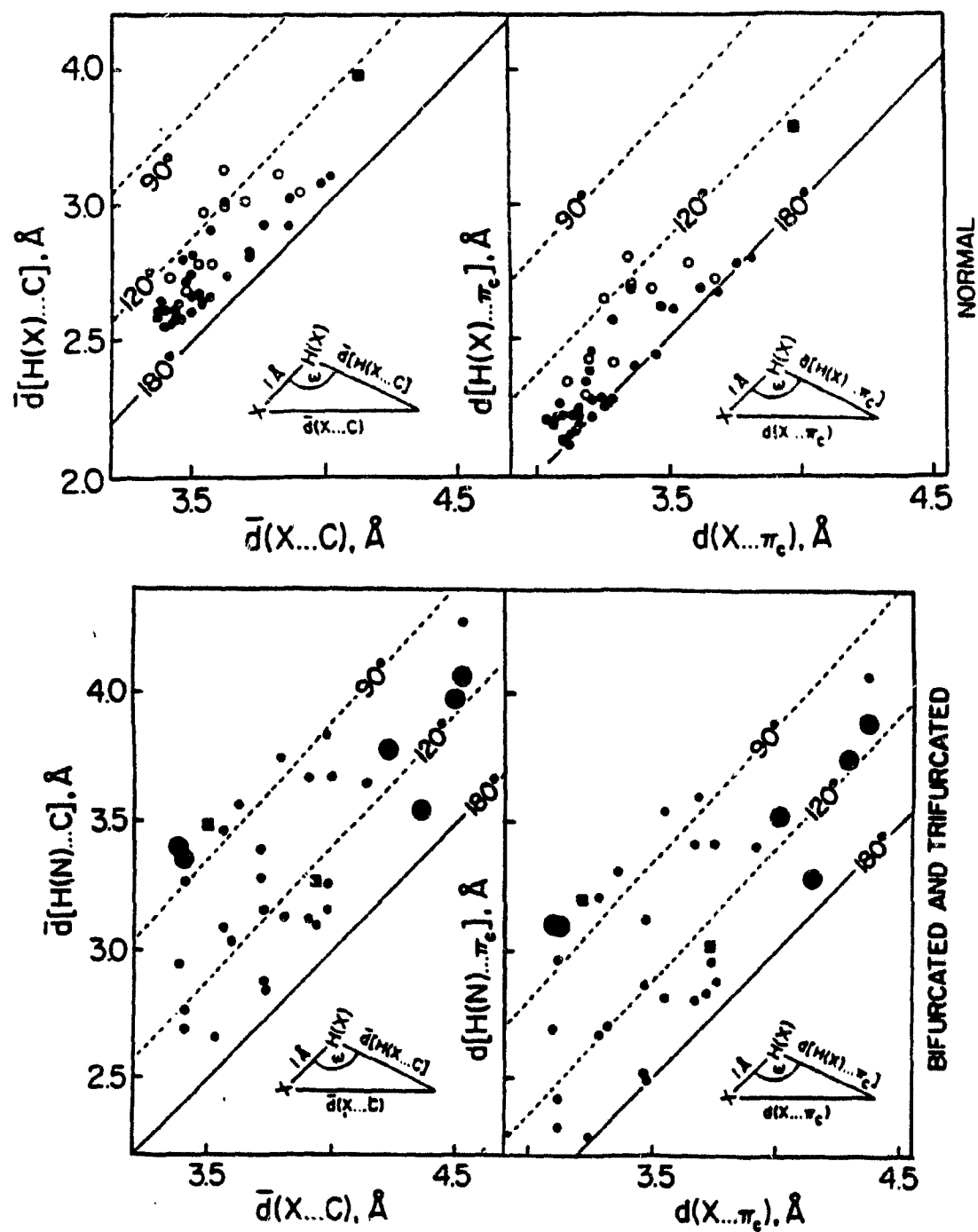


Fig. 45. Plot of $\bar{d}[H(X)...C]$ vs. $\bar{d}(X...C)$ and the $d[H(X)...pi_c]$ vs. $d(X...pi_c)$. Circles for interior $\angle(X)...pi$ bonds: full small, $X = N$, normal or bifurcated; full large, $X = N$, trifurcated bonds, Open, $X = O$, normal bonds. Square box: $X = N$, intracation bonds.

Table 20. X - H... π (X = N, O) bonding: mean distances $\bar{d}(X...C)$ and $\bar{d}[H(X)...C]$, and the distances $d(X...C_c)$ and $d[H(X)...C_c]$ in Å; the angles ω , ϕ and ψ in degrees.

compd	H(X)...R	$\bar{d}(X...C)$	$d(X...C_c)$	$\bar{d}[H(X)...C]$	$d[H(X)...C_c]$	ω	ϕ	ψ
N - H(N)... π bonds								
1	H(N)... R(2,4)	3.60(13)	3.32	3.03(27)	2.70	113	46	27
2	H(N)... R1	3.99(39)	3.76	3.08(44)	2.78	161	79	84
3	H(N)...R3	3.81(18)	3.55	3.13(31)	2.81	109	56	29
	...R4	3.39(15)	3.09	2.94(27)	2.60	130	56	19
5	H(N)...R2	3.50(5)	3.21	2.67(8)	2.27	152	67	0
6	H(N)...R3	3.46(9)	3.17	2.58(3)	2.17	168	76	0
7	H(N1)...R12	3.50(13)	3.21	2.60(9)	2.20	170	75	52
8	H(N2)...R2	3.94(50)	3.72	3.27(65)	3.03	126	73	20
9	H(N2)...R2	3.51(18)	3.23	3.49(34)	3.22	82	10	37
10	H(N11)...R3	3.38(12)	3.08	2.62(7)	2.21	143	57	12
11	H(N1)...R2	3.87(27)	3.61	3.02(31)	2.68	152	70	15
	H(N2)...R4	3.72(1)	3.44	2.81(14)	2.42	177	87	41
12	H(N1)...R2	3.44(9)	3.16	2.57(16)	2.17	162	83	0
	H(N2)...R3	3.37(7)	3.07	2.58(9)	2.18	145	61	0
13	H(N1)...R2	3.80(42)	3.56	3.75(52)	3.52	84	87	12
	...R3	3.54(8)	3.25	2.66(14)	2.26	163	80	6
	H(N2)...R2	3.96(16)	3.69	3.83(33)	3.59	89	17	6
	...R3	3.97(49)	3.75	3.14(59)	2.88	144	75	33
	H(N4)...R1	3.52(2)	3.23	2.83(21)	2.47	131	56	48
	H(N4)...R4	4.02(43)	3.80	3.10(39)	2.79	172	58	63
	H(N7)...R2	3.49(9)	3.20	2.82(15)	2.45	129	49	40
	H(N7)...R6	4.12(86)	3.97	3.47(78)	3.27	127	5	1
14	H(N11)...R21	3.40(4)	3.10	2.55(7)	2.13	158	73	34
	H(N12)...R24	3.45(13)	3.16	2.62(2)	2.22	153	64	64
	H(N21)...R11	3.44(13)	3.15	2.61(9)	2.21	152	64	24
	H(N22)...R12	3.49(11)	3.20	2.74(25)	2.38	138	63	74

Table 20. X - H... π (X = N, O) bonding: mean distances $\bar{d}(X...C)$ and $\bar{d}[H(X)...C]$, and the distances $d(X...C_c)$ and $d[H(X)...C_c]$ in Å; the angles ω , ϕ and ψ in degrees. (continued).

compd	H(X)...R	$\bar{d}(X...C)$	$d(X...C_c)$	$\bar{d}[H(X)...C]$	$d[H(X)...C_c]$	ω	ϕ	ψ
N - H(N)... π bonds								
15	H(N11)...R12	3.55(16)	3.27	2.65(15)	2.26	170	77	28
	H(N12)...R14	3.47(15)	3.17	2.60(8)	2.19	162	69	21
	H(N21)...R11	3.43(7)	3.13	2.57(14)	2.16	159	77	61
	H(N22)...R13	3.66(17)	3.39	2.77(13)	2.40	164	70	2
	H(N23)...R23	3.89(45)	3.65	2.98(44)	2.67	161	58	80
17	H(N)...R2	3.53(12)	3.25	2.67(14)	2.28	157	70	71
18	H(N)...R2	3.77(20)	3.52	2.93(32)	2.61	148	79	11
20	H(N1)...R3	3.54(16)	3.26	2.65(19)	2.26	164	78	8
	H(N2)...R4	3.48(9)	3.19	2.72(11)	2.34	139	56	4
21	H(N1)...R1	3.54(20)	3.26	2.64(18)	2.24	173	76	83
	H(N2)...R3	3.45(5)	3.16	2.63(10)	2.24	149	65	26
22	H(N12)...R2A	3.57(15)	3.29	2.91(26)	2.57	127	51	37
	H(N21)...R3A	3.94(77)	3.72	3.09(57)	2.83	146	83	43
	...R4B'	4.53(67)	4.37	4.26(52)	4.06	101	86	15
	H(N22)...R1A'	4.23(33)	4.01	3.77(35)	3.52	111	28	37
	...R2A'	4.50(35)	4.29	3.96(49)	3.74	116	53	36
	...R4B'	4.53(67)	4.37	4.05(80)	3.88	112	72	43
	H(N31)...R3B	3.74(11)	3.48	2.84(17)	2.49	164	85	47
	...R4B''	3.63(17)	3.36	3.56(33)	3.30	85	77	14
	H(N32)...R4B''	3.63(17)	3.36	3.01(28)	2.69	124	48	9
23	H(N1)...R1B	3.41(15)	3.12	2.69(14)	2.31	136	52	17
	...R3B	4.14(42)	3.92	3.64(48)	3.40	114	35	34
	H(N2)...R4A	3.39(13)	3.09	2.64(30)	2.26	137	67	40
	H(N3)...R1B	3.41(15)	3.12	3.35(40)	3.08	83	16	5
	...R2A	4.36(34)	4.15	3.54(22)	3.27	145	43	70
	...R4A	3.39(13)	3.09	3.39(21)	3.10	80	3	41
24	H(N1,1)...R23B	3.40(3)	3.10	2.61(15)	2.22	145	65	9
	H(N1,2)...R11A	3.41(7)	3.12	2.76(28)	2.42	126	56	43
	...R24B	4.00(19)	3.75	3.67(22)	3.41	101	20	42
	H(N1,3)...R11A	3.41(7)	3.12	3.26(23)	2.96	89	14	33
	...R12A	3.99(24)	3.74	3.25(39)	2.95	134	20	69

Table 20. X - H... π (X = N, O) bonding: mean distances $\bar{d}(X...C)$ and $\bar{d}[H(X)...C]$, and the distances $d(X...C_c)$ and $d[H(X)...C_c]$ in Å; the angles ω , ϕ and ψ in degrees (continued).

compd	H(X)...R	$\bar{d}(X...C)$	$d(X...C_c)$	$\bar{d}[H(X)...C]$	$d[H(X)...C_c]$	ω	ϕ	ψ
N - H(N)... π bonds								
24	H(N2,1)...R22	3.72(37)	3.47	2.92(50)	2.62	141	85	64
	H(N2,2)...R13	3.73(21)	3.47	2.87(22)	2.52	154	66	75
	...R14	3.57(14)	3.29	3.46(40)	3.20	86	22	20
	H(N2,3)...R14	3.57(14)	3.29	3.08(27)	2.67	113	38	43
	...R21	3.91(37)	3.67	3.65(54)	3.41	96	37	47
	H(N2,1)*...R14	3.57(14)	3.29	2.66(15)	2.27	171	25	80
	H(N2,2)*...R21	3.91(37)	3.67	3.11(36)	2.80	142	52	55
	...R22	3.72(37)	3.47	3.27(37)	3.86	110	26	34
	H(N2,3)*...R13	3.73(21)	3.47	3.15(36)	2.86	119	49	51
	...R22	3.72(37)	3.47	3.38(39)	3.11	102	21	20
25	H(N)...R1 (LT)	3.34(6)	3.04	2.58(12)	2.17	141	59	0
	H(N)...R1 (RT)	3.35(6)	3.05	-	-			
O - H(O)... π bonds								
4	H(O1)...R1	3.71(15)	3.44	3.29(32)	2.68	133	65	67
	H(O2)...R2	3.55(10)	3.26	2.98(24)	2.64	120	44	27
14	H(O11)...R22	3.58(12)	3.29	2.78(20)	2.41	147	68	34
	H(O12)...R23	3.63(12)	3.35	3.13(14)	2.81	115	34	58
	H(O21)...R14	3.83(26)	3.58	3.11(12)	2.78	137	42	77
	H(O22)...R13	3.53(9)	3.24	2.78(22)	2.41	139	57	19
16	H(O1)...R1	3.82(26)	3.57					
	H(O1)...R2	3.55(7)	3.27					
	H(O2)...R3	3.58(17)	3.30					
	H(O2)...R4	3.73(16)	3.46					
	H(O3)...R1	4.20(59)	4.13					
	H(O3)...R4	3.79(26)	3.53					
	H(O4)...R1	3.61(18)	3.34					
	H(O4)...R4	4.22(62)	4.03					
19	H(W)...R1	3.42(2)	3.12	2.73(14)	2.34	146	85	38
	H'(W)...R3	3.48(9)	3.19	2.68(14)	2.29	167	85	33
22	H(O1)...R1	3.63(19)	3.36	3.01(39)	2.70	124	60	75
	H(O2)...R2	3.91(43)	3.68	3.04(34)	2.72	161	48	79

Table 21. Mean values of the $\bar{d}(X\cdots\pi_c)$ and $\bar{d}(H(X)\cdots\pi_c)$ distances (Å) and bond angles $\bar{\omega}$ (°) in compounds of Table 11.

Sample	$\bar{d}(X\cdots\pi_c)$	$\bar{d}[H(X)\cdots\pi_c]$	$\bar{\omega}$
Normal bonds, X = N			
All	3.35(17)	2.34(19)	156(16)
A	3.34(20)	2.37(21)	161(8)
B, large ω	3.38(23)	2.38(22)	170(6)
B, small ω	3.25(19)	2.38(18)	143(8)
Competing	3.32(22)	2.38(20)	156(15)
15	3.39(21)	2.41(21)	161(2)
25	3.04	2.20	141
Normal bonds, X = O			
All	3.35(17)	2.58(18)	139(16)
H ₂ O, all	3.35(17)	2.58(18)	139(16)
H ₂ O, large ω	3.37(18)	2.50(17)	149(13)
H ₂ O, small ω	3.33(15)	2.63(21)	128(11)
Bifurcated bonds, X = N			
All	3.50(30)	2.99(48)	118(24)
Large ω	3.42(24)	2.64(22)	137(16)
Small ω	3.58(31)	3.33(37)	98(11)
Trifurcated bonds, X = N			
22 + 23	3.84(53)	3.43(31)	108(22)
22 only	4.22(15)	3.71(15)	113(2)

The inclination of the X - H vector to the ring skeleton plane can also be estimated by the difference, $\Delta(X\cdots C)$, between the longest, $d_{\max}(X\cdots C)$, and the shortest, $d_{\min}(X\cdots C)$, distance from X to the ring carbons, and the corresponding difference, $\Delta[H(X)\cdots C]$,

between $d_{\max}[\text{H(X)}\dots\text{C}]$ and $d_{\min}[\text{H(X)}\dots\text{C}]$. A $\Delta(\text{X}\dots\text{C})$ value of zero corresponds to an X - H vector coincident with the C6 axis. For the normal X - H(X) $\dots\pi$ bonds in the TBs, $\Delta(\text{N}\dots\text{C})$ varies from 0.04 to 1.0 Å, $\Delta[\text{H(N)}\dots\text{C}]$ from 0.04 to ~ 1.3 Å, $\Delta(\text{O}\dots\text{C})$ from 0.04 to 1.14 Å, and $\Delta[\text{H(O)}\dots\text{C}]$ from ~0.3 to ~1.0 Å.

Examples of O - H $\dots\pi$ bonding found in compounds 4, 14, 19 and 22, are all normal (H and J type). The mean O - π_c and H(O) $\dots\pi_c$ distances are 3.35(17) Å and 2.58(18) Å, respectively, consistent with the values estimated from theoretical investigations of the H₂O - C₆H₆ complex. The O - H $\dots\pi_c$ angles range from 115° to 167° (mean 139(16)°). The mean ω_1 and ω_2 angles, for the two H(O) hydrogens of a water molecule forming two asymmetric O - H $\dots\pi$ bonds, are 149(13)° and 128(12)°, respectively.

A scatter plot of the distribution of the angles ϕ and ψ is shown in Fig. 46. In this plot the angle ϕ is presented as $\sin\phi$ in order to emphasize the tendency of the N - H vector to point at the phenyl ring plane at angles approaching perpendicularity. The larger the angle ϕ the smaller the correlation with the angle ψ . The difference in the distribution between what is observed for the normal bonds and for the branched bonds is displaced.

The LiTBw compound is probably the first example containing eight O - H $\dots\pi$ bonds but in absence of hydrogen positions it is difficult to describe the geometry of the H(O) $\dots\pi$ bonds. Infra-red spectral evidence indicates that in LiTBw, six of the O - H $\dots$ phenyl bonds are essentially normal and two are highly bent, possibly bifurcated.

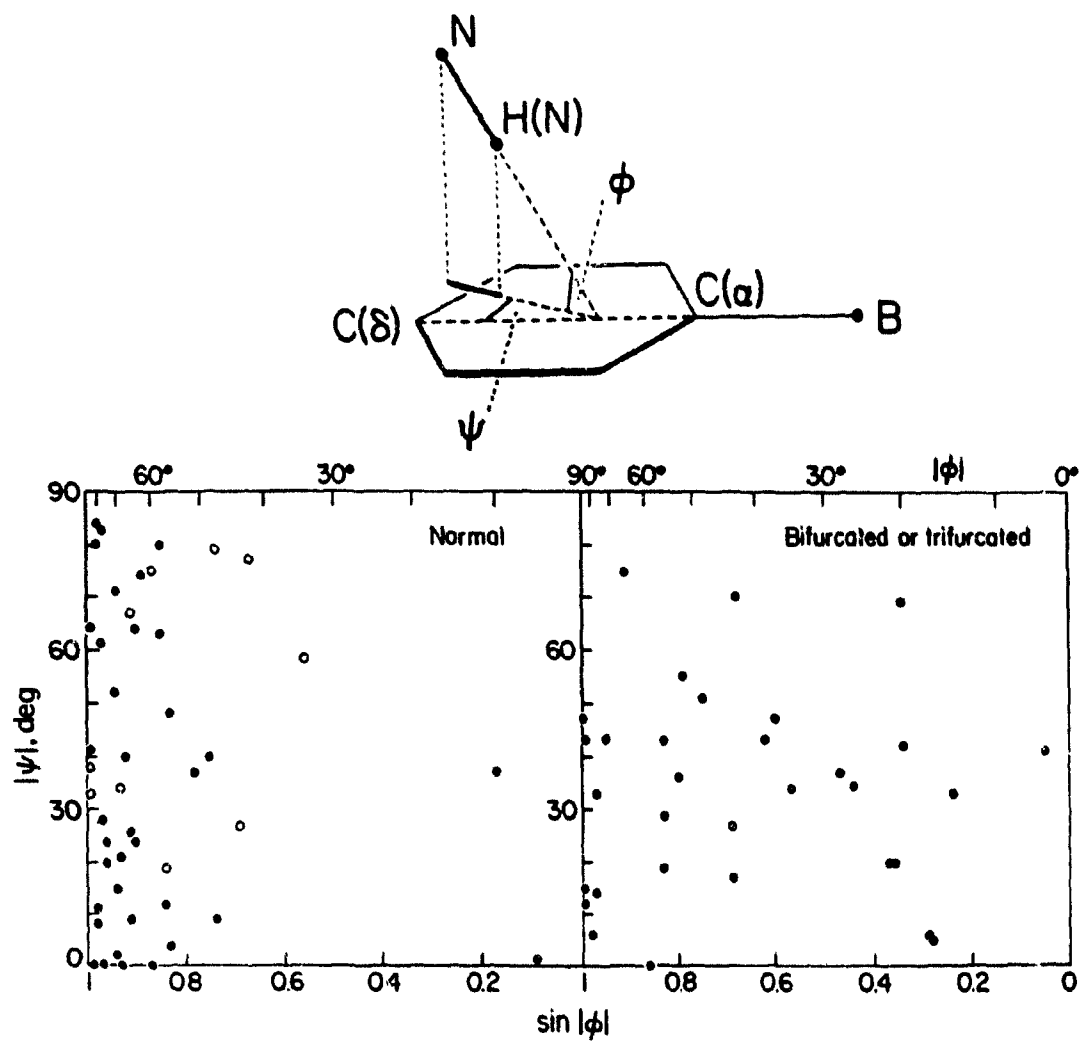


Fig. 46. A scatter plot of the distribution of the angles ϕ and ψ . Full circles, $X = N$; open circles, $X = O$.

3.3.2. Electron Density Studies

The centre of the phenyl ring, π_c , though well-defined by the C atoms of the phenyl rings, is only a point in space, not occupied by an atom. The mean distance $\bar{d}(X...C)$, although a length, does not represent the distance from X to any uniquely defined point in the crystal structure, thus it is just an arithmetic mean, i.e., a number. Therefore, all the parameters, the mean distances [$\bar{d}(X...C)$ and $\bar{d}(X...\pi_c)$] and the angles ω , ϕ and ψ , used in this report are for a qualitative description of the general norm of the X - H... π bonding.

In this situation, an attempt was made to focus on the effect of hydrogen bonding on the electron density distribution of the phenyl ring using the traditional ($X-X_{80}$) and the multipole refinement methods. The compound DaHTB (Fig. 47) was chosen for this

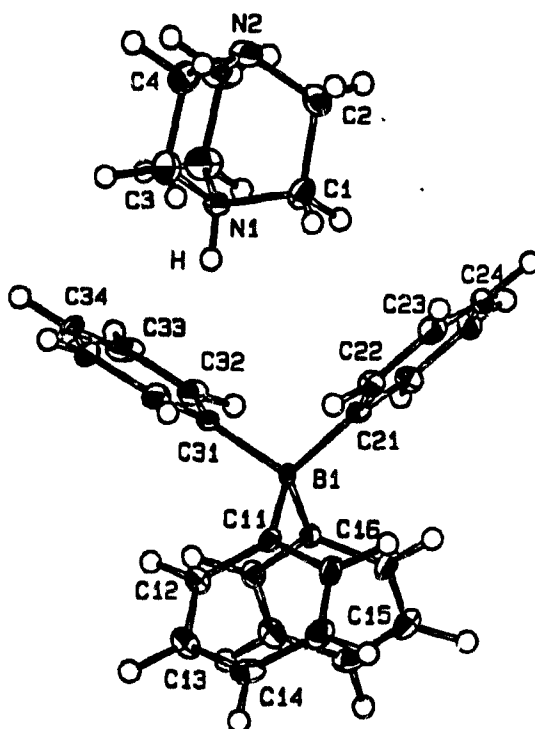


Fig. 47. Molecular structure of DaHTB. Vibrational ellipsoids are at the 50% probability level.

investigation because it is a relatively good scatterer; its room temperature structure is completely ordered, and its high symmetry reduces the number of parameters to refine.

Low temperature data were collected using a RIGAKU diffractometer mounted on an RU200 rotating anode x-ray generator equipped with a Mo anode. A colourless needle crystal (0.09 x 0.08 x 0.15 mm) was used for data collection. The data were collected at a temperature of $-80^{\circ} \pm 1^{\circ}$ C. Three sets of data were collected; the first set ran from 0 to h, 0 to k, 0 to l, the second set ran from -h to h, 0 to k, 0 to l, and the third set ran from 0 to h, 0 to k, -l to l. After careful examination of all three sets of data, only the third set was selected for electron density calculations.

The data were processed using the routine procedure. The merging R was 4.60%. The direct method, SHELXS-86, was used to locate the positions of non-hydrogen atoms. The H(C) hydrogens were placed geometrically (C - H = 1.08 Å); the H(N) were located from the Fourier difference map. During refinement, the positions of the H atoms were kept fixed and assigned fixed isotropic temperature factors $1.2 \times B_{\text{eq}}$ of the atom to which each was bonded. A σ weighting scheme was used and the function minimised was $\sum w(|F_o| - |F_c|)^2$, where w is the weight. No absorption or extinction corrections were applied.

For the calculation of $X - X_{\text{Bo}}$ deformation density maps the positional and thermal parameters were refined first using the high-order reflections ($\theta > 20.3^{\circ}$, $l > 1\sigma(l)$). The parameters from the high order refinement were then used with the low angle data ($3^{\circ} \leq \theta \leq 25^{\circ}$, $l > 3.0\sigma$), to refine the scale factor and calculate the difference Fourier map. The program, TEXSAN⁵², was used for all calculations and refinement.

For multipole deformation density maps, the program MOLLY²⁹ was used. The positional anisotropic thermal parameters of the non-hydrogen atoms were refined first

Table 22. Physical properties and parameters for data collection and refinement of DaHTB (It).

Formula	BC ₃₀ H ₃₃ N ₂
Formula Weight	432.4
Crystal System	orthorombic
<i>a</i> (Å)	18.111(5)
<i>b</i> (Å)	13 234(5)
<i>c</i> (Å)	9.958(6)
<i>V</i> (Å ³)	2387(3)
Space Group	<i>Pnma</i> (No. 62)
<i>Z</i>	4
<i>d</i> _{calc} (g/cm ³)	1.203(2)
<i>F</i> ₀₀₀ (e)	928
μ (MoK α) (cm ⁻¹)	0.63
Radiation	MoK α (λ = 0.71069 Å)
2 θ _{max} (°)	90.0
$\sin\theta/\lambda$	1.41
Reflections:	
Total measured	9,045
Unique total	8,066 (100 <i>R</i> _m = 4.60)
Conventional refinement: (σ weighting scheme, θ = 45)	
Unique used ($I > 3\sigma(I)$)	1444
Parameters refined; d/p	163; 8.9
Agreement Factors:	
100 <i>R</i>	6.97
100 <i>R</i> _w	6.71
G.O.F.	2.33
Residual e.d. (min, max) (e/Å ³)	-0.69, 0.40
Multipole refinement: (σ weighting scheme, θ = 45)	
Unique used ($I > 2\sigma(I)$)	1444
Agreement Factors:	
100 <i>R</i>	6.56
100 <i>R</i> _w	6.80
G.O.F.	1.73
Residual e.d. (min, max) (e/Å ³)	-0.40, 0.30

using the high angle data ($\sin\theta/\lambda > 0.48 \text{ \AA}^{-1}$, $I > 2\sigma(I)$). The hydrogen atoms were placed in their geometrically calculated positions with $C_{\text{aromatic}} - H = 1.08 \text{ \AA}$, $C_{\text{aliphatic}} - H = 1.06 \text{ \AA}$ and $N - H = 1.02 \text{ \AA}$, the distances being derived from neutron structures of similar compounds^{54,55}. The atomic positions and temperature factors were kept fixed and the multipole parameters were refined using all the data ($I > 2\sigma(I)$). There were only 1526 reflections above 2σ , and therefore the multipole refinement was done very carefully in stages; p_v , k' , p_v+k' , p_{lm} of non-hydrogen atoms, p_{lm} of H atoms, k'' were refined separately, then the whole process was repeated. The nitrogen and carbon atoms were refined to octapolar ($l = 3$) and the hydrogen atoms to dipolar ($l = 1$) parameters. Appropriate symmetry constraints were applied to the atoms of the cation and the anion which were found to lie on a mirror plane. To reduce the number of variables to be refined, mirror symmetry was also applied to the phenyl ring, the atoms of which are in general positions. Thus, the multipole parameters of C(2) were made equivalent to those of C(6) and C(3) to C(5). Detailed information concerning the data collection and the refinement procedure is compiled in Table 22. The dynamic deformation, residual maps were calculated using the NF (locally modified NIELSAV) program³³. The multipole population parameters are listed in Appendix 1.

In the compound DaHTB, both the TB anion and DaH cation are on a mirror plane. The mirror plane bisects the anion through the atoms B, C(α) and C(δ) and the associated C(δ) protons; thus one, and one half of two other phenyl rings, are unique. In the cation, the mirror plane passes through the two nitrogen atoms, H(N), and the carbon atoms of one $-\text{CH}_2-\text{CH}_2-$ branched chain. The $X - X_{\text{BO}}$ and dynamic deformation maps of the asymmetric phenyl ring are displayed in Fig. 48. The $X - X_{\text{BO}}$ maps contain more noise, in the form of minor peaks and troughs, however, the general appearance

of the in-plane electron density of the two maps is similar. The deformation density at the C - C bond centre decreases with increasing distance from the B atom which supports the idea that -BPh_3^- is a powerful σ -releasing group. The expected extension of the electron density peaks on the C - C bonds in the direction normal to the ring plane is also visible.

Fig. 49 shows the $X - X_{\text{BO}}$ and dynamic deformation density maps of the phenyl ring which is associated in N - H... π interaction with the cation. The in-plane electron density of both maps is similar. Comparing the $X - X_{\text{BO}}$ map of this ring with the $X - X_{\text{BO}}$ map of the non-hydrogen bonded asymmetric phenyl ring, no significant decrease of electron density is observed. It indicates that the possible H(N)... π interaction is weak. This supports the conclusion reached by Knop *et al.* from their ir spectral investigation of ATB¹²³. The dynamic deformation density map is diffuse and makes it difficult to draw any concrete conclusion from it.

The deformation density maps calculated in the plane of the cation's H(N1), N(1) and N(2), are shown in Fig. 50. In these maps the H-bonded phenyl ring is almost perpendicular to the plane of the paper. In the direction of the N - H vector to the phenyl ring, a charge density contour ($0.15 \text{ e}/\text{\AA}^3$) is found in between the H(N) of the bond donor and the π acceptor. It is located about $1.1 \text{ \AA}$ from the H(N) and $1.6 \text{ \AA}$ from the ring C(α) atom. This would seem to indicate substantial covalent character in the H(N)... π (aromatic) interaction. A similar observation was made by Stevens *et al.*¹⁴³ from the electron density calculations of sodium acetate diacetate. In this map, the expected charge depletion of the N - H bond is also observed. The effect of H-bonding is also visible on the C - C bonding electron density contour of the C atoms close to boron.

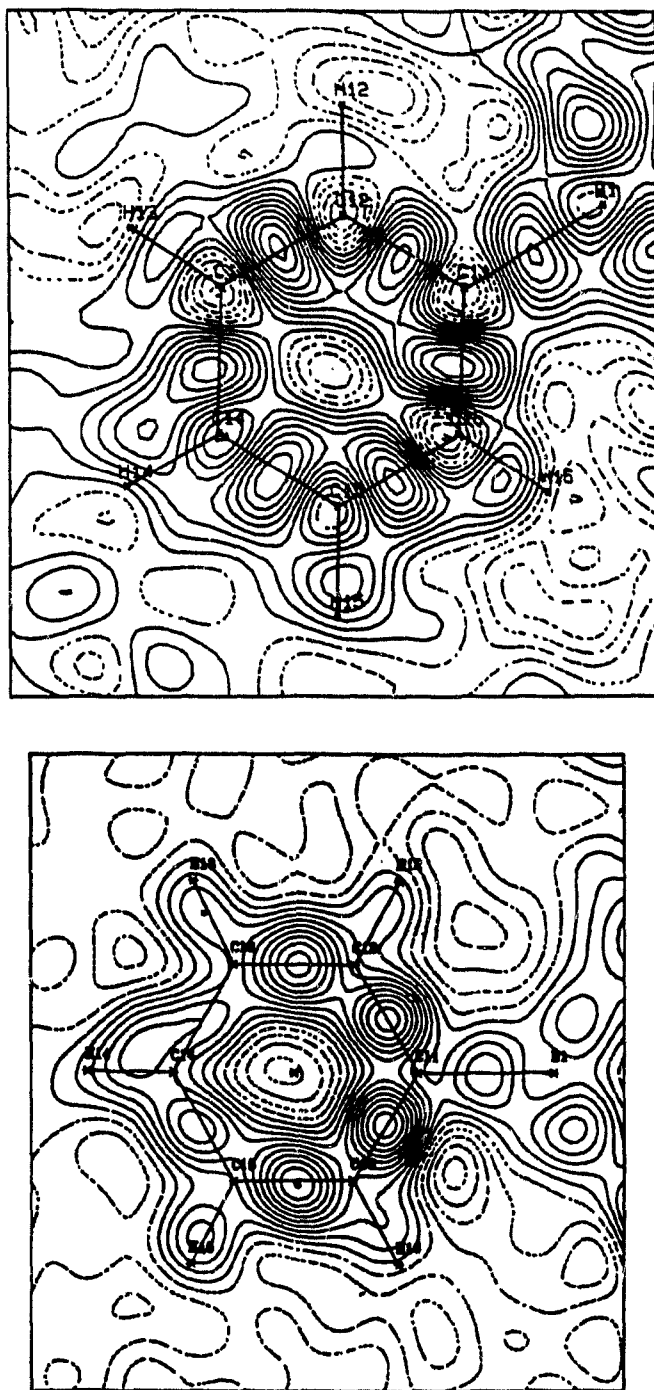


Fig. 48. Deformation density maps in the plane of the asymmetric phenyl ring in the compound DabHTB. Upper diagram - $X - X_{B0}$ map, contours are at 0.06 e/Å³; Lower diagram - dynamic deformation density map, contours are at 0.04 e/Å³.

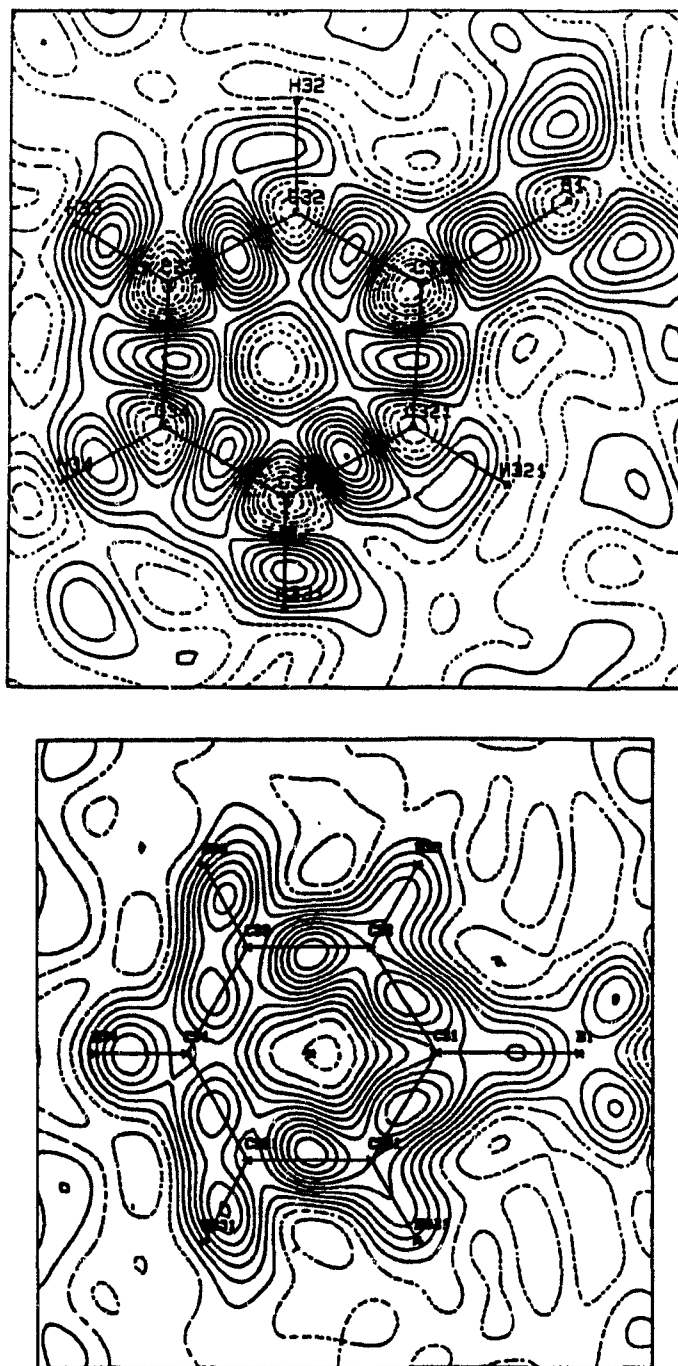


Fig. 49. Deformation density maps in the plane of the phenyl ring which is associated in $H(X) \dots \pi$ interaction. Upper diagram - $X - X_{BO}$ map, contours are at $0.06 \text{ e}/\text{\AA}^3$; Lower diagram - dynamic deformation density map, contours are at $0.04 \text{ e}/\text{\AA}^3$.

The distortion of electron density from the C(31) - C(32) bond became more apparent when the deformation density maps were calculated in the plane passing through C(31), C(33) and the mirror related C(33) atoms of the phenyl ring. Maps were drawn at perpendicular heights of 1.3 Å, 1.6 Å and 2.0 Å, from the plane of the ring (Fig. 51). Electron density increases with increasing perpendicular height from 1.3 Å (0.04 e/Å³) to a maximum at 1.6 Å (0.20 e/Å³) and, then decreases again to about 0.08 e/Å³ at 2.0 Å.

The residual maps (not shown) calculated through the plane of the phenyl rings contain several minor peaks. These unexpected peaks in the residual maps indicate either the pseudoatom model used in the multipole refinement is insufficient or the refinement is incomplete because the refinement was done in stages.

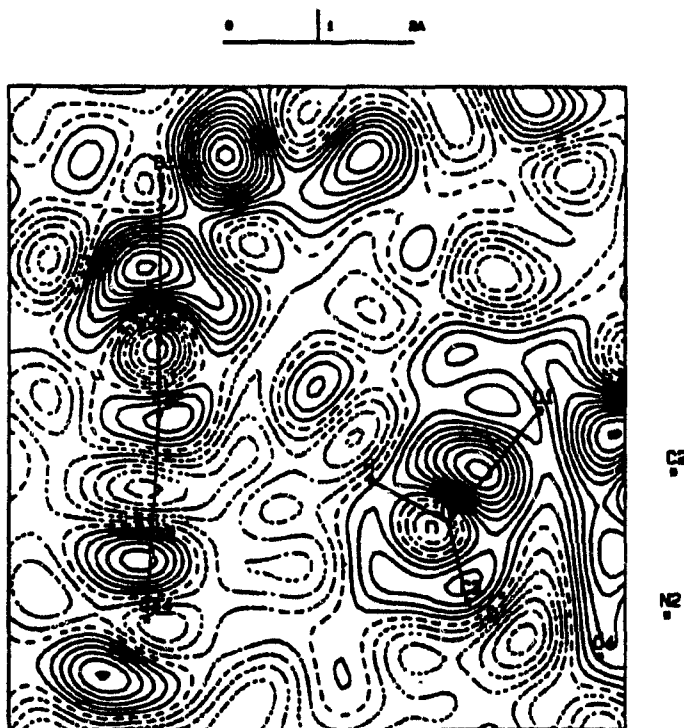


Fig. 50. $X - X_{BO}$ electron density map calculated in the plane of the cation's H(N1), N(1) and N(2). Contours are at 0.05 e/Å³.

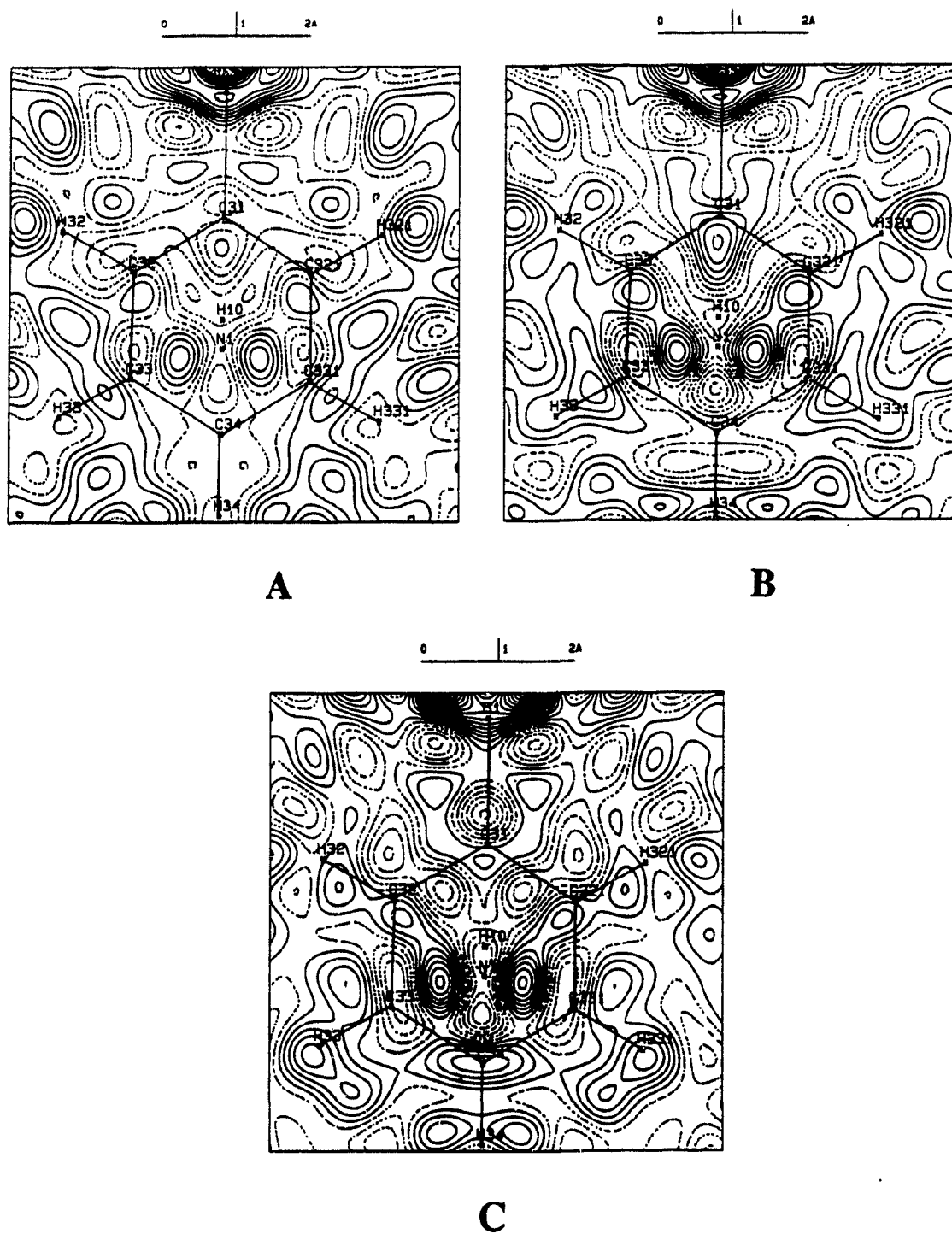


Fig. 51: $X - X_{HO}$ electron density map calculated in the plane of the phenyl ring at perpendicular heights of 1.3 Å (labelled A), 1.6 Å (labelled B) and 2.0 Å (labelled C). Contours are at $0.04 \text{ e}/\text{\AA}^3$.

3.3.3. IR Studies

Formation of an X - H...acc bond will weaken the X - H bond and lead to a lowering of the $\nu(\text{XH})$ stretching frequency relative to the non-H-bonded reference. This lowering can be used to corroborate the presence of an X - H...acc bond in a crystal. Thus the two absorption bands observed in the ir spectrum of the hydrated 3BnTBw, at 3564 and 3506 cm^{-1} (significantly below the $\nu_1(\text{OH}) = 3651.7 \text{ cm}^{-1}$ and $\nu_3(\text{OH}) = 3755.8 \text{ cm}^{-1}$ of the H_2O molecule in water vapour¹⁴⁴) have been assigned to the two $\nu(\text{OH})$ stretching vibrations of the H_2O molecule bonded to phenyl groups. Similarly, the absorption at 3590.5 and 3529.5 cm^{-1} , respectively, in the ir spectrum of ImETBw are assigned to the two O - H...phenyl bonds, identifiable in the crystal structure.

In the case of $\nu(\text{NH})$ vibration in organoammonium compounds the problem of how to establish a reference frequency, to be used for detecting frequency lowering induced by the formation of N - H... π bonds, is much more difficult. A detailed x-ray and ir study of $[\text{NH}_4][\text{BPh}_4]$ ¹²³ indicated that the $\nu(\text{NH})$ is slightly shifted to lower frequency because of the weak N - H... π interaction. By implication, it is reasonable to assume that a $\nu(\text{NH})$ frequency lowering should exist in the compounds of this work, attributable to the presence of such weak N - H... π interactions. The observed N - H stretching frequencies of ImATB are 3246.5 and 3165.5 cm^{-1} , ImCTB are 3238.0 and 3161.0 cm^{-1} and ImDTB are 3228.0 and 3159.0 cm^{-1} .

To clarify the hydrogen bonding situation in BPTB and PTB, their ir spectra were examined (Fig. 52). In the 10K spectrum of PTB, a single sharp $\nu(\text{NH})$ peak was observed at 3278.7 cm^{-1} , well separated from the $\nu(\text{CH})$ absorption. This peak shifted progressively and smoothly to lower frequencies with increasing temperature (the frequency lowering between 10 and 295K is about 6.7 cm^{-1}). The negative $d\nu/dT$

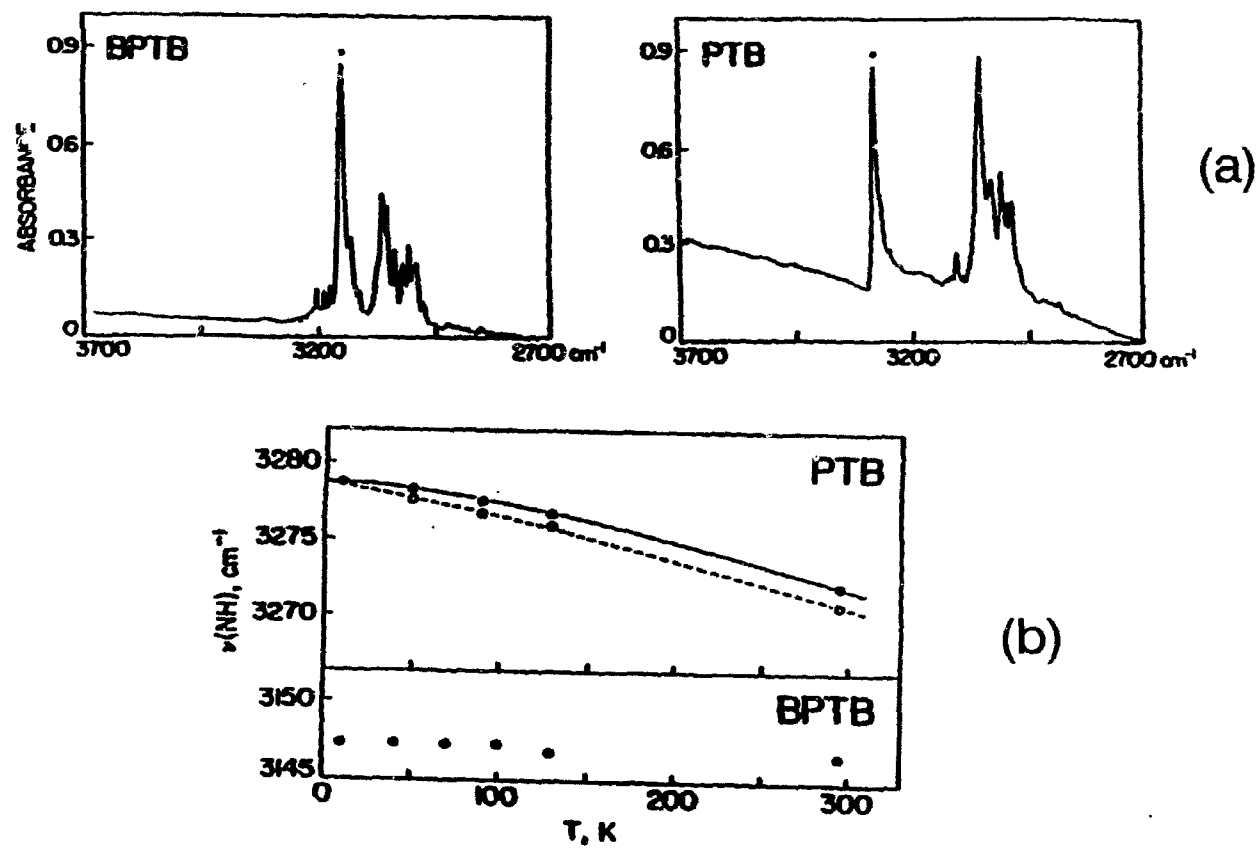


Fig. 52. (a) The $\nu(\text{NH})$ and $\nu(\text{CH})$ region of the FT-ir spectra of BPTB and PTB in fluorocarbon mulls at 10° K. (b) Variation of the $\nu(\text{NH})$ frequency in BPTB and PTB with temperature.

coefficient and in turn, the strengthening of N - H bond with increasing temperature is consistent with the observation of Knop *et al.* in $[\text{NH}_4][\text{BPh}_4]^{123}$ and is suggestive of the presence of a very weak branched hydrogen bond⁸. On the other hand, the $\nu(\text{NH})$ absorption in the 10K spectrum of BPTB showed incipient splitting merged with $\nu(\text{CH})$ absorption. The frequency of the $\nu(\text{NH})$ absorption remained practically unchanged with increasing temperature.

The ir spectrum of the isotopically diluted LiTBw sample was also recorded. Fig. 53 shows the $\nu(\text{OD})$ [of HDO] and the $\delta(\text{HOH})$ [of H_2O] regions of the FT-ir spectrum of the LiTBw sample. In the 10K spectrum, the HOH bending region consists of two resolved doublets with frequencies between 1594 and 1617 cm^{-1} . These four absorptions, of comparable intensities, indicate the presence of four non-equivalent sets of H_2O molecules in the crystal. The doublet at higher frequency (1611.7 and 1616.5

⁸ The effect of cooling on the N - H stretching frequency in N - H... π systems has been well documented and explained (O. Knop and M. Falk, Can. J. Chem., 56, 867, 1980). On cooling the amplitude of the librations about the N - H bond axis decreases. In the case of normal N - H... π bonding, the average distance from acceptor to H shortens thereby allowing the acceptor to increase its pull on the H, away from the bonded atom. The N - H bond becomes weaker and the $\nu(\text{N} - \text{H})$ stretch move to lower frequencies. On the other hand, the $\nu(\text{N} - \text{H})$ frequency for branched hydrogen bond moves higher as the bonds get stronger. In this case, as the amplitude of the libration of the N - H bond decreases the H atom comes to rest between two acceptors and so the average acc...H distance increases. The same argument is also applicable to O - H... π systems.

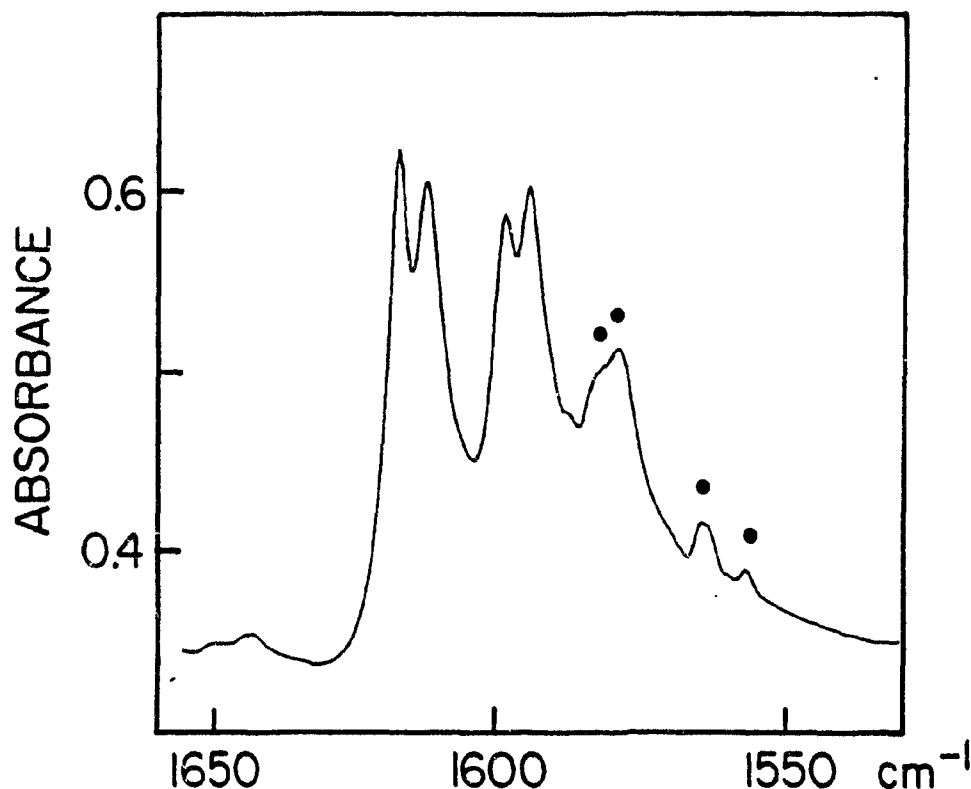


Fig. 53. FT-ir spectrum of H_2O in LBTBw in the HOH bending region at 10 K. Black dots indicate tetraphenylborate absorption.

cm^{-1}) may correspond to the stronger hydrogen bonds, normal $\text{O}(1) - \text{H}\cdots\pi$ and $\text{O}(2) - \text{H}\cdots\pi$, whereas the doublet at lower frequency (1594.1 and 1598.0 cm^{-1}) may correspond to the relatively weak bonds, one normal and one bifurcated $\text{O} - \text{H}\cdots\pi$, each for $\text{O}(3)$ and $\text{O}(4)$. With increasing temperature the four bands all underwent shifts to higher frequencies.

In the $\nu(\text{OD})$ region of the 10K spectrum there were five resolved absorptions observed instead of the expected eight (Fig. 54). Four of these peaks (2619.6 , 2623.4 , 2626.3 and 2631.1 cm^{-1}) were closely-spaced and were of almost equal weight, while

the fifth (2643.9 cm^{-1}) had an approximately fourfold greater weight but showed no sign of incipient splitting. However, with increasing temperature this band split into at least three and possibly four components. The exact number of components was not clear.

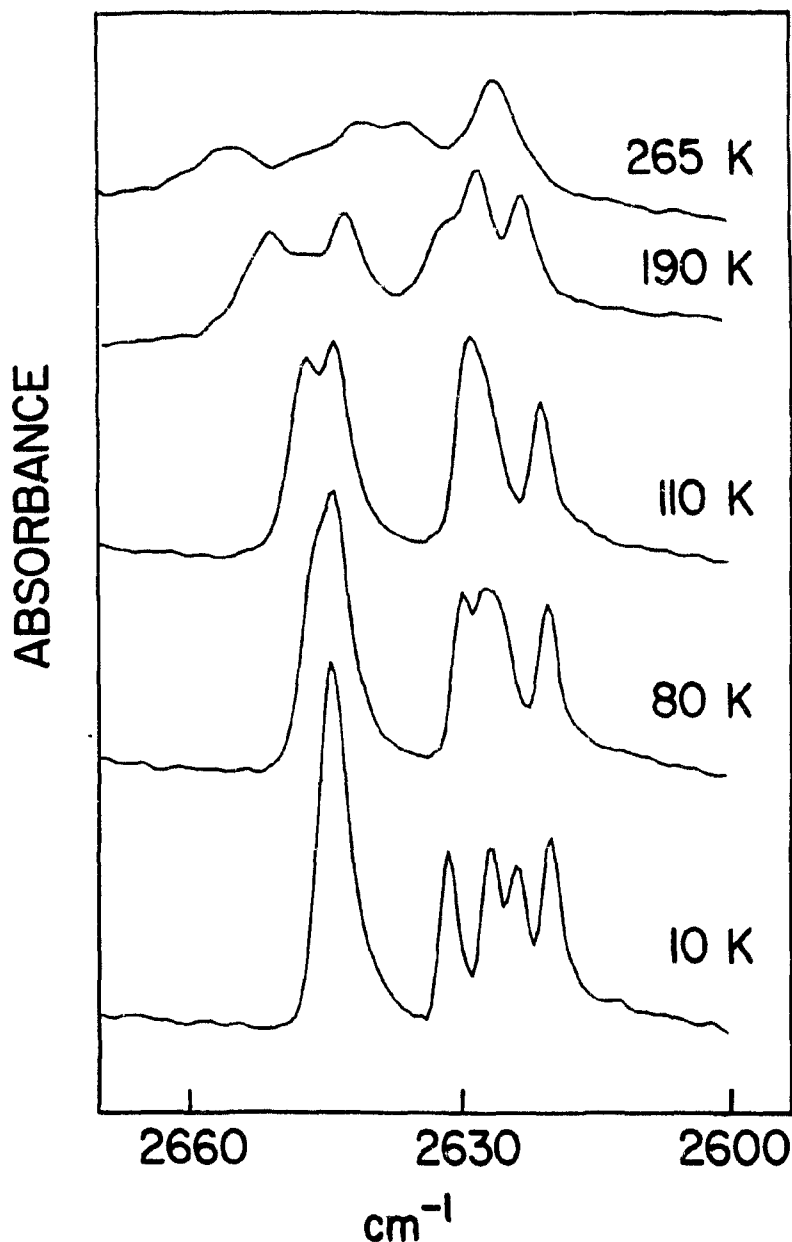


Fig. 54. Ft-ir spectrum of HDO in LiTBw (~3% of the H_2O hydrogen is replaced by D) in the OD stretching frequency region at different temperature.

Fig. 55 shows the temperature coefficient, $d\nu/dT$, of the $\nu(\text{OD})$ frequency. In the lower-frequency quartet, $d\nu(\text{OD})/dT$ is positive for three bands and negative for the fourth. Whereas, $d\nu(\text{OD})/dT$ is positive for two, negative for one and probably positive

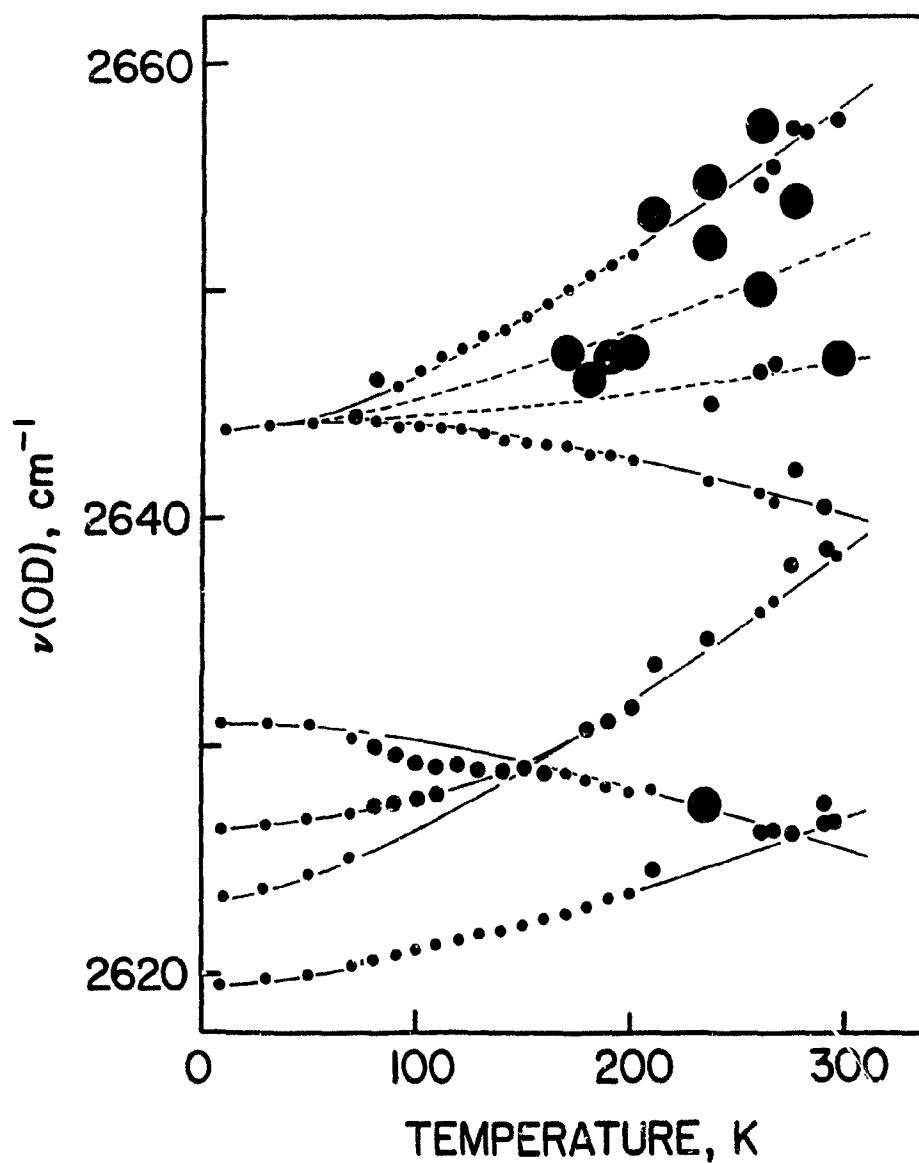


Fig. 55. Variation of the $\nu(\text{OD})$ frequency of HDO in LTBw (~3% D) with temperature.

for the fourth band in the higher-frequency quartet. This observation suggests that at least five ($d\nu/dT > 0$) of the eight O - H... π bonds are normal while two ($d\nu/dT < 0$) are branched.

3.3.4. Hydrogen bonded vs. Nonbonded Cations

It is clear from the above discussion that, given the opportunity, a cation's H(N) (or a H₂O-hydrogen) will form a X - H... π bond to a phenyl group(s) of the tetraphenyl-borate counter anion. However, to understand whether the formation of a hydrogen bond is a positive tendency or not of such a cation, it is necessary to investigate the effect on the cation orientation with respect to the nearest phenyl ring(s) when the N atom is sterically shielded from the anion by alkyl group(s) or when the cation contains regions of high local electron density. To this end, the crystal structures of ImBTB, AzPpTB and 2PhITB have been determined. These structures together with the reported structures of 4MTB, 3MTB, 2MTB.Et₂CO, 3MTeTB, 3MSTB and 3ESTB are presented in Table 23.

Procedures described previously (see page 82-83) have been adopted for the data collection and structure refinement. Only the compound 2PhITB deteriorated by 28% during data collection; a decay correction was applied. The non-hydrogen atoms were refined anisotropically. The hydrogens atoms were placed in their geometrically calculated positions with a C - H distance of 1.08 Å. In ImBTB the hydrogens were refined isotropically riding on corresponding C atoms; otherwise, the hydrogen positions were kept fixed during refinement and assigned fixed isotropic temperature factors of $1.2 \times B_{eq}$ of the atom to which each was bonded. Experimental details are summarised in Tables 24-25. For positional parameters of nonhydrogen atoms and selected bond

Table 23. Crystal structures discussed in this work.

Compound		Abbreviation	Reference
This investigation			
26	$[\text{Me}_2\text{C}=\text{NMe}_2]^+\text{TB}^-$	ImBTB	
27	1-azoniapropellane TB^-	AzPpTB	
28	Diphenyliodonium TB^-	2PhITB	
Cited from the literature			
29	$\text{Me}_4\text{N}^+\text{TB}^-$ (<i>Cmcm</i> , $Z = 4$)	4MTB	145
30	$\text{Me}_3\text{NH}^+\text{TB}^-$ (P2_1 , $Z = 2$)	3MTB	117
31	$\text{Me}_2\text{NH}_2^+\text{TB}^- \cdot \text{Et}_2\text{CO}$ ($\text{P2}_1/n$, $Z = 4$)	2MTB. Et_2CO	117
32	$\text{Me}_3\text{Te}^+\text{TB}^-$ (<i>Cmcm</i> , $Z = 4$)	3MTeTB	146
33	$\text{Me}_3\text{S}^+\text{TB}^-$ ($\text{P2}_1/n$, $Z = 4$)	3MSTB	147
34	$\text{Et}_3\text{S}^+\text{TB}^-$ (<i>Cmcm</i> , $Z = 4$)	3ESTB	147
35	$\text{Et}_2\text{NH}_2^+\text{TB}^-$ ($\text{P2}_12_12_1$, $Z = 4$)	2ETB	117

lengths and angles, see individual structure. The fractional coordinates of the hydrogen atoms and the temperature factors are listed in Appendix 2.

The crystal packing in tetraphenylborate salts is determined largely by the size of the cation. For small organic cations, the packing is symmetric and is often based on the space group *Cmcm* or its subgroups. The structures consist of alternating cation-anion columns and the cation occupies the wedge-shaped tetrahedral cavity formed by four phenyl rings of the anion, either from the same column or from different columns. The freedom of the cation orientation is restricted inside the wedge-shaped space formed by the phenyl rings. The anion system is thus well suited for testing the tendency of a cation to interact with the phenyl groups of the TB and to observe the nature of the cation-anion pair interaction.

It is obvious that in TB compounds the $\text{X} - \text{H} \cdots \pi$ bonding tendency is reinforced by the ionic charge; the question is, to what extent? The tetraphenylborate anion is large,

Table 24. Physical properties and crystal data of ImBTB and AzPpTB.

Formula	BC ₂₉ H ₃₂ N	BC ₃₄ H ₃₈ N
Formula weight	405.4	471.5
Crystal size (mm ³)	0.40 x 0.20 x 0.40	0.35 x 0.32 x 0.42
Crystal system	orthorhombic	monoclinic
Space group	<i>Cmcm</i> (No. 64)	<i>P2₁/n</i> (No. 14)
<i>a</i> (Å)	13.196(4)	9.903(2)
<i>b</i> (Å)	14.469(3)	19.897(2)
<i>c</i> (Å)	25.122(4)	13.630(2)
α (°)	90	90
β (°)	90	92.33(1)
γ (°)	90	90
<i>V</i> (Å ³)	4797(4)	2683(1)
<i>Z</i>	8	4
<i>d</i> _{calc} (g/cm ³)	1.123(2)	1.167(1)
<i>F</i> (000) (e)	1744	1016
Diffractometer	CAD4	RIGAKU
λ (cm ⁻¹)	0.60	0.61
θ range (°)	2 - 23	2 - 23
Reflections:		
total measured	1892	5186
unique total	1887	4891
unique used	832 (<i>I</i> > 3 σ (<i>I</i>))	2134 (<i>I</i> > 3 σ (<i>I</i>))
Parameters refined; <i>d/p</i>	188; 4.4	326; 6.6
Absorption corrections (min, max)	0.71, 1.69	-
Weighting scheme	SHELX	unit
100 <i>R</i> , 100 <i>R</i> _w	4.75, 5.34	4.60, 4.60
G.O.F.	2.09	2.56
Residual <i>e. d.</i> (min, max) (e/Å ³)	-0.20, 0.17	-0.14, 0.26

Table 25. Physical properties and crystal data of 2PhITB (free refinement).

Formula	BC ₃₆ H ₃₀ I
Formula weight	630.4
Crystal size (mm ³)	0.20 x 0.25 x 0.30
Crystal system	orthorhombic
Space group	<i>Pnma</i> (No. 62)
<i>a</i> (Å)	17.731(4)
<i>b</i> (Å)	16.382(6)
<i>c</i> (Å)	9.982(4)
α (°)	90
β (°)	90
γ (°)	90
<i>V</i> (Å ³)	2899(3)
<i>Z</i>	4
<i>d</i> _{calc} (g/cm ³)	1.444(1)
<i>F</i> (000) (e)	1276
Diffractometer	RIGAKU
λ (cm ⁻¹)	11.2
θ range (°)	2 - 30
Reflections:	
total measured	4710
unique total	4710
unique used	1370 (<i>I</i> > 3 σ (<i>I</i>))
Parameters refined; d/p	195; 7.0
Absorption corrections (min, max)	0.57, 1.64
Weighting scheme	unit
100 <i>R</i> , 100 <i>R</i> _w	6.89, 6.89
G.O.F.	3.05
Residual e. d. (min, max) (e/Å ³)	-0.99, 1.05

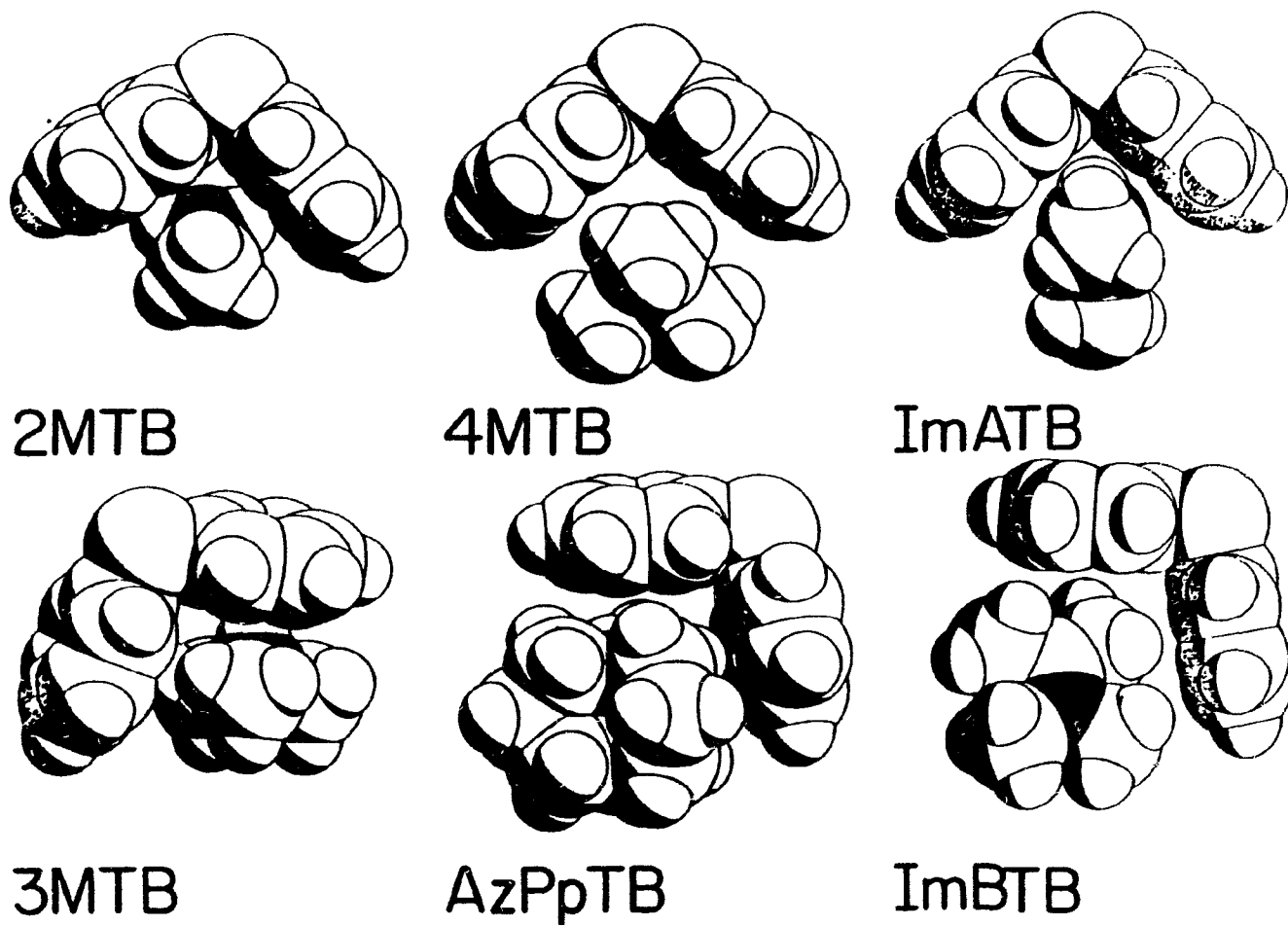


Fig. 56. Space-filling representation of the cation-anion pairs indicating the effect of replacing H(N) by a methyl group(s). The N atoms are shown in black.

so its single negative charge is greatly diluted and each phenyl ring bears at most $\frac{1}{4}$ of the charge. On the other hand, the net charge on the interacting H(N) in the cation, is larger but not dramatically larger than that on a CH_3 or CH_2 hydrogen⁴. Thus it can be assumed that in the hydrogen-bonded TBs, the cation orientation responds mainly to H-bonding interactions and less to Columbic cation-anion interactions. This becomes more clear when a comparison is made between the cation orientations of ImATB and ImBTB, 2MTB.Et₂CO and 4MTB, and 3MTB and AzPpTB (Fig. 56). The planar cation in ImATB is oriented in the plane bisecting the angle between the two phenyl rings in such a way that the H(N) forms a symmetrically bifurcated N - H... π bond. In ImBTB, the Me groups facing the rings are more or less equidistant, with the N - Me groups directed away from the rings. The cations, in the compounds Me_2NH_2^+ and Me_4N^+ , are rotated about their respective N...B axes so as to achieve hydrogen bonding in Me_2NH_2^+ but "antibonding" of the corresponding Me groups in Me_4N^+ . The orientations of the cations in the compounds 3MTB and AzPpTB are comparable with those observed for the cations Me_2NH_2^+ and Me_4N^+ , respectively. All the diagrams in Fig. 56 are on the same scale, therefore it is immediately clear that the H-bonded cations are closer to the phenyl rings than the nonbonded ones. Table 26, which shows the N... π_c and N...B separations for the H-bonded and nonbonded cations, further supports this idea.

The plot of the N... π_c vs. the N...B distance (Fig. 57) also shows the difference between the situations for which N - H... π bonding is claimed and those in which such bonding is absent. For the cations containing two H(N) atoms, both involved in N - H... π bonding, the points fall in a relatively small area, with N...B separations below 4.8 Å. Two points need to be considered for the cations which contain a single H(N) atom, one for the ring which is engaged in a N - H... π bond and the other for the ring which

is nonbonded. The points corresponding to bonding interaction fall in the general 2H(N) - cation region, at slightly longer N...B distances, while the others have $d(\text{N}...\pi_c) > 4.0 \text{ \AA}$, consistent with the absence of H-bonding. The N...B separation is above 5.5 Å for the cations which contain no H(N), and thus no N - H... π bonds, and also for cations in which the N atom is isolated from the associated phenyl rings by -CH₂ or -CH₃ groups. There is no overlap observed between the H-bonded and the nonbonded region of the N... π_c vs. N...B plot.

Table 26. Shortest interatomic distances (Å) between the cation and the centre π_c of the associated phenyl ring(s) or the boron atoms in tetraphenylborates.

Compound	Z...B		Z... π_c		other contacts	
ImATB	N...B	4.32	N... π_c (2)	3.32	H(N)... π_c (2)	2.70
ImBTB	N(C)...B	6.21	N... π_c (1)	4.54		
			N... π_c (4A)	5.13		
2MTB.Et ₂ CO	N...B	4.53	N... π_c (3)	3.26	H(N1)... π_c (3)	2.26
			N... π_c (4)	3.19	H(N2)... π_c (4)	2.34
4MTB	N...B	5.58	N... π_c (2)	4.37	C(1)... π_c (2)	3.90
					H(1')... π_c (2)	3.10
3MTB	N...B	4.74	N... π_c (2)	3.25	H(N)... π_c (2)	2.38
			N... π_c (4)	4.21	H(N)... π_c (4)	4.17
AzPpTB	N...B	5.78	N... π_c (3)	4.32	H(1,11)... π_c (3)	2.82
			N... π_c (4)	4.63	H(1,22)... π_c (4)	3.47
	C...B	6.95	C... π_c (3)	5.82	C(1,1)... π_c (3)	3.75
			C... π_c (4)	5.21	C(1 2)... π_c (4)	4.39
3MeTeTB	Te...B	6.03	Te... π_c (2)	4.38	C(1)... π_c (2)	3.92
	Te*...B	6.03	Te*... π_c (2)	5.05	C(1*)... π_c (2)	3.92
2PhITB	I...B	4.38	I... π_c (1)	3.49	I...C(16)	3.35
					I...C(15)	3.50
					I...C(11)	3.65
					I...C(14)	3.88
3MSTB	S...B	5.54	S... π_c (2)	3.89		
			S... π_c (4)	4.72		
3ESTB	S(B)...B(A)	5.18	S(B)... π_c (2)	3.94		
	S(B)...B	5.72	S(B)... π_c (4)	4.89		
			S(B)... π_c (1A)	5.15		
2ETB	N...B	4.23	N... π_c (1)	3.26	H(N1)... π_c (1)	2.24
			N... π_c (3)	3.16	H(N1)... π_c (3)	2.24

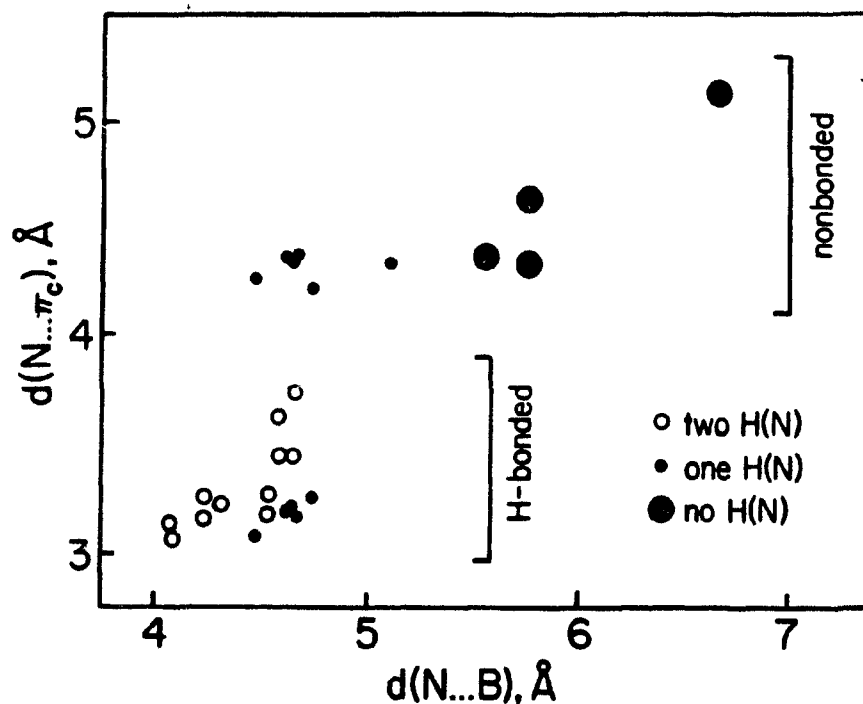


Fig. 57. Plot of the shortest $d(N...π_c)$ against $d(N...B)$ in the tetraphenylborates of Table 26.

How does this situation change when a methyl group is replaced by an oriented lone pair? The answer is provided by comparing 4MTB with 3MTeTB. These two compounds are isostructural with their structures controlled by the anion packing. The Me_4N^+ in 4MTB cation is fully ordered whereas in 3MTeTB the Me_3Te^+ has a twofold orientational disorder across a mirror plane. Fig. 58 shows that the lone pair in Me_3Te^+ is oriented away from the phenyl rings, in preference to an orientation in which it would replace one of the Me groups in 4MTB.

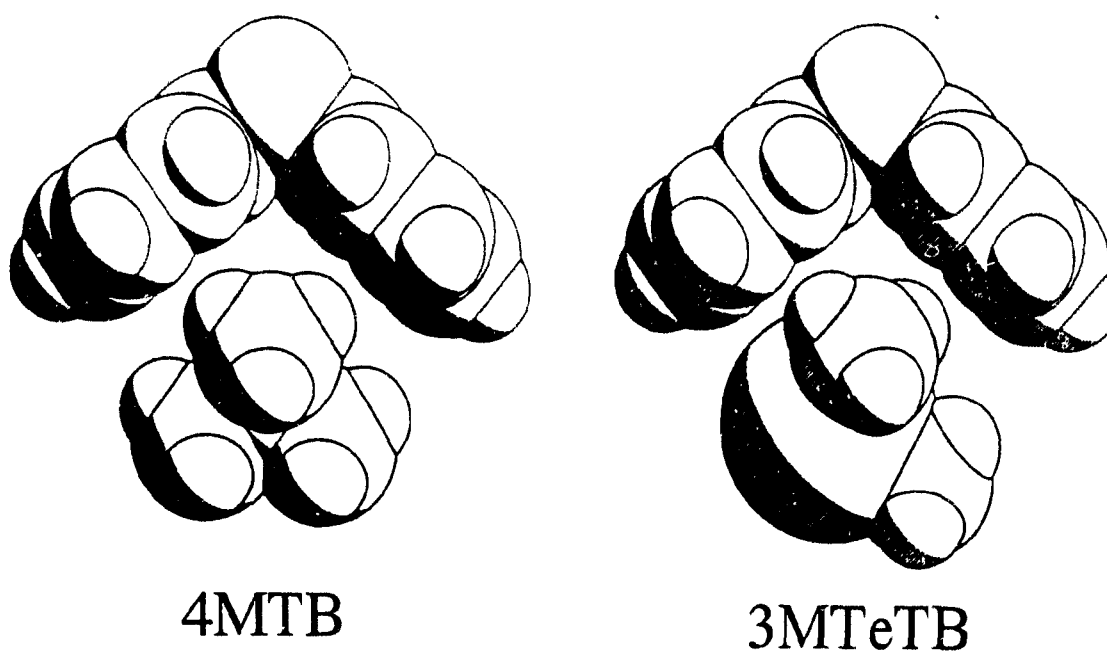


Fig. 58. Cation orientation in the 4MTB and 3MTeTB compounds.

Because of the bulk of the cation phenyl groups, the principle is less clear for the compound 2PhITB. However, it is evident from the Fig. 59 that the two lone pairs on the iodine atom are oriented sideways, away from the rings, so as to minimize the lone pair...phenyl repulsion. The shortest I... π_c distance in 2PhITB is 3.89 Å, greater than the estimated van der Waals contact of 3.7 Å. The compounds 3MSTB and 3ESTB which have been reported in the literature¹⁴⁷, all show a very similar ring-avoiding tendency by the lone pair (Fig. 59).

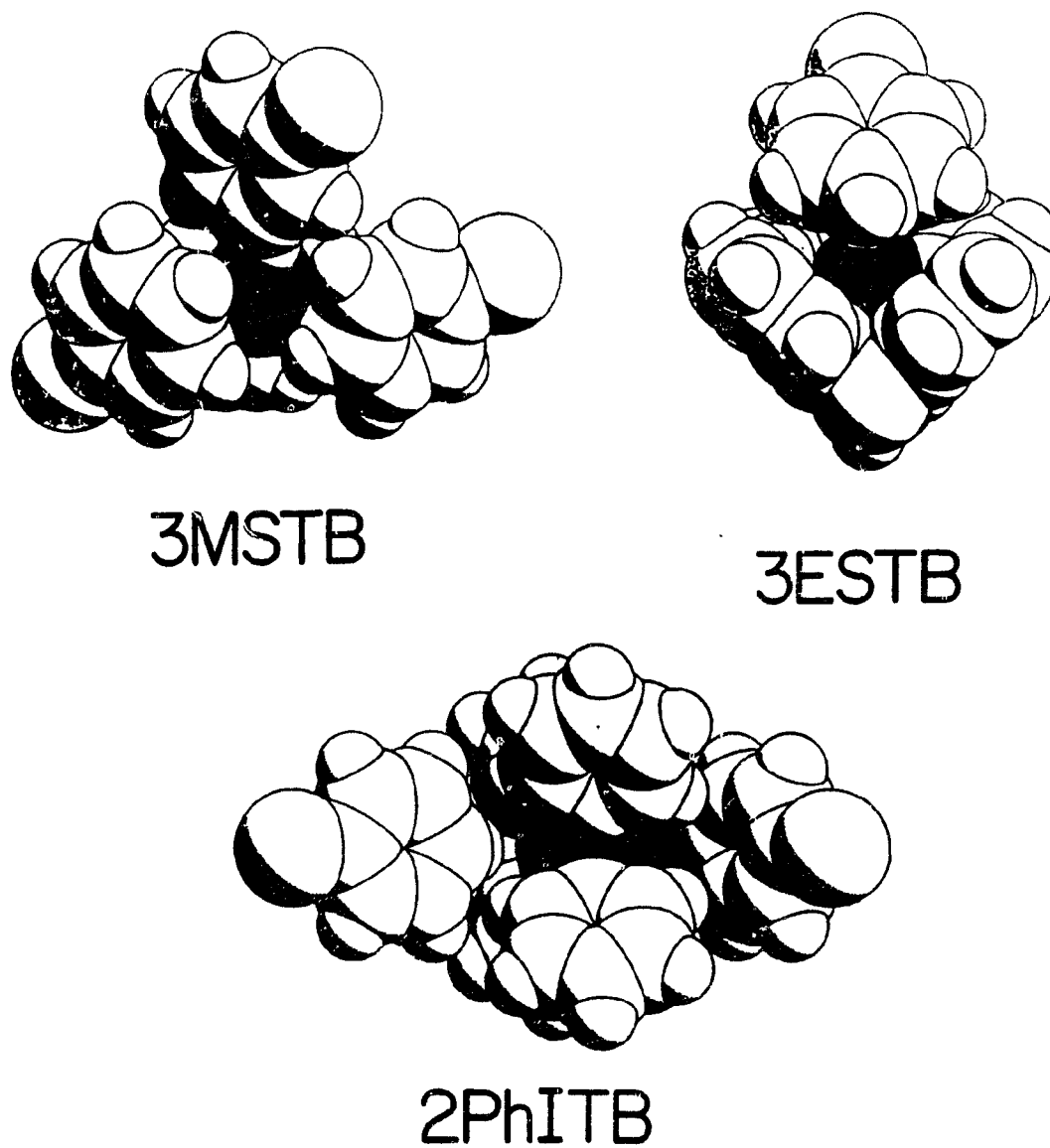


Fig. 59. Avoidance of the phenyl rings by the lone pairs on the S and I atoms in 3MSTB, 3ESTB and 2PhITB.

3.4. Individual Crystal Structures

ImATB, [Me₂C=NHMe]⁺TB

Atomic positions, selected bond lengths and angles involving the non-hydrogen atoms are listed in Table 27-28. The asymmetric unit contains one cation-anion pair. The cation skeleton is planar (C_s) and disordered across a mirror plane perpendicular to the cation plane. An F_{obs} map in the plane of the cation (Fig. 60), clearly shows the twofold positional disorder across the mirror plane parallel to (001) at $z = \pm 1/4$, which interchanges z and $z' = 1/2 - z$. Modelling of the twofold positional disorder across the mirror $\parallel$ (001) improves the U values significantly. However, the U_{11} values of several atoms; particularly C(C1), still remain high, suggesting that these atoms might be disordered about the second mirror plane. Attempts were made to model this disorder but these failed.

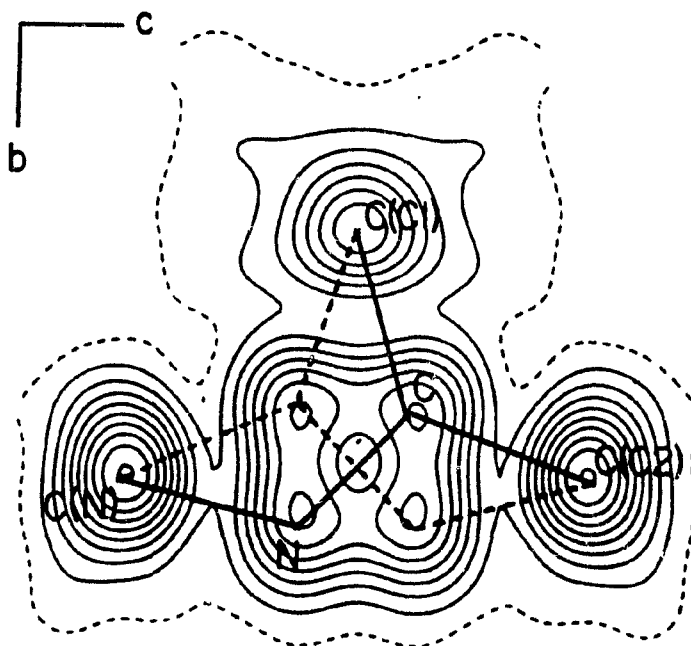
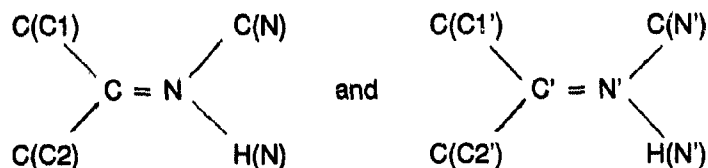


Fig. 60. F_{obs} map in the plane of the cation, [Me₂C = NHMe]⁺. Contour intervals, 0.4 e/Å³. The cation disorder is across the vertical mirror $\parallel$ (001).

The cation consists of two disordered units:



The distance between the disordered atoms C - C' and N - N' are 0.859(7) and 0.955(7) Å, respectively. The C = N⁺ distance is 1.261(7) Å. The cation is inserted between two phenyl rings in such a way that the N - H vector occupies a position which is equidistant from the two phenyl rings formed by C(21) - C(24) and their mirror related carbon atoms. Thus, a bifurcated hydrogen bond (type K) is formed.

In the anion, the B atom lies on the two mirror plane at $x = \frac{1}{2}$ and $z = \frac{3}{4}$. The C(α) and the C(δ) atoms and the associated H(δ) atoms of the phenyl rings also lie on the mirror plane.

Table 27. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for ImATB (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	Ueq
B	1/2	0.1666(4)	3/4	0.0336
C(11)	1/2	0.2313(2)	0.6542(3)	0.0371
C(12)	0.3899(3)	0.2641(1)	0.6127(2)	0.0448
C(13)	0.3893(3)	0.3237(1)	0.5367(2)	0.0509
C(14)	1/2	0.3535(2)	0.4973(3)	0.0543
C(21)	0.3802(4)	0.1024(2)	3/4	0.0378
C(22)	0.3294(3)	0.0694(1)	0.6626(2)	0.0517
C(23)	0.2336(3)	0.0090(1)	0.6622(2)	0.0705
C(24)	0.1871(5)	-0.0215(3)	3/4	0.0728
N	1/2	0.1079(5)	0.2145(5)	0.0701
C(N) = C(C2')	1/2	0.1311(4)	0.1097(4)	0.0916
C	1/2	0.1639(5)	0.2819(5)	0.0549
C(C1) = C(C1')	1/2	0.2566(4)	1/4	0.1110
C(C2) = C(N')	1/2	0.1311(4)	0.3903(4)	0.0916

Table 28. Selected bond lengths (Å), contacts (Å) and angles (°) for ImATB (with e.s.d.'s in parentheses).

C - N	1.261(7)	H(N)...C(21)	2.67
C - C(C1)	1.512(6)	H(N)...C(22)	2.75
C - C(C2)	1.546(6)	H(N)...C(23)	2.75
N - C(N)	1.457(6)	H(N)...C(24)	3.30
		H(N)...C(25)	3.30
B - C(11)	1.640(3)	H(N)...C(26)	3.39
B - C(11)	1.640(3)	Mean	3.03(27)
B - C(21)	1.633(3)		
B - C(21)	1.633(3)	H(N)... $\pi_c(2)$	2.70
Mean	1.637(4)		
		H(N)...C(21)	2.67
N...C(21)	3.564(5)	H(N)...C(22)	2.75
N...C(22)	3.398(6)	H(N)...C(23)	2.75
N...C(22)	3.398(6)	H(N)...C(24)	3.30
N...C(23)	3.781(6)	H(N)...C(25)	3.30
N...C(23)	3.781(6)	H(N)...C(26)	3.39
N...C(24)	3.655(6)	Mean	3.03(27)
Mean	3.60(13)		
		H(N)... $\pi_c(4)$	2.70
N... $\pi_c(2)$	3.32		
N...C(21)	3.564(5)		
N...C(22)	3.398(6)		
N...C(22)	3.398(6)		
N...C(23)	3.781(6)		
N...C(23)	3.781(6)		
N...C(24)	3.655(6)		
Mean	3.60(13)		
N... $\pi_c(4)$	3.32		
C(C1) - C - N	117.5(4)	C(11) - B - C(21)	112.3(2)
C(C2) - C - N	116.6(4)	C(11) - B - C(21)	112.3(2)
C(C1) - C - C(C2)	125.9(4)	C(11) - B - C(21)	112.3(2)
C - N - C(N)	121.5(4)	C(11) - B - C(21)	112.3(2)
H(N) - N - C	118.6	Mean	112.3(0)
H(N) - N - C(N)	119.9		
		C(12) - C(11) - C(12)	114.8(2)
C(11) - B - C(11)	103.7(2)	C(12) - C(11) - C(12)	114.8(2)
C(21) - B - C(21)	104.1(2)	C(22) - C(21) - C(22)	114.9(3)
Mean	103.9(2)	C(22) - C(21) - C(22)	114.9(3)
		Mean	114.9(1)

ImCTB, [Me₂C=NHEt]TB

The compound ImCTB is monoclinic, with space group $P2_1/n$ ($Z = 4$). Each asymmetric unit contains one [Me₂C = NHEt]⁺ cation and one TB anion. All atoms are in general positions. The positional and equivalent isotropic thermal parameters of the non-hydrogen atoms are given in Table 29. Selected bond lengths and angles are listed in Table 30.

The cation is almost planar, the maximum deviation from the plane being 0.057 Å for H(N). The cation is enclosed asymmetrically by four phenyl rings from a pair of TB anions, rings 1 and 4 from one and rings 2 and 3 from another neighbour. Because of its awkward shape, the cation does not fit well into the tetrahedral cavity formed by the four phenyl rings; the fit is worse than that seen in the compounds ImATB or ImDTB. The uncorrected C = N⁺ bond length is 1.277(4) Å. In this case, the N - H vector points toward only one plane of the phenyl ring consisting of atoms from C(11) to C(16). The N(H)... π bonding is normal and of type A.

Table 29. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for ImCTB (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	U _{eq}
B	0.9836(3)	0.1732(3)	0.2504(3)	0.0371
C(11)	0.8671(3)	0.1196(3)	0.2685(2)	0.0396
C(12)	0.8568(3)	0.0240(3)	0.2907(3)	0.0540
C(13)	0.7575(4)	-0.0164(3)	0.3119(3)	0.0710
C(14)	0.6642(4)	0.0375(4)	0.3122(3)	0.0737
C(15)	0.6694(3)	0.1321(4)	0.2901(3)	0.0683
C(16)	0.7686(3)	0.1717(3)	0.2687(3)	0.0510
C(21)	1.0797(3)	0.0973(2)	0.2284(2)	0.0372
C(22)	1.1902(3)	0.0975(3)	0.2682(2)	0.0495
C(23)	1.2683(3)	0.0338(3)	0.2401(3)	0.0649
C(24)	1.2398(4)	-0.0321(3)	0.1717(3)	0.0722
C(25)	1.1316(4)	-0.0348(3)	0.1291(3)	0.0653
C(26)	1.0548(3)	0.0289(3)	0.1572(3)	0.0504
C(31)	0.9685(3)	0.2412(2)	0.1562(2)	0.0361
C(32)	0.8872(3)	0.2266(3)	0.0800(3)	0.0490
C(33)	0.8804(3)	0.2802(3)	-0.0028(3)	0.0639
C(34)	0.9554(4)	0.3516(3)	-0.0119(3)	0.0699
C(35)	1.0363(3)	0.3684(3)	0.0604(3)	0.0632
C(36)	1.0429(3)	0.3142(3)	0.1429(3)	0.0508
C(41)	1.0155(3)	0.2359(2)	0.3475(2)	0.0375
C(42)	1.0657(3)	0.1962(3)	0.4316(3)	0.0496
C(43)	1.0898(3)	0.2480(3)	0.5152(3)	0.0601
C(44)	1.0611(4)	0.3418(3)	0.5176(3)	0.0697
C(45)	1.0083(4)	0.3828(3)	0.4375(3)	0.0673
C(46)	0.9868(3)	0.3305(3)	0.3551(3)	0.0514
N	0.7840(3)	0.2335(3)	0.5070(2)	0.0659
C(N1)	0.7441(4)	0.3298(3)	0.5198(3)	0.0848
C(N2)	0.6830(5)	0.3676(4)	0.4330(4)	0.1357
C	0.8349(3)	0.1806(3)	0.5706(3)	0.0607
C(C1)	0.8657(4)	0.2149(3)	0.6692(3)	0.0855
C(C2)	0.8624(4)	0.0831(3)	0.5472(3)	0.0864

Table 30. Selected bond lengths (Å), contacts (Å) and angles (°) for ImCTB (with e.s.d.'s in parentheses).

C - N	1.277(4)	H(N)...C(11)	3.07
C - C(C1)	1.489(5)	H(N)...C(12)	3.56
C - C(C2)	1.461(5)	H(N)...C(13)	3.62
N - C(N1)	1.460(5)	H(N)...C(14)	3.17
C(N1) - C(N2)	1.467(6)	H(N)...C(15)	2.56
		H(N)...C(16)	2.48
		Mean	3.08(44)
B - C(11)	1.648(5)		
B - C(21)	1.638(5)	H(N)... $\pi_c(1)$	2.78
B - C(31)	1.637(5)		
B - C(41)	1.647(5)		
Mean	1.65(21)		
N...C(11)	3.970(5)		
N...C(12)	4.414(5)		
N...C(13)	4.469(6)		
N...C(14)	4.063(6)		
N...C(15)	3.536(5)		
N...C(16)	3.473(5)		
Mean	3.99(39)		
N... $\pi_c(1)$	3.76		
C(C1) - C - N	121.7(4)	C(11) - B - C(21)	111.8(3)
C(C2) - C - N	119.7(4)	C(11) - B - C(31)	111.9(3)
C(C1) - C - C(C2)	118.6(4)	C(21) - B - C(41)	113.7(3)
C(N1) - N - C	126.7(4)	C(31) - B - C(41)	111.3(3)
N - C(N1) - C(N2)	112.2(4)	Mean	112.2(9)
H(N) - N - C	116.7		
H(N) - N - C(N1)	116.7	C(12) - C(11) - C(16)	114.0(3)
		C(22) - C(21) - C(26)	114.5(3)
C(11) - B - C(41)	104.1(3)	C(32) - C(31) - C(36)	114.7(3)
C(21) - B - C(31)	104.3(3)	C(42) - C(41) - C(46)	114.2(3)
Mean	104.2(1)	Mean	114.4(3)

ImDTB, [MeEtC=NHMe]TB

As was discussed in the experimental section, organic ammonium tetraphenylborate crystals are generally weak scatterers; significant reflections were seldom observed above a $(\sin\theta)/\lambda$ limit of $0.48 \text{ \AA}^{-1}$ ($\theta = 20^\circ$ for Mo radiation). Compound ImDTB was no exception. The intensities were first collected at room temperature. After solving the structure it was found that the ratio of the number of observed reflections (d) ($I > 3\sigma(I)$) to the number of parameters (p) was only 4.28 even after fixing both the positions and the temperature factors of the hydrogen atoms. The intensities were therefore re-collected at low temperature (-70°C), with a view to improving the d/p ratio. However, after data processing it was found that the number of observed reflections ($I > 3\sigma(I)$) at low temperature, relative to room temperature, was increased by only 27 reflections (i.e. 3.81 % of the total unique data used). The coordinates of the non-hydrogen atoms, obtained from the low temperature data refinement, are listed in Table 31. Selected bond lengths and angles are listed in Table 32.

In compound ImDTB, all atoms of the cation are in general positions, while the B, C(11), C(14), C(21), and C(24) of the anion lie on a mirror plane at $x = 0$. The cation is disordered, across the mirror at (100) making $x' = -x$. The cation skeleton is essentially planar. The C = N⁺ distance is $1.271(11) \text{ \AA}$.

As in the compound ImATB, the N - H vector in ImDTB is directed between the plane of the two phenyl rings (ring C(31) - C(36) and its mirror related counterpart). Thus the H(N)..... π bonding is bifurcated and of type K.

Table 31. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for ImDTB (It) (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	Ueq
B	0	0.3346(4)	0.0904(0)	0.0297
C(11)	0	0.2713(6)	-0.0101(7)	0.0262
C(12)	0.1094(6)	0.2366(4)	-0.0488(5)	0.0356
C(13)	0.1091(8)	0.1764(5)	-0.1242(6)	0.0503
C(14)	0	0.1418(8)	-0.1629(10)	0.0603
C(21)	0	0.2688(6)	0.1815(8)	0.0331
C(22)	0.1051(7)	0.2381(4)	0.2245(5)	0.0395
C(23)	0.1072(7)	0.1767(4)	0.2989(5)	0.0385
C(24)	0	0.1473(6)	0.3371(7)	0.0333
C(31)	0.1173(3)	0.3998(2)	0.0859(7)	0.0345
C(32)	0.1673(8)	0.4316(4)	-0.0017(5)	0.0485
C(33)	0.2620(10)	0.4933(5)	0.0034(8)	0.0760
C(34)	0.3082(4)	0.5227(2)	0.0915(9)	0.0636
C(35)	0.2619(7)	0.4920(4)	0.1786(6)	0.0529
C(36)	0.1682(7)	0.4322(4)	0.1746(5)	0.0432
N	0.0295(0)	0.3923(4)	-0.4504(6)	0.0509
C(N)	-0.0034(4)	0.3746(7)	-0.5543(7)	0.0688
C	0.0197(10)	0.3373(5)	-0.3812(6)	0.0491
C(C1)	0.0295(0)	0.3636(8)	-0.2710(10)	0.0650
C(C21)	0.0515(6)	0.2484(5)	-0.4119(15)	0.0494
C(C22)	-0.0624(8)	0.1944(6)	-0.4145(14)	0.0718

Table 32. Selected bond lengths (Å), contacts (Å) and angles (°) for ImDTB (with e.s.d.'s in parentheses).

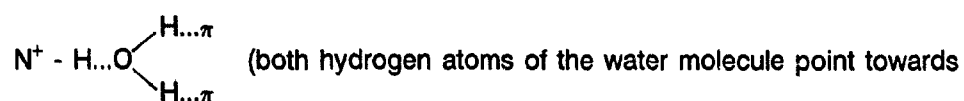
C - N	1.271(11)	H(N)...C(31)	2.70
C - C(C1)	1.539(12)	H(N)...C(32)	2.82
C - C(C21)	1.49(2)	H(N)...C(33)	3.23
C(C21)-C(C22)	1.51(2)	H(N)...C(34)	3.54
N - C(N)	1.47(2)	H(N)...C(35)	3.45
		H(N)...C(36)	3.01
		Mean	3.13(31)
B - C(11)	1.674(6)		
B - C(21)	1.598(7)	H(N)... $\pi_c(3)$	2.81
B - C(31)	1.642(6)		
B - C(31)	1.642(6)	H(N)...C(31)	2.58
Mean	1.639(27)	H(N)...C(32)	2.65
		H(N)...C(33)	3.00
N...C(31)	3.662(7)	H(N)...C(34)	3.29
N...C(32)	3.566(9)	H(N)...C(35)	3.23
N...C(33)	3.716(11)	H(N)...C(36)	2.86
N...C(34)	3.975(9)	Mean	2.94(27)
N...C(35)	4.061(10)		
N...C(36)	3.880(9)	H(N)... $\pi_c(3)$	2.60
Mean	3.81(18)		
N... $\pi_c(3)$	3.55		
N...C(31)	3.427(7)		
N...C(32)	3.216(9)		
N...C(33)	3.176(11)		
N...C(34)	3.381(9)		
N...C(35)	3.574(10)		
N...C(36)	3.559(9)		
Mean	3.39(15)		
N... $\pi_c(3)$	3.09		
C(C1) - C - N	121.0(8)	C(11) - B - C(31)	109.7(3)
C(C21) - C - N	114.1(8)	C(11) - B - C(31)	109.7(3)
C(C1) - C - C(C21)	119.9(8)	C(21) - B - C(31)	115.3(2)
C(C22) - C(21) - C	109.6(10)	C(21) - B - C(31)	115.3(2)
C(N) - N - C	123.2(10)	Mean	112.5(28)
H(N) - N - C	116.2		
H(N) - N - C(N)	111.6	C(12) - C(11) - C(12)	115.9(6)
		C(22) - C(21) - C(22)	113.8(7)
C(11) - B - C(21)	103.7(3)	C(32) - C(31) - C(36)	115.4(6)
C(31) - B - C(31)	103.1(3)	C(32) - C(31) - C(36)	115.4(6)
Mean	103.4(3)	Mean	115.1(8)

ImETBw, [Me₂C=NH(-CH₂CH₂Ph)]TB.H₂O

This structure consists of the iminium cation, the tetraphenylborate anion and a water molecule. The atomic positions, selected bond lengths and bond angles are listed in Tables 33-34.

In this compound, the cation, the anion and the water molecule are all arranged in layers parallel to (100). Within a layer the anions form columns generated by the *c* glide plane and the water molecules are dispersed between the anion columns. The iminium fragment of the cation which consists of atoms C(N1), H(N1), N, C, C(C1) and C(C2), is essentially planar, the maximum distance from the best plane being 0.042 Å for N. The C = N⁺ distance is 1.291(11) Å.

Since the cation is too bulky to allow proper penetration into the cavity formed by the phenyl rings, as is also the case with tributylammonium tetraphenylborate¹²², a water molecule of solvation is included in the crystal. Thus the interaction between the iminium ion and the tetraphenylborate anion is mediated by a water molecule according to the scheme:



the π -electron cloud of the two phenyl rings). The H(N1)...O distance in the N⁺-H...O grouping is 1.76 Å.

Table 33. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for ImETBw (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	U _{eq}
B	0.1465(3)	0.0469(9)	0.0669(4)	0.0325
C(11)	0.1041(2)	-0.0201(8)	0.0962(4)	0.0376
C(12)	0.0883(2)	-0.1494(9)	0.0754(4)	0.0543
C(13)	0.0553(3)	-0.2150(10)	0.1050(5)	0.0634
C(14)	0.0365(2)	-0.1550(10)	0.1575(5)	0.0631
C(15)	0.0514(3)	-0.0290(10)	0.1805(4)	0.0615
C(16)	0.0848(2)	0.0353(9)	0.1501(4)	0.0488
C(21)	0.1889(2)	-0.0318(9)	0.1075(4)	0.0387
C(22)	0.2057(2)	0.0050(10)	0.1742(4)	0.0536
C(23)	0.2385(3)	-0.0690(10)	0.2130(4)	0.0651
C(24)	0.2563(3)	-0.1830(10)	0.1852(6)	0.0683
C(25)	0.2403(3)	-0.2230(10)	0.1206(5)	0.0600
C(26)	0.2076(2)	-0.1486(9)	0.0821(4)	0.0503
C(31)	0.1487(2)	0.2112(8)	0.0771(4)	0.0391
C(32)	0.1881(2)	0.2840(10)	0.0907(4)	0.0515
C(33)	0.1899(3)	0.4250(10)	0.0934(4)	0.0576
C(34)	0.1518(3)	0.5023(9)	0.0821(4)	0.0567
C(35)	0.1122(3)	0.4360(10)	0.0674(4)	0.0554
C(36)	0.1112(2)	0.2950(10)	0.0642(4)	0.0433
C(41)	0.1424(2)	0.0289(8)	-0.0168(4)	0.0379
C(42)	0.1019(2)	0.0290(10)	-0.0583(4)	0.0558
C(43)	0.0978(3)	0.0270(10)	-0.1306(4)	0.0660
C(44)	0.1344(3)	0.0240(10)	-0.1613(4)	0.0700
C(45)	0.1751(3)	0.0250(10)	-0.1230(5)	0.0661
C(46)	0.1792(2)	0.0294(9)	-0.0529(4)	0.0502
N	0.1469(2)	0.5106(7)	-0.2018(3)	0.0490
C(N1)	0.1243(2)	0.6137(9)	-0.2477(4)	0.0542
C(N2)	0.0751(3)	0.5770(10)	-0.2625(4)	0.0615
C(N3)	0.0529(2)	0.5800(10)	-0.1997(4)	0.0523
C(N4)	0.0498(3)	0.4650(10)	-0.1612(5)	0.0659
C(N5)	0.0328(3)	0.4720(10)	-0.1004(6)	0.0864
C(N6)	0.0197(3)	0.5960(20)	-0.0748(6)	0.0925
C(N7)	0.0220(3)	0.7110(10)	-0.1144(6)	0.0841
C(N8)	0.0391(3)	0.7020(10)	-0.1745(5)	0.0652
C	0.1577(2)	0.5190(10)	-0.1366(4)	0.0549
C(C1)	0.1798(3)	0.4000(10)	-0.1018(5)	0.0729
C(C2)	0.1494(2)	0.6400(10)	-0.0950(4)	0.0605
O	0.6506(2)	0.2240(6)	0.2218(3)	0.0791

Table 34. Selected bond lengths (Å), contacts (Å) and angles (°) for ImETBw (with s.s.d.'s in parentheses).

C - N	1.291(11)	O...C(21)	3.594(9)
C - C(C1)	1.48(1)	O...C(22)	3.435(10)
C - C(C2)	1.48(1)	O...C(23)	3.410(11)
		O...C(24)	3.535(11)
N - C(N1)	1.475(9)	O...C(25)	3.637(11)
C(N1) - C(N2)	1.55(1)	O...C(26)	3.668(10)
C(N2) - C(N3)	1.49(1)	Mean	3.55(10)
C(N3) - C(N4)	1.38(1)		
C(N4) - C(N5)	1.37(1)	O... π_c (2)	3.26
C(N5) - C(N6)	1.40(1)		
C(N6) - C(N7)	1.38(1)	H(O1)...C(11)	2.92
C(N7) - C(N8)	1.36(1)	H(O1)...C(12)	2.53
C(N8) - C(N3)	1.38(1)	H(O1)...C(13)	2.69
		H(O1)...C(14)	3.17
		H(O1)...C(15)	3.43
		H(O1)...C(16)	3.29
		Mean	3.01(32)
B - C(11)	1.629(11)		
B - C(21)	1.638(11)	H(O1)... π_c (1)	2.68
B - C(31)	1.631(11)		
B - C(41)	1.652(11)	H(O2)...C(21)	3.34
Mean	1.638(11)	H(O2)...C(22)	3.14
N...O	2.769(9)	H(O2)...C(23)	2.81
		H(O2)...C(24)	2.66
H(N)...O	1.757	H(O2)...C(25)	2.82
		H(O2)...C(26)	3.15
O...C(11)	3.697(9)	Mean	2.98(24)
O...C(12)	3.494(10)		
O...C(13)	3.551(11)	H(O2)... π_c (2)	2.65
O...C(14)	3.774(11)		
O...C(15)	3.906(11)		
O...C(16)	3.846(10)		
Mean	3.71(15)		
O... π_c (1)	3.44		
C(C1) - C - N	117.2(9)	C(11) - B - C(21)	105.0(6)
C(C2) - C - N	124.3(9)	C(31) - B - C(41)	103.1(6)
C(C1) - C - C(C2)	118.5(8)	Mean	104.1(10)
C(N) - N - C(N1)	127.7(8)		

Table 34. Selected bond lengths (Å), contacts (Å) and angles (°) for *ImETBw* (with e.s.d.'s in parentheses - continued).

N - C(N1) - C(N2)	109.3(7)	C(11) - B - C(31)	112.4(6)
H(N) - N - C	118.8	C(11) - B - C(41)	110.3(6)
H(N) - N - C(N1)	112.9	C(21) - B - C(31)	113.0(6)
C(N1) - C(N2) - C(N3)	112.3(6)	C(21) - B - C(41)	113.3(6)
C(N2) - C(N3) - C(N4)	120.8(9)	Mean	112.3(6)
C(N2) - C(N3) - C(N8)	120.8(9)		
C(N3) - C(N4) - C(N5)	120.2(9)	C(12) - C(11) - C(16)	114.4(7)
C(N4) - C(N5) - C(N6)	121.2(11)	C(22) - C(21) - C(26)	115.4(7)
C(N5) - C(N6) - C(N7)	118.3(11)	C(32) - C(31) - C(36)	113.5(7)
C(N6) - C(N7) - C(N8)	119.4(10)	C(42) - C(41) - C(46)	114.5(7)
C(N7) - C(N8) - C(N3)	122.8(9)	Mean	114.5(7)
C(N8) - C(N3) - C(N4)	118.0(8)		
		H(O1) - O - H(O2)	104.8

QTB, [C₇H₁₄N]TB

The diffraction intensities of QTB were first collected using Mo radiation. After anisotropic refinement of the nonhydrogen atoms it was found that the data ($I > 3.0\sigma$) to parameter ratio was only 3.00. However, when data were collected using Cu radiation, a significant improvement was achieved ($d/p = 5.19$).

Each crystal consists of quinuclidinium cations and tetraphenylborate anions. The cation has mirror symmetry; the crystallographic mirror plane passes through the N, C, C(2,1), C(2,2), and H(N) atoms. In the anion, the B atom, the C(α) and C(δ) atoms of two of the phenyl rings and the associated H(δ) protons all lie on the mirror plane. Atomic positions of the non hydrogen atoms are given in Table 35. The selected bond lengths and angles of this compound are listed in Table 36.

The geometry of the quinuclidinium cage of QTB is normal and comparable with that of quinuclidinium chloride (QCl)¹⁴⁸. In particular, mean $\bar{d}(\text{N} - \text{C}) = 1.504(7)$ Å, mean $\bar{d}(\text{C} - \text{C}) = 1.521(10)$ Å and non-bonded $d(\text{N} \cdots \text{C}) = 2.505(7)$ Å are found in QTB while

in QCl the corresponding values are mean $\bar{d}(\text{N} - \text{C}) = 1.508(1) \text{ \AA}$, mean $\bar{d}(\text{C} - \text{C}) = 1.536(3) \text{ \AA}$ and non-bonded $d(\text{N} \cdots \text{C}) = 2.534(8) \text{ \AA}$.

The results of a TLS analysis (Fig. 61) indicate that the cation can be modelled reasonably well as a rigid body; $R(U_{ij}) = 10.1\%$, $R_w(U_{ij}) = 10.6\%$, $\text{rms}(U_{ij}) = 0.0061$, $\text{rms}[\text{esd}(U_{ij})] = 0.0044$. The mean librational amplitude about L_1 it is 4.1° , about L_2 it is 6.2° , and about L_3 it is 8.4° .

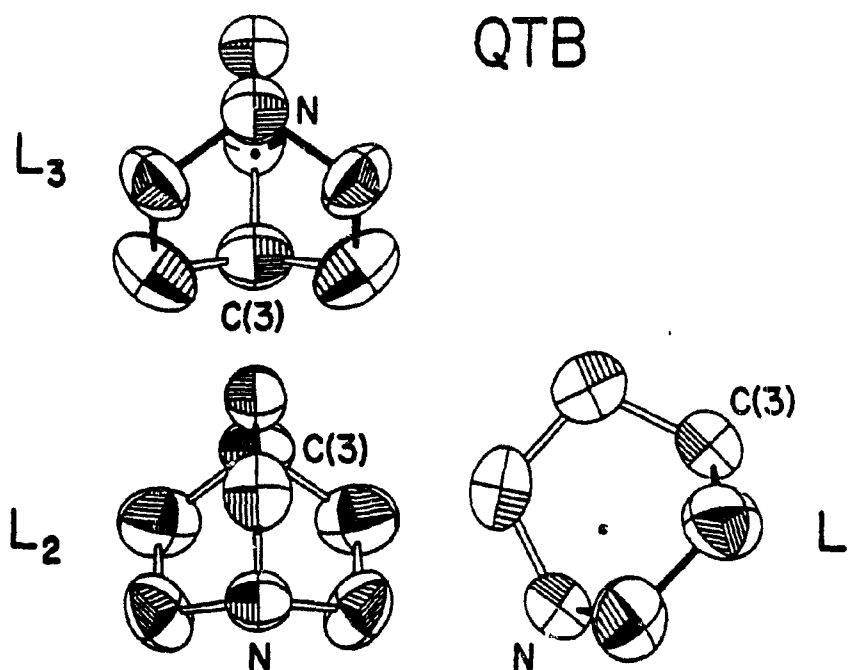


Fig. 61. Rigid-body libration of the cation in QTB. Small black circle indicates the points of intersection of the librational axes with the projection plane.

In QTB, the $\text{H}(\text{N})$ is bonded directly to one phenyl ring of the TB anion. The $\text{H}(\text{N}) \cdots \pi$ bonding is of type A.

Table 35. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for QTB (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	Ueq
B	0.8280(4)	1/4	0.0738(9)	0.0452
C(11)	0.8652(3)	0.3466(4)	0.1542(5)	0.0463
C(12)	0.9337(3)	0.3857(4)	0.1209(5)	0.0546
C(13)	0.9694(3)	0.4574(4)	0.1982(6)	0.0597
C(14)	0.9389(3)	0.4915(4)	0.3151(6)	0.0616
C(15)	0.8716(3)	0.4547(4)	0.3505(5)	0.0651
C(16)	0.8358(3)	0.3838(4)	0.2729(5)	0.0586
C(21)	0.8486(4)	1/4	-0.0848(7)	0.0463
C(22)	0.8592(3)	0.3391(4)	-0.1576(5)	0.0606
C(23)	0.8806(3)	0.3407(5)	-0.2914(6)	0.0768
C(24)	0.8930(5)	1/4	-0.357(1)	0.0861
C(31)	0.7402(4)	1/4	0.0851(7)	0.0456
C(32)	0.6991(3)	0.3390(4)	0.0909(5)	0.0559
C(33)	0.6240(3)	0.3402(4)	0.1041(5)	0.0596
C(34)	0.5859(4)	1/4	0.1123(8)	0.0631
N	0.7937(3)	3/4	0.1682(7)	0.0646
C(1,1)	0.7901(3)	0.6560(5)	0.0839(6)	0.0809
C(1,2)	0.8534(3)	0.6562(5)	-0.0110(6)	0.0909
C(2,1)	0.8621(5)	3/4	0.2483(8)	0.0758
C(2,2)	0.9278(5)	3/4	0.1543(9)	0.0686
C(3)	0.8996(4)	3/4	0.0111(8)	0.0723

Table 36. Selected bond lengths (Å), contacts (Å) and angles (°) for QTB (with e.s.d.'s in parentheses).

N - C(1,1)	1.512(7)	N...C(21)	3.601(8)
N - C(1,1)	1.512(7)	N...C(22)	3.517(7)
N - C(2,1)	1.493(7)	N...C(22)	3.517(7)
Mean	1.506(9)	N...C(23)	3.455(8)
		N...C(23)	3.455(8)
C(3) - C(1,2)	1.529(8)	N...C(24)	3.448(7)
C(3) - C(1,2)	1.529(8)	Mean	3.50(4)
C(3) - C(2,2)	1.522(8)		
Mean	1.527(3)	N... π_c (2)	3.21
B - C(11)	1.665(7)	H(N)...C(21)	2.58
B - C(11)	1.665(7)	H(N)...C(22)	2.59
B - C(21)	1.630(7)	H(N)...C(22)	2.59
B - C(31)	1.623(7)	H(N)...C(23)	2.72
Mean	1.646(19)	H(N)...C(23)	2.72
		H(N)...C(24)	2.79
		Mean	2.67(8)
		H(N)... π_c (2)	2.27
C(1,1) - N - C(2,1)	109.6(4)	C(11) - B - C(21)	112.0(4)
C(1,1) - N - C(1,1)	112.0(4)	C(11) - B - C(21)	112.0(4)
C(1,1) - N - C(2,1)	109.6(4)	C(11) - B - C(31)	112.1(4)
Mean	110.4(11)	C(11) - B - C(31)	112.1(4)
		Mean	112.1(1)
C(1,2) - C(3) - C(2,2)	109.0(5)	C(12) - C(11) - C(16)	114.7(5)
C(1,2) - C(3) - C(1,2)	109.8(5)	C(12) - C(11) - C(16)	114.7(5)
C(1,2) - C(3) - C(2,2)	109.0(5)	C(22) - C(21) - C(22)	115.3(4)
Mean	109.3(4)	C(32) - C(31) - C(32)	114.7(4)
		Mean	114.9(2)
C(11) - B - C(11)	101.4(4)		
C(21) - B - C(31)	107.4(4)		
Mean	104.4(32)		

DaHTB, $[C_6H_{13}N_2]TB$

The TB salt of the DabcoH⁺ cation is isostructural with QTB; both belong to the orthorhombic crystal system, space group *Pnma*. This is not unexpected, since the stereochemical difference between the quinuclidinium cation $[HC(-CH_2CH_2)_3NH^+]$ and the singly protonated DabcoH⁺ cation $[N(-CH_2CH_2)_3NH^+]$ is minor. The -CH group in the quinuclidinium cation is replaced by -N in DabcoH⁺.

Atomic positions and equivalent isotropic temperature factors are quoted in Table 37 and selected bond lengths and angles are given in Table 38. The crystals consist of monoprotonated 1,4-diazabicyclo[2.2.2]octane cations and tetraphenylborate anions. As in QTB, the mirror plane, in this compound, passes through the barrel-shaped diazabicyclo-octane moiety along the quasi C_3 -axis, while in the anion, the B atom, the C(α) and C(δ) atoms of two of the phenyl rings and the associated H(δ) protons all lie in the mirror plane.

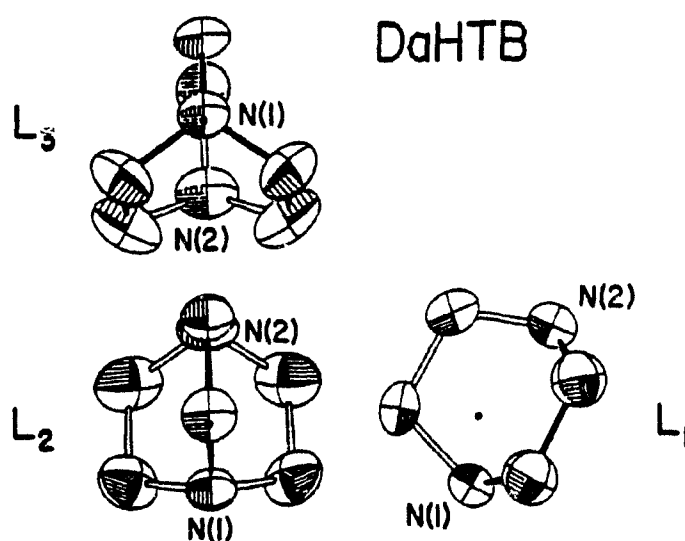


Fig. 62. Rigid-body libration of the DaH⁺ cation in DaHTB. Small black circle, points of intersection of the librational axes with the projection plane.

In the cation, the bonds around the tetrahedrally coordinated N atom (mean 1.493(2) Å) are comparable with those reported in other monoprotonated Dabco compounds¹⁴⁹. They are significantly longer than those around the amine N-atom (mean 1.456(2) Å). The hydrogen bonding geometry is similar to those of QTB.

The thermal motion of DabcoH⁺ is consistent with a rigid body model (Fig. 62). The results of a TLS analysis are better than those for the cation in QTB; $R(U_{ij}) = 5.1\%$, $R_w(U_{ij}) = 5.2\%$, $\text{rms}(U_{ij}) = 0.0025$, $\text{rms}[\text{esd}(U_{ij})] = 0.0021$. The mean librational amplitude about L_1 it is 5.0° , about L_2 it is 6.2° , and about L_3 it is 8.0° . The corresponding mean translational displacement is 0.2 Å.

Table 37. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for DaHTB (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	Ueq
B	0.6714(3)	3/4	0.0794(5)	0.0327
C(11)	0.6341(1)	0.6540(2)	0.1579(3)	0.0341
C(12)	0.5643(2)	0.6166(2)	0.1257(3)	0.0416
C(13)	0.5285(2)	0.5448(3)	0.2022(3)	0.0500
C(14)	0.5602(2)	0.5072(2)	0.3172(3)	0.0508
C(15)	0.6294(2)	0.5422(2)	0.3538(3)	0.0519
C(16)	0.6649(2)	0.6139(2)	0.2753(3)	0.0440
C(21)	0.7617(2)	3/4	0.0910(4)	0.0353
C(22)	0.8030(2)	0.6613(2)	0.0942(3)	0.0425
C(23)	0.8795(2)	0.6605(3)	0.1054(3)	0.0491
C(24)	0.9176(2)	3/4	0.1128(5)	0.0494
C(31)	0.6507(2)	3/4	-0.0809(4)	0.0355
C(32)	0.6416(2)	0.6613(3)	-0.1545(3)	0.0480
C(33)	0.6217(2)	0.6606(3)	-0.2895(3)	0.0630
C(34)	0.6109(3)	3/4	-0.3565(5)	0.0707
N(1)	0.2947(2)	3/4	-0.1686(4)	0.0475
C(1)	0.3603(3)	3/4	-0.2592(5)	0.0556
C(2)	0.4290(3)	3/4	-0.1689(5)	0.0562
C(3)	0.2956(2)	0.8426(3)	-0.0839(4)	0.0679
C(4)	0.3659(2)	0.8392(3)	0.0010(4)	0.0763
N(2)	0.4096(2)	3/4	-0.0278(4)	0.0617

Table 38. Selected bond lengths (Å), contacts (Å) and angles (°) for DaHTB (with e.s.d.'s in parentheses).

N(1) - C(1)	1.499(6)	N(1)...C(31)	3.625(5)
N(1) - C(3)	1.495(5)	N(1)...C(32)	3.506(5)
N(1) - C(3)	1.495(5)	N(1)...C(32)	3.506(5)
Mean	1.496(2)	N(1)...C(33)	3.393(5)
		N(1)...C(33)	3.393(5)
N(2) - C(2)	1.453(7)	N(1)...C(34)	3.357(6)
N(2) - C(4)	1.457(7)	Mean	3.46(9)
N(2) - C(4)	1.457(7)		
Mean	1.456(2)	N(1)... $\pi_c(3)$	3.12
B - C(11)	1.645(4)	H(N1)...C(31)	2.65
B - C(11)	1.645(4)	H(N1)...C(32)	2.57
B - C(21)	1.647(6)	H(N1)...C(32)	2.57
B - C(31)	1.645(6)	H(N1)...C(33)	2.55
Mean	1.646(1)	H(N1)...C(33)	2.55
		H(N1)...C(34)	2.56
		Mean	2.58(3)
		H(N1)... $\pi_c(3)$	2.11
C(1) - N(1) - C(3)	109.5(2)	C(11) - B - C(21)	112.2(2)
C(1) - N(1) - C(1)	111.0(4)	C(11) - B - C(21)	112.2(2)
C(1) - N(1) - C(3)	109.5(2)	C(11) - B - C(31)	111.6(2)
Mean	110.0(7)	C(11) - B - C(31)	111.6(2)
		Mean	111.9(3)
C(2) - N(2) - C(4)	108.9(3)	C(12) - C(11) - C(16)	114.7(3)
C(2) - N(2) - C(2)	109.0(4)	C(12) - C(11) - C(16)	114.7(3)
C(2) - N(2) - C(4)	108.9(3)	C(22) - C(21) - C(22)	114.9(4)
Mean	108.9(1)	C(32) - C(31) - C(32)	114.8(4)
		Mean	114.8(1)
C(11) - B - C(11)	101.8(3)		
C(21) - B - C(31)	107.3(3)		
Mean	104.6(28)		

1MPzBTB.Me₂CO, [C₂₃H₂₈N₂]TB.Me₂CO

In 1MPzBTB.Me₂CO, the asymmetric unit contains a [MeHN(-CH₂CH₂)₂NHBPh₃]⁺ cation, a TB⁻ anion, and an solvent molecule. It was reported in the experimental section that our aim was to prepare [N-Me-piperazinium]2TB. However, the product obtained from an acidic solution of N-Me-piperazine and sodium tetraphenylborate at room temperature had the composition [MeHN(-CH₂CH₂)₂NHBPh₃]⁺[BPh₄]⁻. A tetraphenylborate anion had lost one phenyl group and then formed a usual B - N bond with one apical nitrogen of the monoprotonated piperazinium cation. Abstraction of a phenyl group from tetraphenylborate anion usually occurs at a relatively high temperature. Surprisingly, in this case, the process took place at room temperature.

Positional parameters and equivalent isotropic temperature factors of compound 1MPzBTB.Me₂CO are listed in Table 39 and selected bond lengths and angles are given in Table 40.

This compound thus contains both Ph₃B - N⁺ and Ph₄B⁻ groups. Comparison of their stereochemistries indicates that the B - C bond of the Ph₃B - N⁺ group is

	Ph ₃ B - N	Ph ₄ B ⁻	Ph ₄ B ⁻ (overall)
mean (B - C) Å	1.618(11)	1.653(9)	1.646(18)
mean <C - B - C>°	112.3(33)	111.7(1)	104.4(17)
mean <C - B - C>°	112.3(33)	108.4(8)	112.1(12)
mean <C - B - N>°	106.5(8)		
mean <C(2) - C(1) - C(6)>°	114.9(3)	114.6(9)	

significantly shorter than the corresponding distance observed in the Ph₄B⁻ anion (Table 40). The N - B bond length is normal, 1.683(8) Å, close to the values observed in

$\text{Ph}_3\text{B} - \text{NH}_2\text{Me}$ (1.675(8) Å) and $\text{Ph}_3\text{B} - \text{NHMe}_2$ (1.670(7) Å) (both crystals are monoclinic, $\text{P2}_1/\text{c}$, unpublished results).

The singly charged piperazinium fragment of the cation exists in the chair conformation with the two nitrogens at the apices. The nitrogen atoms, N(1) and N(2), deviate from the plane of the four carbon atoms in the ring by 0.727 and -0.630 Å, respectively. The dimensions of the piperazinium fragment are comparable with those reported previously¹⁵⁰⁻¹⁵³.

All seven phenyl rings exhibit satisfactory planarity, the mean deviation of the C atoms from the respective best planes through the seven rings being 0.007 Å. The deviation of the B atoms from the planes of the phenyl ring ranges, from -0.088 to 0.134 Å for B(1) and from -0.001 to 0.119 Å for B(2), in the cation and anion, respectively.

The N(1) - H(N1)... π_c (12) bond is of type A. The second N-hydrogen of the cation is weakly bonded to the O atom of the acetone molecule, N(2) - H(N₂)...O: $d[\text{N}(2)\cdots\text{O}] = 3.091(11)$ Å, $d[\text{H}(\text{N}2)\cdots\text{O}] = 2.11$ Å.

Table 39. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for 1MPzBTB.Me₂CO (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	Ueq
B(1)	0.3020(6)	0.9085(3)	0.1264(2)	0.0430
C(111)	0.2941(5)	0.8607(3)	0.0670(2)	0.0398
C(112)	0.2375(6)	0.7896(3)	0.0583(2)	0.0561
C(113)	0.2345(6)	0.7530(3)	0.0071(2)	0.0666
C(114)	0.2850(6)	0.7356(4)	-0.0374(2)	0.0632
C(115)	0.3393(6)	0.8576(3)	-0.0314(2)	0.0576
C(116)	0.3432(5)	0.8934(3)	0.0201(2)	0.0470
C(121)	0.4656(5)	0.9194(3)	0.1486(2)	0.0401
C(122)	0.5383(5)	0.8766(3)	0.1906(2)	0.0473
C(123)	0.6746(6)	0.8895(3)	0.2093(2)	0.0550
C(124)	0.7450(6)	0.9470(3)	0.1874(2)	0.0597
C(125)	0.6812(6)	0.9908(3)	0.1456(2)	0.0597
C(126)	0.5446(6)	0.9770(3)	0.1270(2)	0.0534
C(131)	0.2258(5)	0.9899(3)	0.1137(2)	0.0428
C(132)	0.2655(6)	1.0566(3)	0.1408(2)	0.0532
C(133)	0.1943(7)	1.1242(3)	0.1307(2)	0.0674
C(134)	0.0765(6)	1.1259(3)	0.0945(2)	0.0614
C(135)	0.0311(5)	1.0604(3)	0.0685(2)	0.0539
C(136)	0.1046(5)	0.9935(3)	0.0773(2)	0.0465
C(141)	0.2258(5)	0.8626(3)	0.1742(2)	0.0421
C(142)	0.1288(5)	0.8979(3)	0.2046(2)	0.0500
C(143)	0.0715(6)	0.8640(3)	0.2482(2)	0.0576
C(144)	0.1029(6)	0.7900(4)	0.2623(2)	0.0618
C(145)	0.1947(6)	0.7520(3)	0.2332(2)	0.0596
C(146)	0.2551(5)	0.7868(3)	0.1901(2)	0.0506
N(1)	0.7235(4)	0.8397(2)	0.0690(1)	0.0479
C(N1)	0.7223(6)	0.8997(3)	0.0248(2)	0.0656
C(1)	0.8679(5)	0.8159(3)	0.0880(2)	0.0495
C(2)	0.6385(5)	0.7735(3)	0.0484(2)	0.0492
C(3)	0.8691(5)	0.7523(3)	0.1294(2)	0.0458
C(4)	0.6471(5)	0.7099(3)	0.0904(2)	0.0484
N(2)	0.7926(4)	0.6848(2)	0.1054(1)	0.0407
B(2)	0.8079(6)	0.6075(3)	0.1460(2)	0.0414
C(211)	0.7469(6)	0.6308(3)	0.2026(2)	0.0459
C(212)	0.8287(6)	0.6627(3)	0.2476(2)	0.0631
C(213)	0.7755(7)	0.6881(4)	0.2956(2)	0.0827
C(214)	0.6384(8)	0.6806(4)	0.3008(3)	0.0888
C(215)	0.5539(7)	0.6495(4)	0.2582(3)	0.0875
C(216)	0.6072(6)	0.6246(3)	0.2103(2)	0.0630

Table 39. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for 1MPzBTB.Me₂CO (with e.s.d.'s in parentheses - continued).

Atom	x/a	y/b	z/c	U _{eq}
C(221)	0.7272(5)	0.5391(3)	0.1124(2)	0.0443
C(222)	0.6815(7)	0.4771(3)	0.1414(2)	0.0701
C(223)	0.6225(8)	0.4135(4)	0.1153(3)	0.0892
C(224)	0.6067(6)	0.4091(3)	0.0589(3)	0.0725
C(225)	0.6499(6)	0.4678(4)	0.0282(2)	0.0661
C(226)	0.7107(6)	0.5316(3)	0.0548(2)	0.0564
C(231)	0.9700(5)	0.5864(3)	0.1526(2)	0.0421
C(232)	1.0177(5)	0.5371(3)	0.1964(2)	0.0525
C(233)	1.1511(7)	0.5125(3)	0.2037(2)	0.0689
C(234)	1.2434(6)	0.5346(3)	0.1680(3)	0.0678
C(235)	1.2012(6)	0.5808(3)	0.1242(2)	0.0640
C(236)	1.0659(5)	0.6060(3)	0.1167(2)	0.0474
O	0.6281(4)	0.1804(2)	0.5150(1)	0.0807
C(11)	0.6152(6)	0.1487(3)	0.5576(2)	0.0664
C(12)	0.7219(10)	0.1625(5)	0.6064(4)	0.1974
C(13)	0.5026(8)	0.0925(5)	0.5632(4)	0.1817

Table 40. Selected bond lengths (Å), contacts (Å) and angles (°) for 1MPzBTB.Me₂CO (with e.s.d.'s in parentheses).

B(1) - C(111)	1.665(8)	H(N1)...C(121)	2.67
B(1) - C(121)	1.656(9)	H(N1)...C(122)	2.70
B(1) - C(131)	1.640(9)	H(N1)...C(123)	2.67
B(1) - C(141)	1.650(9)	H(N1)...C(124)	2.59
Mean	1.653(9)	H(N1)...C(125)	2.48
		H(N1)...C(126)	2.50
B(2) - C(211)	1.603(9)	Mean	2.60(9)
B(2) - C(221)	1.623(9)		
B(2) - C(231)	1.628(9)	H(N1)... $\pi_c(12)$	2.21
Mean	1.618(11)		
		N(2)...O	3.091(11)
B(2) - N(2)	1.683(8)	H(N2)...O	2.11
N(1)...C(121)	3.612(7)		
N(1)...C(122)	3.665(7)		
N(1)...C(123)	3.585(8)		
N(1)...C(124)	3.429(8)		
N(1)...C(125)	3.304(8)		
N(1)...C(126)	3.382(8)		
Mean	3.50(13)		
N(1)... $\pi_c(12)$	3.21		
C(111) - B(1) - C(121)	107.7(4)	C(211) - B(2) - N(2)	105.7(4)
C(111) - B(1) - C(131)	107.5(5)	C(221) - B(2) - N(2)	107.6(4)
C(121) - B(1) - C(141)	108.7(5)	C(231) - B(2) - N(2)	106.1(4)
C(131) - B(1) - C(141)	109.6(5)	Mean	106.5(8)
Mean	108.4(8)		
		C(112) - C(111) - C(116)	114.6(5)
C(111) - B(1) - C(141)	111.7(5)	C(122) - C(121) - C(126)	113.5(5)
C(121) - B(1) - C(131)	111.7(5)	C(132) - C(131) - C(136)	116.0(5)
Mean	111.7(0)	C(142) - C(141) - C(146)	114.1(5)
		Mean	114.6(9)
C(211) - B(2) - C(221)	114.6(5)		
C(211) - B(2) - C(231)	114.6(5)	C(212) - C(211) - C(216)	114.8(5)
C(221) - B(2) - C(231)	107.7(5)	C(222) - C(221) - C(226)	114.6(5)
Mean	112.3(33)	C(232) - C(231) - C(236)	115.3(5)
		Mean	114.9(3)

BPTB, $[\text{C}_{10}\text{H}_9\text{N}_2]^+\text{TB}^-$

In the solid state, the free base 2,2'-bipyridine adopts a *trans*-coplanar conformation¹⁵⁴. Literature reports^{155,156} indicate that the BP cation in 2,2'-bipyridinium salts can exist in various conformations between the *cis*- and the *trans*- extremes. Monoprotonation of the base (BP^+) allows a nearly *cis*- conformation to be adopted, owing to a strong intracation N - H...N hydrogen bonding interaction. The ψ_{cis} angle varies from 1.3° to 19.0°. The diprotonated 2,2'-bipyridine cation (BP^{2+}) can adopt a *trans*- conformation. This is usually observed in the 1:2 salts formed with relatively strong acids ($18.9^\circ \leq \psi_{\text{trans}} \leq 44.4^\circ$).

While our aim was to prepare the 1:2 compound, mixing a dilute acidic (HCl) solution of 2,2'-bipyridyl with an aqueous solution of sodium tetraphenylborate gave a 1:1 product of composition $(\text{C}_{10}\text{H}_9\text{N}_2)\text{BPh}_4$ (= BPTB). The BP^+ cation lies in a very nearly planar, *cis*-conformation (the dihedral angle between the best planes of ring 1 and 1' is only 5.4°). The formation of a product with 1:1 stoichiometry was not unexpected; the ionization constants¹⁵⁷ of 2,2'-bipyridine and the necessity of using strong acids to stabilize the BP^{2+} cation¹⁵⁸ both pointed to the likelihood of the 1:1 candidate being formed.

Crystals of BPTB are unsolvated and belong to the monoclinic, $\text{P}2_1/\text{c}$ crystal system. Each asymmetric unit contains one cation/anion pair. All atoms are in general position. The final atomic parameters of nonhydrogen atoms along with their estimated standard deviations are listed in Table 41 and the selected bond lengths and angles are given in Table 42.

In the cation, the ring skeleton (1) is planar to within 0.003 Å and the ring skeleton (1') to 0.002 Å. They are twisted by 5.4° about the 2,2'-carbon bond. If the BP^+ cation

is treated as planar, the mean deviation of the nonhydrogen atoms from the best plane is 0.041 Å and the angles of ring 1 and ring 1' with the cation plane are 2.6° and 2.5°, respectively.

Because of the strong σ -electron withdrawing effect of the proton, the protonation of a ring nitrogen is associated with an increase in the CNC angle¹⁵⁹. The BP⁺ cation in BPTB is no exception. While the angle at the unprotonated nitrogen is 117.9(4)°, the CNC angle at the protonated N atom is 124.5(5)°. Like other mono-protonated BP⁺ salts, the proton H(N(2')) is involved in intracation hydrogen bonding with N(2), which forces the cation to adopt a *cis*-conformation. In comparison with Phen⁺, the N...N separation in BP⁺ is 4% shorter, indicative of the stronger H(N2')...N(2) interaction. As far as the interion H(N)... π bonding is concerned, in BPTB, only two distances (H(N2')...C(25) = 2.47 Å and H(N2')...C(26) = 2.40 Å) appear to qualify for possible hydrogen bonds. All the other H(N2')...C distances are longer than 3.3 Å. However, the distances, H(N2')... π_c = 3.03 Å and N(2')... π_c = 3.72 Å, and the angle N(2') - H(N2')... π_c (2) = 126.3° are all consistent with the statistics of a bifurcated H(N)... π bond. Thus the N(2') - H(N2')...acc bond may be regarded as bifurcated, with an intracation component engaging the lone pair on N(2) and an interion component pointing at R2 of the nearest anion^h.

^h The structure of BPTB was determined at low temperature (-20°C) by x-ray diffraction (not reported here). The position of the H(N2') atom was located from the Fourier difference map, so the distances and angles involving the H(N2') atom differ slightly from the room temperature determination. The other bond lengths and angles differ only within the stated e.s.d.'s.

A TLS analysis of the cation indicates that the thermal motion of the cation atoms can be accounted for by a rigid body model, with $R(U_{ij}) = 5.7\%$, $R_w(U_{ij}) = 5.8\%$, $\text{rms}(U_{ij}) = 0.0029$ and $\text{rms}[\text{esd}(U_{ij})] = 0.0029$; the mean libration about three principal axes are L_1 , 2.8° ; L_2 , 3.4° ; L_3 , 6.5° . The axis of the largest amplitude libration (L_3) is almost parallel to the long cation axis, as shown in Fig. 63. The corresponding mean translational displacement is $0.2 \text{ \AA}$.

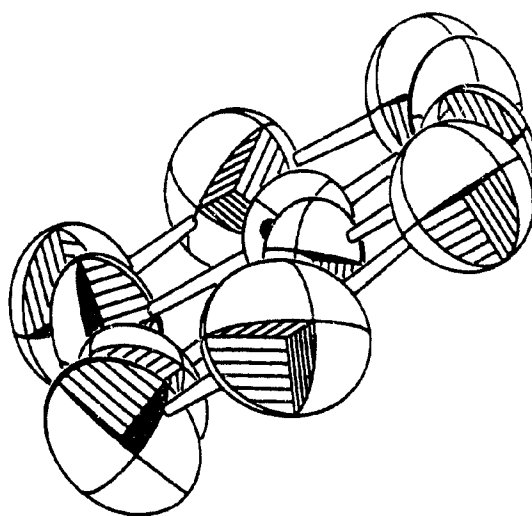


Fig. 63. Projection of the BP^+ cation down its principal axis (L_3) of libration. Black circle, points of intersection of the librational axes with the projection plane.

Table 41. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for BPTB (with e.s.d's in parentheses).

Atom	x/a	y/b	z/c	U _{eq}
B	-0.0316(5)	0.7378(3)	0.8708(2)	0.0308
C(11)	-0.1428(4)	0.6545(3)	0.8945(2)	0.0400
C(12)	-0.0905(4)	0.5685(3)	0.9207(2)	0.0478
C(13)	-0.1809(6)	0.4997(3)	0.9455(2)	0.0619
C(14)	-0.3285(6)	0.5144(4)	0.9453(2)	0.0692
C(15)	-0.3848(5)	0.5984(4)	0.9210(2)	0.0684
C(16)	-0.2930(4)	0.6679(3)	0.8964(2)	0.0527
C(21)	0.0347(4)	0.7811(2)	0.9411(2)	0.0383
C(22)	0.1555(4)	0.7385(3)	0.9745(2)	0.0478
C(23)	0.2020(5)	0.7641(3)	1.0385(2)	0.0590
C(24)	0.1323(5)	0.8354(3)	1.0711(2)	0.0586
C(25)	0.0161(5)	0.8810(3)	1.0401(2)	0.0529
C(26)	-0.0321(4)	0.8534(3)	0.9763(2)	0.0454
C(31)	-0.1134(4)	0.8160(3)	0.8220(2)	0.0396
C(32)	-0.2148(4)	0.7870(3)	0.7718(2)	0.0474
C(33)	-0.2777(5)	0.8503(4)	0.7255(2)	0.0598
C(34)	-0.2402(5)	0.9447(4)	0.7275(2)	0.0657
C(35)	-0.1415(5)	0.9756(3)	0.7754(2)	0.0599
C(36)	-0.0783(4)	0.9123(3)	0.8218(2)	0.0485
C(41)	0.1031(4)	0.6981(3)	0.8275(2)	0.0455
C(42)	0.1088(5)	0.6105(3)	0.7963(2)	0.0617
C(43)	0.2250(7)	0.5844(4)	0.7578(2)	0.0883
C(44)	0.3367(7)	0.6484(6)	0.7499(3)	0.1074
C(45)	0.3340(5)	0.7356(5)	0.7796(3)	0.0974
C(46)	0.2201(5)	0.7600(4)	0.8182(2)	0.0667
C(1)	0.0831(4)	0.6031(3)	0.6015(2)	0.0513
N(2)	0.1701(4)	0.5569(3)	0.5611(2)	0.0622
C(3)	0.1495(5)	0.4639(3)	0.5527(2)	0.0702
C(4)	0.0419(5)	0.4144(3)	0.5823(2)	0.0711
C(5)	-0.0493(5)	0.4622(4)	0.6222(2)	0.0721
C(6)	-0.0284(5)	0.5585(4)	0.6327(2)	0.0639
C(1')	0.1170(4)	0.7046(3)	0.6101(2)	0.0518
N(2')	0.2238(4)	0.7381(3)	0.5732(2)	0.0610
C(3')	0.2722(6)	0.8278(4)	0.5748(2)	0.0748
C(4')	0.2110(6)	0.8917(3)	0.6161(2)	0.0804
C(5')	0.1021(6)	0.8604(4)	0.6549(2)	0.0786
C(6')	0.0546(5)	0.7677(4)	0.6519(2)	0.0646

Table 42. Selected bond lengths (Å), contacts (Å) and angles (°) for BPTB (with e.s.d.'s in parentheses).

N(2) - C(1)	1.346(5)	N(2')...C(21)	4.040(5)
N(2) - C(3)	1.335(5)	N(2')...C(22)	4.570(5)
C(3) - C(4)	1.378(6)	N(2')...C(23)	4.516(6)
C(4) - C(5)	1.375(6)	N(2')...C(24)	3.922(6)
C(5) - C(6)	1.387(5)	N(2')...C(25)	3.282(5)
C(6) - C(1)	1.388(6)	N(2')...C(26)	3.328(5)
		Mean	3.94(15)
N(2') - C(1')	1.355(5)		
N(2') - C(3')	1.342(5)	N(2')... $\pi_c(2)$	3.723
C(3') - C(4')	1.372(6)		
C(4') - C(5')	1.383(7)	H(N2')...C(21)	3.29
C(6') - C(5')	1.380(7)	H(N2')...C(22)	4.00
C(6') - C(1')	1.377(6)	H(N2')...C(23)	4.04
		H(N2')...C(24)	3.39
N(2)...N(2')	2.612(5)	H(N2')...C(25)	2.49
C(6)...C(6')	3.068(8)	H(N2')...C(26)	2.40
		Mean	3.27(65)
H(N2')...N(2)	2.16		
		H(N2')... $\pi_c(2)$	3.03
B - C(11)	1.649(5)		
B - C(21)	1.642(5)		
B - C(31)	1.641(6)		
B - C(41)	1.658(5)		
Mean	1.648(7)		
C(1) - N(2) - C(3)	117.9(4)	C(11) - B - C(31)	112.3(3)
N(2) - C(3) - C(4)	122.9(4)	C(11) - B - C(41)	114.3(3)
C(3) - C(4) - C(5)	119.1(5)	C(21) - B - C(31)	114.5(3)
C(4) - C(5) - C(6)	119.1(5)	C(21) - B - C(41)	109.1(3)
C(5) - C(6) - C(1)	118.3(4)	Mean	112.6(22)
C(6) - C(1) - N(2)	122.7(4)		
		C(12) - C(11) - C(16)	115.4(4)
C(1') - N(2') - C(3')	124.5(4)	C(22) - C(21) - C(26)	114.9(3)
N(2') - C(3') - C(4')	119.1(4)	C(32) - C(31) - C(36)	115.2(4)
C(3') - C(4') - C(5')	118.3(5)	C(42) - C(41) - C(46)	116.2(4)
C(4') - C(5') - C(6')	121.1(5)	Mean	115.4(5)
C(5') - C(6') - C(1')	119.8(4)		
C(6') - C(1') - N(2')	117.2(4)		
C(11) - B - C(21)	102.9(3)		
C(31) - B - C(41)	104.1(3)		
Mean	103.5(6)		

PTB, [C₁₂H₉N₂]⁺TB⁻

Atomic positions and equivalent isotropic temperature factors of the 1,10-phenanthroline salt of TB are listed in Table 43 and selected bond lengths and angles are given in Table 44.

In contrast to the colourless BPTB, the product that was obtained on combining the dilute acidic solutions (acidified with HCl) of 1,10-phenanthroline and sodium tetraphenylborate was yellow in colour. The crystals obtained after recrystallization from an acetone/water mixture were also yellow. Inspection of the crystal packing reveals that the phenyl rings (R2) from two neighbouring anions are aligned approximately parallel to the cation planes (the angle between the R2 and the cation planes is 9.5°) and partially overlapping the phenH⁺ rings (Fig. 64). This arrangement favours a π - π interaction between the cation and anion rings which gives rise to the yellow colour observed in solid PTB. The perpendicular distances of N(10), C(11) and C(12) in the cation from the R2 plane are 3.17, 3.38 and 3.34 Å, respectively.

Another interesting feature of the structure is that the cation planes are nearly perpendicular (91°) to the phenyl rings (R4) in adjacent four-stacks. The ring-centre separations are $\pi_c(\text{cat } 1) \dots \pi_c(\text{R4}) = 5.78 \text{ Å}$ and $\pi_c(\text{cat } 3) \dots \pi_c(\text{R4}) = 5.00 \text{ Å}$. The T-shaped edge-to-face orientation of cation/anion pairs is believed to lower the crystal energy¹⁶⁰. A similar arrangement of phenyl and cation rings in four-stacks has been observed in the red N,N'-Me₂-4,4'-bipyridinium tetraphenylborate (PQTB)¹⁶¹, in which the planar, centrosymmetric cation is sandwiched between two pairs of phenyl rings, one pair from each anion.

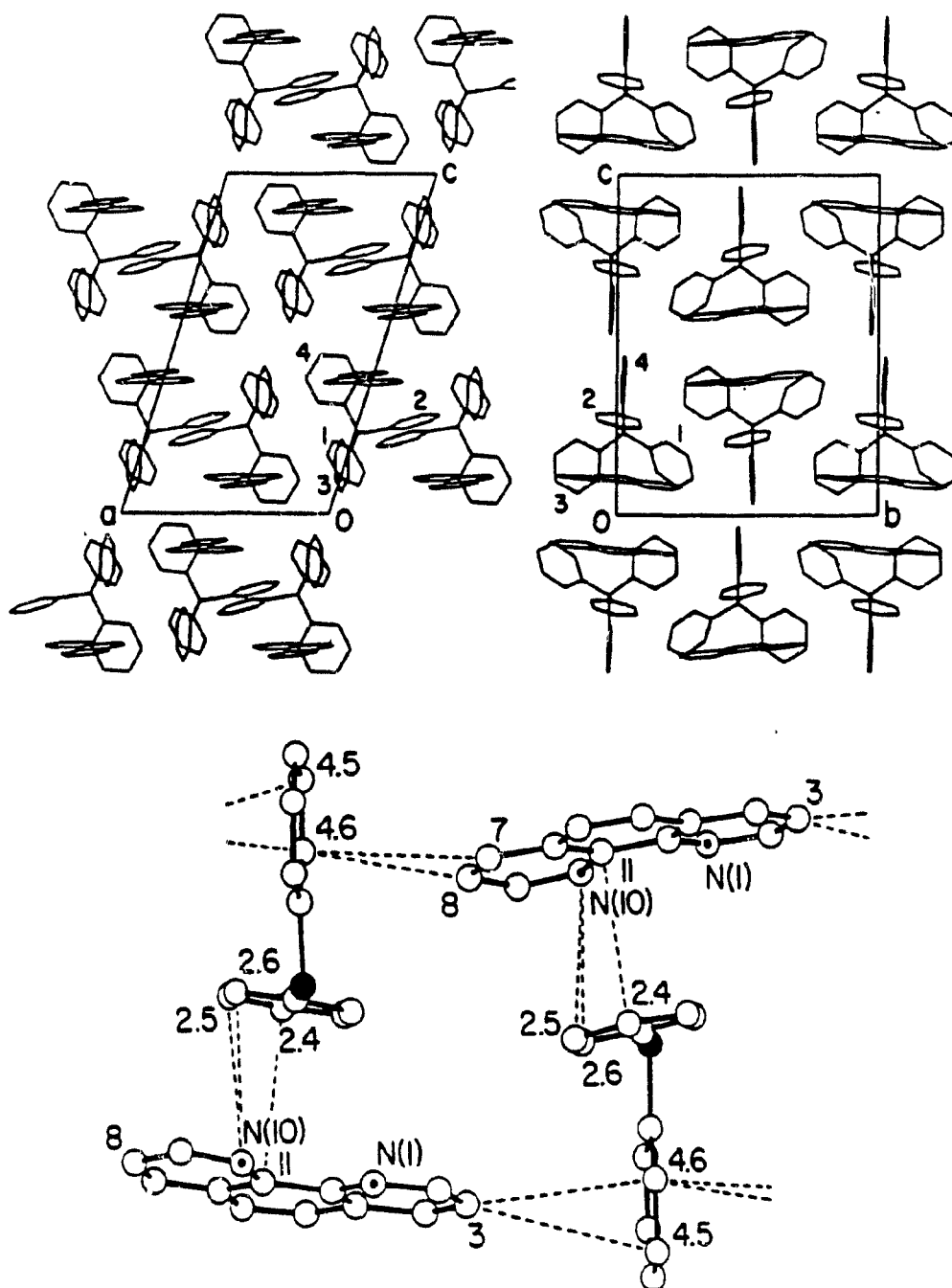


Fig. 64. Upper diagram - Projection of portions of the PTB structure on (010) (left) and (100) (right). Lower diagram - Projection of two cat-an pairs in neighbouring four-stacks approximately on (100). Filled circles, B; circles with dots, N. H atoms are not shown.

The phenH⁺ skeleton in the PTB structure is planar to 0.029(17) Å; the individual rings R1, R2, and R3 are planar to 0.008(3), 0.015(9), and 0.009(3) Å, respectively. The dihedral angles are R2/R1 = 3.1°, R3/R1 = 1.3°, and R3/R2 = 2.0°. As in the BP⁺ ion, the CNC angle in the protonated pyridinium ring is noticeably increased (8.3°), compared with the unprotonated one.

The shortest interatomic H(N)...acc approach is H(N10)...N(1), at 2.30 Å with an N(10) - H(N10)...N(1) angle of 101.8°. This intracation situation is even less favourable for an effective hydrogen bonding interaction than that in BPTB. The shortest H(N10)...C(anion) distance is H(N10)...C(32) equal to 3.09 Å (N(10) - H(N10)...C(32) = 122°). The distances, N(10)... $\pi_c(3)$ = 3.23 Å and H(N10)... $\pi_c(3)$ = 3.22 Å, though long, still can be regarded as weak bifurcation, with an intraion component engaging the lone pair on N(1)[‡]. Very recently, a similar situation has been reported in the structure of *cis*-1-(N-Me₂-amino)-2-(N-Me₂-ammonio)cyclopentane monopicrate¹⁶², where the N - H - N angle is only 97° and the H(N)...N distance is 2.56 Å. The H(N10)...C(R2) distances vary from 3.01 to 3.96 Å, suggestive of an interion H(N10)... π interaction.

[‡] The structure of PTB was also determined at low temperature (-20°C) by x-ray diffraction (not reported here). The position of the H(N10) atom was located from the Fourier difference map, so the distances and angles involving the H(N10) atom differ slightly from the room temperature determination. The other bond lengths and angles differ only within the stated e.s.d.'s. For details see reference 158.

Table 43. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for PTB (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	Ueq
B	-0.0179(5)	0.0274(5)	0.2391(3)	0.0380
C(11)	-0.0100(5)	0.1287(4)	0.1931(3)	0.0399
C(12)	-0.1053(5)	0.1553(4)	0.1261(3)	0.0450
C(13)	-0.0987(5)	0.2368(4)	0.0833(3)	0.0477
C(14)	0.0027(6)	0.2974(4)	0.1071(3)	0.0531
C(15)	0.0966(5)	0.2771(4)	0.1735(3)	0.0526
C(16)	0.0891(5)	0.1935(4)	0.2155(3)	0.0453
C(21)	-0.1546(4)	0.0164(4)	0.2547(3)	0.0400
C(22)	-0.2327(5)	0.0949(4)	0.2543(3)	0.0466
C(23)	-0.3412(5)	0.0856(5)	0.2763(3)	0.0620
C(24)	-0.3781(6)	-0.0029(6)	0.2961(3)	0.0719
C(25)	-0.3036(6)	-0.0825(5)	0.2955(3)	0.0638
C(26)	-0.1953(5)	-0.0724(4)	0.2752(3)	0.0505
C(31)	-0.0001(4)	-0.0662(4)	0.1859(3)	0.0391
C(32)	-0.0370(5)	-0.0672(4)	0.1068(3)	0.0497
C(33)	-0.0280(5)	-0.1491(5)	0.0638(3)	0.0640
C(34)	0.0216(6)	-0.2341(5)	0.1007(4)	0.0610
C(35)	0.0604(5)	-0.2358(4)	0.1788(3)	0.0512
C(36)	0.0511(5)	-0.1504(4)	0.2205(3)	0.0481
C(41)	0.0906(5)	0.0251(4)	0.3224(3)	0.0435
C(42)	0.2183(5)	0.0177(4)	0.3290(3)	0.0532
C(43)	0.3119(5)	0.0183(5)	0.3998(4)	0.0685
C(44)	0.2818(7)	0.0245(5)	0.4669(4)	0.0755
C(45)	0.1575(7)	0.0313(5)	0.4634(3)	0.0689
C(46)	0.0645(5)	0.0310(4)	0.3926(3)	0.0476
N(1)	-0.4354(4)	0.1218(4)	0.0806(3)	0.0580
C(2)	-0.4613(7)	0.2158(5)	0.0763(4)	0.0744
C(3)	-0.5720(7)	0.2551(5)	0.0824(4)	0.0802
C(4)	-0.6613(6)	0.1950(6)	0.0932(4)	0.0786
C(5)	-0.7254(7)	0.0245(7)	0.1116(4)	0.0905
C(6)	-0.6986(8)	-0.0700(7)	0.1169(4)	0.0899
C(7)	-0.5476(8)	-0.2017(6)	0.1180(4)	0.0884
C(8)	-0.4326(9)	-0.2304(5)	0.1158(4)	0.0903
C(9)	-0.3453(6)	-0.1616(6)	0.1084(3)	0.0764
C(1.1)	-0.4955(5)	-0.0379(5)	0.1018(3)	0.0529
C(1.2)	-0.5243(5)	0.0630(5)	0.0936(3)	0.0532
C(1.3)	-0.6384(6)	0.0950(5)	0.0997(3)	0.0661
C(1.4)	-0.5822(7)	-0.1048(5)	0.1122(4)	0.0691
N(10)	-0.3820(5)	-0.0687(4)	0.1007(3)	0.0611

Table 44. Selected bond lengths (Å), contacts (Å) and angles (°) for PTB (with e.s.d.'s in parentheses).

N(1) - C(2)	1.329(7)	N(10)...C(21)	3.385(6)
N(1) - C(1.2)	1.362(7)	N(10)...C(22)	3.600(7)
C(2) - C(3)	1.390(9)	N(10)...C(23)	3.769(8)
C(3) - C(4)	1.361(9)	N(10)...C(24)	3.679(8)
C(4) - C(1.3)	1.405(9)	N(10)...C(25)	3.409(8)
C(1.2) - C(1.3)	1.390(8)	N(10)...C(26)	3.243(7)
		Mean	3.51(18)
N(10) - C(1.1)	1.348(7)		
N(10) - C(9)	1.343(8)	N(10)... $\pi_c(2)$	3.21
C(8) - C(9)	1.401(9)		
C(7) - C(8)	1.361(10)	H(N10)...C(21)	3.01
C(7) - C(1.4)	1.389(10)	H(N10)...C(22)	3.21
C(1.1) - C(1.4)	1.396(8)	H(N10)...C(23)	3.71
		H(N10)...C(24)	3.96
N(1)... N(10)	2.701(7)	H(N10)...C(25)	3.76
C(1.3)...C(1.4)	2.827(10)	H(N10)...C(26)	3.28
		Mean	3.49(34)
H(N10)...N(1)	2.16		
		H(N10)... $\pi_c(2)$	2.27
B - C(11)	1.650(8)		
B - C(21)	1.651(7)		
B - C(31)	1.667(8)		
B - C(41)	1.637(7)		
Mean	1.651(11)		
C(12) - N(1) - C(2)	115.8(5)	C(11) - B - C(21)	111.3(4)
N(1) - C(2) - C(3)	124.2(6)	C(11) - B - C(31)	109.0(4)
C(2) - C(3) - C(4)	119.1(7)	C(11) - B - C(41)	110.6(5)
C(3) - C(4) - C(1.3)	119.3(6)	C(21) - B - C(31)	108.2(4)
C(4) - C(1.3) - C(1.2)	117.0(6)	C(21) - B - C(41)	107.6(4)
C(1.3) - C(1.2) - N(1)	124.4(6)	C(31) - B - C(41)	110.0(4)
		Mean	109.5(13)
C(1.1) - N(10) - C(9)	124.1(6)	C(12) - C(11) - C(16)	114.6(5)
N(10) - C(9) - C(8)	117.3(7)	C(22) - C(21) - C(26)	115.3(5)
C(9) - C(8) - C(7)	120.1(7)	C(32) - C(31) - C(36)	114.7(5)
C(8) - C(7) - C(1.4)	121.6(7)	C(42) - C(41) - C(46)	114.6(5)
C(7) - C(1.4) - C(1.1)	117.3(7)	Mean	114.8(3)
C(1.4) - C(1.1) - N(10)	119.5(6)		

2MTB.MeCN, [Me₂NH₂]⁺TB.MeCN

The crystals of 2MTB, obtained after recrystallization from MeCN or Et₂CO, were solvated whereas the crystals of 1MTB, 1ETB, 2ETB, 2PITB, 3MTB and 3ETB were all unsolvated, even though a similar preparative procedure was followed in all cases. The reason for the formation of a solvate is not yet clear and further study is needed. In a recent paper, Gruwel and Wasylshen¹⁶³ reported that the precipitate obtained from aqueous (D₂O) solutions of Me₂ND₂Cl and NaBPh₄ had the composition [Me₂ND₂]⁺[BPh₄]⁻.

The asymmetric unit in 2MTB.MeCN contains a cation, an anion and an acetonitrile molecule. The anions, cations and solvent molecules are arranged in columns generated by the *a* glide reflection in the direction of *c*. The coordinates of the non-hydrogen atoms are listed in Table 45 and the selected bond lengths and angles are gathered in Table 46. The cation geometry is normal with a mean N - C distance of 1.471(9) Å and the angle C - N - C of 114.2(5)°. In 2MTB.MeCN, one H(N) of the cation is bonded to a phenyl ring (N(1) - H(N11)...π_c(3)) whereas the other forms a bond to the N atom of the solvent molecule (N(1) - H(N12)...N(2)). Both are normal hydrogen bonds of type D.

The crystal packing of the previously reported 2MTB.Et₂CO¹¹⁷ is unique and is significantly different from that of 2MTB.MeCN. In contrast to 2MTB.MeCN, the solvent molecule in 2MTB.Et₂CO does not participate in the hydrogen bonding, and in the unit cell it orients in such a way that the repulsion between the lone pair on the O atom and the electron cloud of the phenyl ring is minimized. The H(N)...π hydrogen bonding in 2MTB.Et₂CO is of type B; both H(N)'s are linearly bonded to the phenyl rings of the same anion.

Table 45. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for 2MTB.MeCN (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	Ueq
B	0.6297(3)	0.1055(3)	0.7631(3)	0.0430
C(11)	0.5343(3)	0.0326(3)	0.7677(3)	0.0466
C(12)	0.4491(3)	0.0094(3)	0.6840(3)	0.0633
C(13)	0.3729(4)	-0.0598(3)	0.6822(3)	0.0745
C(14)	0.3811(3)	-0.1113(3)	0.7672(4)	0.0700
C(15)	0.4634(3)	-0.0910(3)	0.8529(3)	0.0687
C(16)	0.5392(3)	-0.0209(3)	0.8521(3)	0.0580
C(21)	0.7014(3)	0.0345(3)	0.7193(3)	0.0465
C(22)	0.7713(3)	-0.0345(3)	0.7790(3)	0.0593
C(20)	0.8288(3)	-0.1012(3)	0.7436(3)	0.0715
C(24)	0.8159(4)	-0.1021(3)	0.6449(4)	0.0764
C(25)	0.7460(4)	-0.0379(3)	0.5828(3)	0.0734
C(26)	0.6896(3)	0.0289(3)	0.6190(3)	0.0583
C(31)	0.5839(3)	0.2039(3)	0.6962(3)	0.0489
C(32)	0.6453(4)	0.2598(3)	0.6537(3)	0.0630
C(33)	0.6070(4)	0.3482(3)	0.6008(3)	0.0788
C(34)	0.5084(5)	0.3823(4)	0.5918(3)	0.0873
C(35)	0.4471(4)	0.3313(4)	0.6334(4)	0.0872
C(36)	0.4844(3)	0.2442(3)	0.6842(3)	0.0655
C(41)	0.6992(3)	0.1508(3)	0.8707(3)	0.0474
C(42)	0.8076(3)	0.1659(3)	0.9008(3)	0.0650
C(43)	0.8654(4)	0.2077(3)	0.9899(4)	0.0816
C(44)	0.8152(5)	0.2374(3)	1.0540(3)	0.0859
C(45)	0.7085(4)	0.2264(3)	1.0278(4)	0.0810
C(46)	0.6510(4)	0.1845(3)	0.9370(3)	0.0627
N(1)	0.1421(3)	0.0625(3)	0.8181(3)	0.0975
C(N11)	0.0765(5)	0.0441(4)	0.8803(5)	0.1270
C(N12)	0.2556(4)	0.0608(4)	0.8716(4)	0.1224
N(2)	0.1028(4)	-0.1159(3)	0.7005(3)	0.1095
C(N21)	0.0856(3)	-0.1895(4)	0.6662(4)	0.0769
C(N22)	0.0595(4)	-0.2889(3)	0.6160(4)	0.1104

Table 46. Selected bond lengths (Å), contacts (Å) and angles (°) for 2MTB.MeCN (with e.s.d.'s in parentheses).

N(1) - C(N11)	1.479(9)	H(N11)...C(31)	2.55
N(1) - C(N12)	1.462(8)	H(N11)...C(32)	2.52
Mean	1.471(9)	H(N11)...C(33)	2.63
		H(N11)...C(34)	2.72
N(2) - C(N21)	1.097(8)	H(N11)...C(35)	2.69
C(N21) - C(N22)	1.506(8)	H(N11)...C(36)	2.58
		Mean	2.62(7)
B - C(11)	1.638(7)		
B - C(21)	1.633(7)	H(N11)... $\pi_c(3)$	2.21
B - C(31)	1.634(7)		
B - C(41)	1.635(7)	N(1)...N(2)	2.887(7)
Mean	1.635(2)		
		H(N12)...N(2)	1.90
N(1)...C(31)	3.562(7)		
N(1)...C(32)	3.382(7)		
N(1)...C(33)	3.239(8)		
N(1)...C(34)	3.238(8)		
N(1)...C(35)	3.366(8)		
N(1)...C(36)	3.503(7)		
Mean	3.38(12)		
N(1)... $\pi_c(3)$	3.08		
C(N11) - N(1) - C(N12)	114.2(5)	C(12) - C(11) - C(16)	115.1(4)
		C(22) - C(21) - C(26)	114.7(4)
C(11) - B - C(21)	103.8(4)	C(32) - C(31) - C(36)	114.8(4)
C(31) - B - C(41)	103.9(4)	C(42) - C(41) - C(46)	114.8(4)
Mean	103.9(1)	Mean	114.9(2)
C(11) - B - C(31)	111.5(4)	N(2) - C(N21) - C(N22)	178.1(6)
C(11) - B - C(41)	113.1(4)	N(1) - H(N12) - N(2)	161.6
C(21) - B - C(31)	113.7(4)		
C(21) - B - C(41)	111.2(4)		
Mean	112.4(11)		

2PiTB, [(iso-Pr)₂NH₂]⁺TB⁻

In 2PiTB, all atoms are in general positions. Each crystal consists of one diisopropylammonium cation and one TB anion. The coordinates of the nonhydrogen atoms and the selected bond lengths and angles are tabulated in Tables 47 and 48.

The geometry of the cation is normal; the mean N - C bond length is 1.55(1) Å (slightly longer than that observed in 2PiCl¹⁶⁴ where the mean is 1.506(3) Å) and the C - N - C bond angle is 117.1(7)° (117.6(3) in 2PiCl).

The hydrogen bonding is of type B, the two H(N⁺)'s of the cation form two normal hydrogen bonds with two phenyl rings of the same anion, N - H(N1)...π_c(R2) and N - H(N2)...π_c(R4).

Table 47. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for 2PiTB (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	Ueq
B	0.5159(8)	0.8227(8)	0.2470(7)	0.0386
C(11)	0.4320(7)	0.9104(7)	0.2630(6)	0.0354
C(12)	0.3232(7)	0.9041(7)	0.2319(6)	0.0487
C(13)	0.2544(7)	0.9769(8)	0.2552(7)	0.0536
C(14)	0.2900(8)	1.0559(8)	0.3097(7)	0.0591
C(15)	0.3960(8)	1.0646(7)	0.3421(6)	0.0595
C(16)	0.4646(7)	0.9930(8)	0.3186(6)	0.0504
C(21)	0.4737(7)	0.7581(8)	0.1544(7)	0.0366
C(22)	0.4291(7)	0.8062(8)	0.0729(8)	0.0529
C(23)	0.3957(8)	0.7530(10)	-0.0071(7)	0.0687
C(24)	0.4067(8)	0.6500(10)	-0.0095(8)	0.0798
C(25)	0.4504(8)	0.6021(7)	0.0680(10)	0.0696
C(26)	0.4838(7)	0.6534(8)	0.1491(7)	0.0511
C(31)	0.5307(8)	0.7554(7)	0.3389(6)	0.0386
C(32)	0.4579(7)	0.6803(8)	0.3531(7)	0.0479
C(33)	0.4649(9)	0.6269(8)	0.4327(8)	0.0612
C(34)	0.5450(10)	0.6459(9)	0.5033(8)	0.0675
C(35)	0.6178(8)	0.7175(9)	0.4930(7)	0.0640
C(36)	0.6109(7)	0.7725(7)	0.4128(7)	0.0494
C(41)	0.6302(7)	0.8681(7)	0.2251(6)	0.0422
C(42)	0.6364(7)	0.9617(8)	0.1853(6)	0.0549
C(43)	0.7360(10)	0.9951(8)	0.1620(7)	0.0631
C(44)	0.8250(10)	0.9370(10)	0.1769(8)	0.0663
C(45)	0.8178(8)	0.8438(9)	0.2138(7)	0.0584
C(46)	0.7214(7)	0.8100(7)	0.2377(6)	0.0478
N	0.1869(5)	0.7700(6)	0.5117(5)	0.0508
C(N1)	0.1792(7)	0.7109(8)	0.4225(7)	0.0571
C(N11)	0.1396(7)	0.6066(7)	0.4388(7)	0.0806
C(N12)	0.1103(8)	0.7672(8)	0.3476(6)	0.0768
C(N2)	0.2429(7)	0.8723(7)	0.5153(6)	0.0503
C(N21)	0.2413(6)	0.9183(7)	0.6071(7)	0.0717
C(N22)	0.3531(7)	0.8598(7)	0.4947(7)	0.0793

Table 48. Selected bond lengths (Å), contacts (Å) and angles (°) for 2PiTB (with e.s.d.'s in parentheses).

N - C(N1)	1.54(1)	H(N1)...C(21)	2.88
N - C(N2)	1.55(1)	H(N1)...C(22)	2.83
Mean	1.55(1)	H(N1)...C(23)	2.79
		H(N1)...C(24)	2.77
B - C(11)	1.64(1)	H(N1)...C(25)	2.76
B - C(21)	1.65(1)	H(N1)...C(26)	2.81
B - C(31)	1.63(1)	Mean	2.81(4)
B - C(41)	1.67(1)		
Mean	1.648(15)	H(N2)... $\pi_c(2)$	2.44
N...C(21)	3.74(1)	H(N2)...C(41)	3.16
N...C(22)	3.72(1)	H(N2)...C(42)	3.41
N...C(23)	3.73(1)	H(N2)...C(43)	3.32
N...C(24)	3.73(1)	H(N2)...C(44)	2.95
N...C(25)	3.70(1)	H(N2)...C(45)	2.57
N...C(26)	3.71(1)	H(N2)...C(46)	2.68
Mean	3.72(13)	Mean	3.02(31)
N... $\pi_c(2)$	3.45	H(N2)... $\pi_c(4)$	2.69
N...C(41)	3.85(1)		
N...C(42)	4.15(1)		
N...C(43)	4.20(1)		
N...C(44)	3.95(1)		
N...C(45)	3.56(1)		
N...C(46)	3.50(1)		
Mean	3.87(27)		
N... $\pi_c(4)$	3.62		
C(N1) - N - C(N2)	117.1(7)	C(12) - C(11) - C(16)	115.6(8)
		C(22) - C(21) - C(26)	116.0(10)
C(11) - B - C(31)	105.6(7)	C(32) - C(31) - C(36)	115.1(9)
C(21) - B - C(41)	102.5(7)	C(42) - C(41) - C(46)	115.6(9)
Mean	104.1(16)	Mean	115.6(3)
C(11) - B - C(21)	111.0(8)		
C(11) - B - C(41)	112.8(8)		
C(21) - B - C(31)	113.3(8)		
C(31) - B - C(41)	111.9(8)		
Mean	112.3(9)		

AC7TB, [C₆H₁₄N]TB

Initially, the structure of this compound was determined by B. R. Vincent¹⁶⁵. The *R*-factor was 7.60%, high for such a relatively simple, slightly disordered structure. The data were therefore recollected using a new crystal and the structure was redetermined. This time the *R* factor was 5.69%. The asymmetric unit contains an azacycloheptane cation and a tetraphenylborate anion, both of C_s symmetry. In the cation, only the N atom and its two hydrogens lie on the mirror plane, which bisect the C - C bond at the opposite end of the ring, whereas, in the anion the B atom, the C(α) and C(δ) atoms of two of the phenyl rings and the associated H(δ) atoms all lie in the mirror plane at $y = 1/4$ (Table 49).

After refinement, it was found that in the cation the U_{11} values of the C atoms increased consistently with increasing distance from the N atom. Modelling the atoms C(2) and C(3) in twofold orientational disorder with respect to the crystallographic mirror plane significantly reduced the U_{11} of these atoms, even though some of them still remained large. The high U_{11} values of the ring atoms may be a indication of compromise between two commonly observed conformations C_s and C₂, of azacycloheptane¹⁶⁶.

The structure consists of alternating columns of ions parallel to (101). The quasi-spherical cation occupies the tetrahedral cavity formed by four phenyl rings. Two of the rings belong to a neighbouring anion in the same cation-anion column while the other two come, one each, from anions in the neighbouring cation-anion columns. As in 2PiTB, the two N - H vectors point at two phenyl rings R2 (C(21) - C(24) and their mirror related carbon atoms) and R3 (C(31) - C(34) and their mirror related carbon atoms).

Table 49. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for AC7TB (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	U _{eq}
B	0.1800(5)	1/4	0.8153(5)	0.0394
C(11)	0.2491(3)	0.1570(1)	0.7599(2)	0.0398
C(12)	0.1799(3)	0.1213(2)	0.6191(3)	0.0525
C(13)	0.2466(3)	0.0504(2)	0.5641(3)	0.0611
C(14)	0.3864(3)	0.0132(2)	0.6487(3)	0.0596
C(15)	0.4566(3)	0.0456(2)	0.7882(3)	0.0578
C(16)	0.3899(3)	0.1166(2)	0.8412(3)	0.0506
C(21)	-0.0071(4)	1/4	0.7486(4)	0.0414
C(22)	-0.0917(3)	0.1648(2)	0.7266(3)	0.0541
C(23)	-0.2495(3)	0.1647(3)	0.6831(3)	0.0731
C(24)	-0.3282(5)	1/4	0.6636(5)	0.0759
C(31)	0.2255(4)	1/4	0.9916(4)	0.0429
C(32)	0.2375(3)	0.1650(2)	1.0691(3)	0.0586
C(33)	0.2631(4)	0.1639(3)	1.2180(3)	0.0799
C(34)	0.2754(6)	1/4	1.2902(5)	0.0798
N	-0.0965(4)	1/4	1.0393(4)	0.0535
C(1)	-0.1704(4)	0.1584(2)	1.0559(3)	0.0316
C(2)	-0.1798(7)	0.1330(5)	1.1989(7)	0.0826
C(2*)	-0.1300(7)	0.1417(6)	1.2155(6)	0.0771
C(3)	-0.2703(7)	0.2013(5)	1.2492(7)	0.0840
C(3*)	-0.2034(10)	0.1982(7)	1.2971(8)	0.1257

Table 50. Selected bond lengths (Å), contacts (Å) and angles (°) for AC7TB (with e.s.d.'s in parentheses).

N - C(1)	1.499(4)	H(N1)...C(21)	2.35
		H(N1)...C(22)	2.44
B - C(11)	1.642(4)	H(N1)...C(22)	2.44
B - C(11)	1.642(4)	H(N1)...C(23)	2.69
B - C(21)	1.651(4)	H(N1)...C(23)	2.69
B - C(31)	1.651(4)	H(N1)...C(24)	2.80
Mean	1.647(5)	Mean	2.57(16)
N...C(21)	3.335(4)	H(N1)... $\pi_c(2)$	2.16
N...C(22)	3.367(4)		
N...C(22)	3.367(4)	H(N2)...C(31)	2.74
N...C(23)	3.507(5)	H(N2)...C(32)	2.63
N...C(23)	3.507(5)	H(N2)...C(32)	2.63
N...C(24)	3.565(4)	H(N2)...C(33)	2.52
Mean	3.44(9)	H(N2)...C(33)	2.52
		H(N2)...C(34)	2.46
N... $\pi_c(2)$	3.15	Mean	2.58(9)
N...C(31)	3.288(4)	H(N2)... $\pi_c(3)$	2.18
N...C(32)	3.306(4)		
N...C(32)	3.306(4)		
N...C(33)	3.426(5)		
N...C(33)	3.426(5)		
N...C(34)	3.481(4)		
Mean	3.37(7)		
N... $\pi_c(3)$	3.07		
C(11) - B - C(11)	103.9(2)	C(12) - C(11) - C(16)	115.0(3)
C(21) - B - C(31)	103.6(2)	C(12) - C(11) - C(16)	115.0(3)
Mean	103.8(2)	C(22) - C(21) - C(22)	115.2(3)
		C(32) - C(31) - C(32)	115.8(3)
C(11) - B - C(21)	112.1(2)	Mean	115.3(3)
C(11) - B - C(21)	112.1(2)		
C(11) - B - C(31)	112.7(2)		
C(11) - B - C(31)	112.7(2)		
Mean	112.4(3)		

TMTB.MeCN, [C₁₁H₁₂N₇]TB.MeCN

TMTB.MeCN crystallises in the monoclinic crystal system with space group $P2_1/n$ ($Z = 4$). The asymmetric unit contains a cation, an anion and an acetonitrile solvent molecule. All atoms are in general positions. Final atomic coordinates are given in Table 51, and selected bond lengths and angles in Table 52. In the cation, the exocyclic C - N distances are significantly short (average 1.338(12) Å), which may be due to donation of electrons from the exocyclic amino groups to the ring π system. The effect of protonation at N(1) is clearly visible in the C - N bonds and the C - N - C angle related to N(1); the distances, N(1) - C(2) = 1.361(7) Å and N(2) - C(9) = 1.379(7) Å, are longer than the other C - N distances within the pyrimidine ring, and the intraannular bond angle at the protonated N(1) is 3.9° larger than in the reported unprotonated compound, 2,4-diaminopteridine monohydrate¹⁶⁷. Both the pyrimidine and the pyrazine rings are satisfactorily planar and the dihedral angle between the best planes passing through the rings is 4.2°.

The phenyl ring of the cation is also planar; it is twisted by 50.2° and 46.9° from the pyrimidine and pyrazine ring planes, respectively. With the exception of H(7,2), all the other H(N) atoms are involved in hydrogen bonding either to the tetraphenylborate anion or to the solvent molecule. The H(N(1)) is asymmetrically bifurcated between ring 2 and ring 3 of the same anion. In the pyrimidine moiety, the N(4) amino group forms normal hydrogen bonds with ring 1 and ring 4 of the same anion, while, the N(2) amino group directs one of its protons between R2 and R3 and the other toward the N(9) of the acetonitrile solvent molecule. The H(7,1) of the amino group of the pyrazine moiety is involved in normal hydrogen bonding with R2, while the other H(7,2) forms a normal

intracation N(7) - H(7,2)... π hydrogen bond.

A TLS analysis indicates that the thermal motion of the cation is reasonably consistent with a rigid body model, regardless of whether the exocyclic nitrogen atom is excluded or included:

	$R(U_{ij})$	$R_w(U_{ij})$	$\text{rms}(U_{ij})$	L_1	L_2	L_3
N excluded	10.1%	9.7%	0.0035	1.4°	2.3°	3.2°
N included	11.3%	11.2%	0.0043	1.5°	2.6°	4.6°

Table 51. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for TMTB.MeCN (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	Ueq
B	0.5063(5)	0.1467(7)	0.7371(3)	0.0344
C(11)	0.5494(4)	0.1373(6)	0.6722(3)	0.0364
C(12)	0.5327(5)	0.0276(6)	0.6351(3)	0.0494
C(13)	0.5623(5)	0.0175(7)	0.5783(3)	0.0612
C(14)	0.6105(5)	0.1171(9)	0.5564(3)	0.0644
C(15)	0.6283(5)	0.2247(8)	0.5909(3)	0.0612
C(16)	0.5973(4)	0.2354(6)	0.6477(3)	0.0448
C(21)	0.5527(4)	0.2644(5)	0.7804(2)	0.0334
C(22)	0.5003(4)	0.3424(6)	0.8144(3)	0.0418
C(23)	0.5420(5)	0.4378(7)	0.8535(3)	0.0523
C(24)	0.6384(6)	0.4580(7)	0.8601(3)	0.0563
C(25)	0.6930(5)	0.3809(6)	0.8283(3)	0.0505
C(26)	0.6507(4)	0.2860(6)	0.7898(3)	0.0417
C(31)	0.5331(4)	0.0197(5)	0.7792(3)	0.0345
C(32)	0.4846(4)	-0.0100(6)	0.8281(3)	0.0407
C(33)	0.5112(5)	-0.1093(6)	0.8683(3)	0.0529
C(34)	0.5885(5)	-0.1841(6)	0.8615(3)	0.0614
C(35)	0.6379(5)	-0.1581(7)	0.8143(3)	0.0582
C(36)	0.6108(4)	-0.0573(6)	0.7745(3)	0.0432
C(41)	0.3909(4)	0.1626(6)	0.7168(2)	0.0355
C(42)	0.3516(4)	0.2793(6)	0.6938(3)	0.0438
C(43)	0.2547(5)	0.2936(7)	0.6738(3)	0.0569
C(44)	0.1946(5)	0.1918(8)	0.6755(3)	0.0627
C(45)	0.2304(5)	0.0760(7)	0.6962(3)	0.0599
C(46)	0.3269(4)	0.0623(6)	0.7168(3)	0.0473

Table 51. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for TMTB.MeCN (with e.s.d.'s in parentheses - continued).

Atom	x/a	y/b	z/c	Ueq
N(1)	0.7130(4)	0.1013(5)	0.9024(2)	0.0441
C(2)	0.6798(5)	0.1516(6)	0.9516(3)	0.0441
N(2)	0.5864(4)	0.1460(6)	0.9521(2)	0.0620
N(3)	0.7340(4)	0.2021(5)	0.9996(2)	0.0442
C(4)	0.8270(5)	0.2094(6)	0.9983(3)	0.0427
N(4)	0.8826(4)	0.2568(6)	1.0460(2)	0.0614
N(5)	0.9608(4)	0.1800(5)	0.9433(2)	0.0435
C(6)	0.9913(5)	0.1453(6)	0.8923(3)	0.0415
C(7)	0.9261(5)	0.0936(6)	0.8423(3)	0.0441
N(7)	0.9550(4)	0.0571(5)	0.7896(2)	0.0589
N(8)	0.8340(4)	0.0766(5)	0.8452(2)	0.0465
C(9)	0.8073(5)	0.1145(6)	0.8974(3)	0.0400
C(10)	0.8673(4)	0.1668(6)	0.9459(3)	0.0389
C(61)	1.0948(5)	0.1573(6)	0.8916(3)	0.0461
C(62)	1.1303(5)	0.2112(7)	0.8417(3)	0.0578
C(63)	1.2270(6)	0.2224(7)	0.8433(3)	0.0650
C(64)	1.2884(5)	0.1802(7)	0.8935(4)	0.0661
C(65)	1.2543(5)	0.1284(7)	0.9428(4)	0.0643
C(66)	1.1567(5)	0.1158(6)	0.9419(3)	0.0549
N(9)	-0.0396(5)	0.1661(7)	0.5058(3)	0.0797
C(91)	-0.0992(6)	0.0974(8)	0.4892(3)	0.0655
C(92)	-0.1750(6)	0.0085(8)	0.4680(4)	0.0859

Table 52. Selected bond lengths (Å), contacts (Å) and angles (°) for TMTB.MeCN (with e.s.d.'s in parentheses).

N(1) - C(2)	1.361(7)	N(2)...C(21)	3.960(8)
C(2) - N(3)	1.329(7)	N(2)...C(22)	3.736(8)
N(3) - C(4)	1.339(7)	N(2)...C(23)	3.771(9)
C(4) - C(10)	1.444(8)	N(2)...C(24)	3.999(9)
C(10) - N(5)	1.357(7)	N(2)...C(25)	4.154(9)
N(5) - C(6)	1.322(7)	N(2)...C(26)	4.117(8)
C(6) - C(7)	1.443(8)	Mean	3.96(16)
C(7) - N(8)	1.344(8)		
N(8) - C(9)	1.333(7)	N(2)... $\pi_c(2)$	3.69
C(9) - C(10)	1.384(8)		
C(9) - N(1)	1.379(7)	N(2)...C(31)	4.014(7)
C(6) - C(61)	1.491(8)	N(2)...C(32)	3.339(8)
N(9) - C(91)	1.138(9)	N(2)...C(33)	3.353(8)
		N(2)...C(34)	4.020(7)
C(2) - N(2)	1.341(7)	N(2)...C(35)	4.562(8)
C(4) - N(4)	1.321(7)	N(2)...C(36)	4.538(7)
C(7) - N(7)	1.351(7)	Mean	3.97(49)
Mean	1.338(12)		
		N(2)... $\pi_c(3)$	3.75
B - C(11)	1.651(8)		
B - C(21)	1.645(9)	N(4)...C(11)	3.567(7)
B - C(31)	1.643(9)	N(4)...C(12)	3.520(8)
B - C(41)	1.655(8)	N(4)...C(13)	3.499(9)
Mean	1.649(5)	N(4)...C(14)	3.501(9)
		N(4)...C(15)	3.515(8)
N(1)...C(21)	3.693(7)	N(4)...C(16)	3.526(8)
N(1)...C(22)	4.212(8)	Mean	3.52(3)
N(1)...C(23)	4.354(9)		
N(1)...C(24)	3.982(9)	N(4)... $\pi_c(1)$	3.23
N(1)...C(25)	3.364(8)		
N(1)...C(26)	3.181(8)	N(4)...C(41)	3.858(7)
Mean	3.80(43)	N(4)...C(42)	3.388(8)
		N(4)...C(43)	3.635(8)
N(1)... $\pi_c(2)$	3.56	N(4)...C(44)	4.255(9)
		N(4)...C(45)	4.595(9)
N(1)...C(31)	3.560(7)	N(4)...C(46)	4.413(8)
N(1)...C(32)	3.627(8)	Mean	4.02(44)
N(1)...C(33)	3.634(8)		
N(1)...C(34)	3.546(7)	N(4)... $\pi_c(4)$	3.80
N(1)...C(35)	3.436(8)		
N(1)...C(36)	3.419(7)		
Mean	3.54(85)		
N(1)... $\pi_c(3)$	3.25		

Table 52. Selected bond lengths (Å), contacts (Å) and angles (°) for TMTB.MeCN (with e.s.d.'s in parentheses - continued).

N(7)...C(21)	3.448(8)	H(2,1)...C(21)	3.46
N(7)...C(22)	3.360(8)	H(2,1)...C(22)	3.39
N(7)...C(23)	3.415(8)	H(2,1)...C(23)	3.81
N(7)...C(24)	3.537(8)	H(2,1)...C(24)	4.23
N(7)...C(25)	3.617(8)	H(2,1)...C(25)	4.24
N(7)...C(26)	3.570(8)	H(2,1)...C(26)	3.87
Mean	3.49(9)	Mean	3.83(33)
N(7)... $\pi_c(2)$	3.20	H(2,1)... $\pi_c(2)$	3.59
N(7)...C(61)	2.975(7)	H(2,1)...C(31)	3.11
N(7)...C(62)	3.066(8)	H(2,1)...C(32)	2.33
N(7)...C(63)	4.270(8)	H(2,1)...C(33)	2.47
N(7)...C(64)	5.143(9)	H(2,1)...C(34)	3.31
N(7)...C(65)	5.102(9)	H(2,1)...C(35)	3.87
N(7)...C(66)	4.139(8)	H(2,1)...C(36)	3.77
Mean	4.12(86)	Mean	3.14(59)
N(7)... $\pi_c(6)$	3.97	H(2,1)... $\pi_c(3)$	2.88
H(1)...C(21)	3.24	H(4,1)...C(11)	3.08
H(1)...C(22)	3.95	H(4,1)...C(12)	3.09
H(1)...C(23)	4.42	H(4,1)...C(13)	2.89
H(1)...C(24)	4.28	H(4,1)...C(14)	2.61
H(1)...C(25)	3.59	H(4,1)...C(15)	2.53
H(1)...C(26)	3.00	H(4,1)...C(16)	2.76
Mean	3.75(52)	Mean	2.83(21)
H(1)... $\pi_c(2)$	3.52	H(4,1)... $\pi_c(1)$	2.47
H(1)...C(31)	2.59	H(4,2)...C(41)	2.99
H(1)...C(32)	2.74	H(4,2)...C(42)	2.52
H(1)...C(33)	2.84	H(4,2)...C(43)	2.71
H(1)...C(34)	2.76	H(4,2)...C(44)	3.28
H(1)...C(35)	2.56	H(4,2)...C(45)	3.60
H(1)...C(36)	2.44	H(4,2)...C(46)	3.47
Mean	2.65(14)	Mean	3.10(39)
H(1)... $\pi_c(3)$	2.26	H(4,2)... $\pi_c(4)$	2.79

Table 52. Selected bond lengths (Å), contacts (Å) and angles (°) for TMTB.MeCN (with e.s.d.'s in parentheses - continued).

H(7,1)...C(21)	3.03	H(7,2)...C(61)	2.58
H(7,1)...C(22)	2.97	H(7,2)...C(62)	2.39
H(7,1)...C(23)	2.78	H(7,2)...C(63)	3.43
H(7,1)...C(24)	2.61	H(7,2)...C(64)	4.31
H(7,1)...C(25)	2.66	H(7,2)...C(65)	4.43
H(7,1)...C(26)	2.86	H(7,2)...C(66)	3.68
Mean	2.82(15)	Mean	3.47(78)
H(7,1)... $\pi_c(2)$	2.45	H(7,2)... $\pi_c(6)$	3.27
C(2) - N(1) - C(9)	119.4(5)	C(11) - B - C(21)	112.4(5)
C(2) - N(3) - C(4)	117.9(6)	C(11) - B - C(31)	111.1(5)
C(6) - N(5) - C(10)	117.7(5)	C(21) - B - C(41)	112.3(5)
C(7) - N(8) - C(9)	114.6(6)	C(31) - B - C(41)	112.0(5)
		Mean	112.0(5)
C(11) - B - C(41)	105.1(5)	C(12) - C(11) - C(16)	115.4(6)
C(21) - B - C(31)	104.2(4)	C(22) - C(21) - C(26)	115.4(5)
Mean	104.7(5)	C(32) - C(31) - C(36)	114.9(5)
		C(42) - C(41) - C(46)	115.5(5)
		Mean	115.3(2)

[1-Ad]TBw, [C₁₀H₁₈N]TB.H₂O

The atomic positions and equivalent isotropic temperature factors of [1-Ad]TBw are listed in Table 53. Selected bond lengths and angles are given in Table 54. The asymmetric unit contains two sets of anions, cations and water molecules. The anions, the cations and the water molecules are arranged in layers in the *b* direction; each layer contains all three component species and one is related to the other by 2_1 . The adamantane cation skeleton consists of four fused cyclohexane rings, each ring having a nearly chair conformation. The C - C bond lengths and C - C - C bond angles range from 1.505(3) - 1.543(4) Å (mean 1.534(3) Å) and 103.4(1) - 111.5(3)° (mean 109.4(3)°),

respectively. The mean distance N - C is 1.505(12) Å, and the three nearly equal C - C - N bond angles average 108.5(1)°. All these values agree well with the corresponding values in related compounds such as 1-adamantanamine hydrochloride¹⁶⁸, 1-adamantanol¹⁶⁹, 2-iodoadamantanol¹⁷⁰. In spite of being a cage-like entity, the cations fit poorly in the rigid body model, regardless of whether the nitrogen atom is excluded from or included in the TLS analysis:

		$R(U_{ij})$	$R_w(U_{ij})$	$rms(U_{ij})$	L_1	L_2	L_3	T
Cation(1)	(N excluded)	14.0%	13.9	0.0095	3.0°	5.3°	7.1°	0.2 Å
	(N included)	13.8%	13.9	0.0092	3.5°	5.1°	7.1°	0.2 Å
Cation(2)	(N excluded)	10.4%	11.0	0.0063	3.5°	3.7°	8.8°	0.25 Å
	(N included)	10.7%	11.2	0.0063	3.4°	3.8°	8.8°	0.25 Å

The hydrogen bonding patterns are similar in both sets. There are three H(N) protons in each cation, one of which is hydrogen bonded to the solvent water molecule, which in turn forms hydrogen bonds to an anion. The remaining 2H(N)'s of each cation are bonded to the π system. Thus, N of each cation is engaged in normal N - H(N)... π (type F) and normal N - H(N)...O (type H) bonding.

Like other TBs, this compound also is a weak scatterer. To obtain a reasonable d/p ratio during refinement, all eight phenyl rings of the two sets of TB anions were constrained to regular hexagons. Thus, the phenyl rings are perfectly planar. All the C - C distances and all the C - C - C angles inside the rings are 1.395 Å and 120°, respectively. The deviation of the B atom from the ring planes ranges from -0.172 to 0.189 Å.

Table 53. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for [1-Ad]TBw (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	Ueq
B(1)	0.9166(6)	0.8771(0)	1.0394(6)	0.0457
C(111)	0.8369(3)	0.8936(2)	0.9331(2)	0.0536
C(112)	0.8602(3)	0.9558(2)	0.8701(2)	0.0542
C(113)	0.7921(3)	0.9759(2)	0.7870(2)	0.0726
C(114)	0.7007(3)	0.9337(2)	0.7670(2)	0.0711
C(115)	0.6773(3)	0.8715(2)	0.8301(2)	0.0721
C(116)	0.7454(3)	0.8515(2)	0.9131(2)	0.0568
C(121)	0.8850(3)	0.9543(2)	1.1114(3)	0.0476
C(122)	0.9354(3)	1.0326(2)	1.1207(3)	0.0611
C(123)	0.9045(3)	1.0985(2)	1.1751(3)	0.0841
C(124)	0.8232(3)	1.0861(2)	1.2202(3)	0.0869
C(125)	0.7729(3)	1.0077(2)	1.2109(3)	0.0740
C(126)	0.8038(3)	0.9418(2)	1.1566(3)	0.0630
C(131)	1.0355(3)	0.8838(3)	1.0274(3)	0.0570
C(132)	1.1075(3)	0.9059(3)	1.1068(3)	0.0682
C(133)	1.2074(3)	0.9098(3)	1.0986(3)	0.0921
C(134)	1.2353(3)	0.8916(3)	1.0109(3)	0.1041
C(135)	1.1633(3)	0.8694(3)	0.9315(3)	0.1006
C(136)	1.0634(3)	0.8655(3)	0.9398(3)	0.0667
C(141)	0.9053(3)	0.7773(2)	1.0819(3)	0.0491
C(142)	0.8907(3)	0.7073(2)	1.0194(3)	0.0647
C(143)	0.8877(3)	0.6242(2)	1.0558(3)	0.0749
C(144)	0.8993(3)	0.6112(2)	1.1546(3)	0.0799
C(145)	0.9139(3)	0.6813(2)	1.2170(3)	0.0882
C(146)	0.9169(3)	0.7643(2)	1.1807(3)	0.0726
B(2)	0.5533(6)	1.1697(5)	0.4450(6)	0.0429
C(211)	0.6437(3)	1.1838(2)	0.5418(2)	0.0433
C(212)	0.6274(3)	1.2392(2)	0.6148(2)	0.0526
C(213)	0.7052(3)	1.2589(2)	0.6901(2)	0.0729
C(214)	0.7991(3)	1.2234(2)	0.6925(2)	0.0740
C(215)	0.8154(3)	1.1680(2)	0.6196(2)	0.0816
C(216)	0.7376(3)	1.1482(2)	0.5443(2)	0.0541
C(221)	0.5560(3)	1.0712(2)	0.3984(3)	0.0454
C(222)	0.5974(3)	1.0007(2)	0.4520(3)	0.0640
C(223)	0.5918(3)	0.9192(2)	0.4102(3)	0.0805
C(224)	0.5449(3)	0.9084(2)	0.3149(3)	0.0943
C(225)	0.5035(3)	0.9790(2)	0.2613(3)	0.0807
C(226)	0.5091(3)	1.0604(2)	0.3031(3)	0.0609

Table 53. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for [1-Ad]TBw (with e.s.d.'s in parentheses - continued).

Atom	x/a	y/b	z/c	Ueq
C(231)	0.4383(2)	1.1778(3)	0.4718(3)	0.0446
C(232)	0.3608(2)	1.2100(3)	0.4029(3)	0.0751
C(233)	0.2644(2)	1.2129(3)	0.4218(3)	0.0945
C(234)	0.2455(2)	1.1835(3)	0.5096(3)	0.0823
C(235)	0.3230(2)	1.1513(3)	0.5785(3)	0.0748
C(236)	0.4194(2)	1.1485(3)	0.5596(3)	0.0569
C(241)	0.5751(2)	1.2479(2)	0.3705(2)	0.0384
C(242)	0.5421(2)	1.3313(2)	0.3819(2)	0.0497
C(243)	0.5710(2)	1.3982(2)	0.3276(2)	0.0599
C(244)	0.6329(2)	1.3816(2)	0.2619(2)	0.0630
C(245)	0.6659(2)	1.2982(2)	0.2505(2)	0.0627
C(246)	0.6370(2)	1.2313(2)	0.3048(2)	0.0498
N(1)	0.2293(5)	0.8579(0)	0.5042(5)	0.0587
C(11)	0.1265(5)	0.8878(4)	0.5081(5)	0.0443
C(12)	0.1360(6)	0.9709(5)	0.5690(6)	0.0725
C(12')	0.0703(6)	0.8189(6)	0.5505(6)	0.0778
C(12'')	0.0741(6)	0.9077(5)	0.4041(5)	0.0600
C(13)	0.0297(7)	1.0035(7)	0.5689(7)	0.0955
C(13')	-0.0342(8)	0.8514(7)	0.5521(8)	0.1100
C(13'')	-0.0303(7)	0.9401(6)	0.4057(7)	0.0907
C(14)	-0.0247(9)	0.9333(9)	0.6135(9)	0.1351
C(14')	-0.0867(7)	0.8708(8)	0.4491(8)	0.1134
C(14'')	-0.0231(7)	1.0213(7)	0.4664(7)	0.1035
N(2)	0.2948(4)	0.5664(4)	0.0293(4)	0.0555
C(21)	0.3972(5)	0.6069(4)	0.0419(4)	0.0453
C(22)	0.4728(6)	0.5379(5)	0.0321(6)	0.0727
C(22')	0.3953(6)	0.6770(6)	-0.0332(6)	0.0762
C(22'')	0.4203(6)	0.6463(5)	0.1412(6)	0.0702
C(23)	0.5745(6)	0.5800(7)	0.0464(7)	0.0859
C(23')	0.4992(7)	0.7169(6)	-0.0194(6)	0.0889
C(23'')	0.5232(6)	0.6869(5)	0.1555(5)	0.0684
C(24)	0.5754(7)	0.6493(7)	-0.0290(7)	0.1024
C(24')	0.5236(7)	0.7571(5)	0.0813(6)	0.0784
C(24'')	0.5983(7)	0.6212(6)	0.1450(7)	0.0854
O(1)	0.6726(5)	0.4773(4)	0.5877(4)	0.0951
O(2)	0.8544(3)	0.1828(3)	0.9393(3)	0.0760

Table 54. Selected bond lengths (Å), contacts (Å) and angles (°) for [1-Ad]TBw (with e.s.d.'s in parentheses).

N(1) - C(11)	1.493(8)	N(2)...C(111)	3.336(8)
N(2) - C(21)	1.517(10)	N(2)...C(112)	3.260(8)
		N(2)...C(113)	3.367(8)
C(11) - C(12)	1.548(11)	N(2)...C(114)	3.542(8)
C(11) - C(12')	1.509(12)	N(2)...C(115)	3.612(8)
C(11) - C(12'')	1.546(11)	N(2)...C(116)	3.512(8)
Mean	1.534(18)	Mean	3.44(13)
C(21) - C(22)	1.517(12)		
C(21) - C(22')	1.521(12)	N(2)... $\pi_c(11)$	3.14
C(21) - C(22'')	1.515(11)		
Mean	1.518(3)	N(2)...C(121)	3.356(8)
		N(2)...C(122)	3.498(8)
B(1) - C(111)	1.707(7)	N(2)...C(123)	3.627(8)
B(1) - C(121)	1.685(7)	N(2)...C(124)	3.619(8)
B(1) - C(131)	1.670(7)	N(2)...C(125)	3.482(8)
B(1) - C(141)	1.684(7)	N(2)...C(126)	3.347(8)
Mean	1.687(13)	Mean	3.49(12)
B(2) - C(211)	1.683(10)	N(2)... $\pi_c(12)$	3.20
B(2) - C(221)	1.673(10)		
B(2) - C(231)	1.690(10)	N(1)...O(1)	2.757(8)
B(2) - C(241)	1.673(10)	N(2)...O(2)	2.827(9)
Mean	1.680(7)		
		O(1)...C(221)	3.493(8)
N(1)...C(211)	3.349(6)	O(1)...C(222)	3.652(8)
N(1)...C(212)	3.366(6)	O(1)...C(223)	3.736(8)
N(1)...C(213)	3.417(6)	O(1)...C(224)	3.666(8)
N(1)...C(214)	3.451(6)	O(1)...C(225)	3.508(8)
N(1)...C(215)	3.435(6)	O(1)...C(226)	3.418(8)
N(1)...C(216)	3.383(6)	Mean	3.58(12)
Mean	3.40(4)		
		O(1)... $\pi_c(22)$	3.30
N(1)... $\pi_c(21)$	3.10		
		O(1)...C(231)	3.505(8)
N(1)...C(241)	3.390(6)	O(1)...C(232)	3.657(8)
N(1)...C(242)	3.270(6)	O(1)...C(233)	3.775(8)
N(1)...C(243)	3.337(6)	O(1)...C(234)	3.746(8)
N(1)...C(244)	3.518(6)	O(1)...C(235)	3.598(8)
N(1)...C(245)	3.629(6)	O(1)...C(236)	3.474(8)
N(1)...C(246)	3.568(6)	Mean	3.63(12)
Mean	3.45(13)		
		O(1)... $\pi_c(23)$	3.35
N(1)... $\pi_c(24)$	3.16		

Table 54. Selected bond lengths (Å), contacts (Å) and angles (°) for [1-Ad]TBw (with e.s.d.'s in parentheses - continued).

O(2)...C(131)	3.467(7)	H(N21)...C(111)	2.69
O(2)...C(132)	3.590(7)	H(N21)...C(112)	2.57
O(2)...C(133)	3.651(7)	H(N21)...C(113)	2.49
O(2)...C(134)	3.590(7)	H(N21)...C(114)	2.53
O(2)...C(135)	3.467(7)	H(N21)...C(115)	3.65
O(2)...C(136)	3.403(7)	H(N21)...C(116)	2.73
Mean	3.53(9)	Mean	2.61(9)
O(2)... $\pi_c(13)$	3.24	H(N21)... $\pi_c(11)$	2.21
O(2)...C(141)	3.665(7)	H(N22)...C(121)	2.65
O(2)...C(142)	3.450(7)	H(N22)...C(122)	2.98
O(2)...C(143)	3.633(7)	H(N22)...C(123)	3.08
O(2)...C(144)	4.005(8)	H(N22)...C(124)	2.66
O(2)...C(145)	4.192(8)	H(N22)...C(125)	2.50
O(2)...C(146)	4.034(8)	H(N22)...C(126)	2.39
Mean	3.83(26)	Mean	2.74(25)
O(2)... $\pi_c(14)$	3.58	H(N22)... $\pi_c(12)$	2.38
H(N11)...C(211)	2.61	H(N23)...O(2)	1.83(1)
H(N11)...C(212)	2.65		
H(N11)...C(213)	2.58	H(O11)...C(221)	2.83
H(N11)...C(214)	2.48	H(O11)...C(222)	3.04
H(N11)...C(215)	2.45	H(O11)...C(223)	3.00
H(N11)...C(216)	2.51	H(O11)...C(224)	2.74
Mean	2.55(7)	H(O11)...C(225)	2.51
		H(O11)...C(226)	2.56
H(N11)... $\pi_c(21)$	2.13	Mean	2.78(20)
H(N12)...C(241)	2.64	H(O11)... $\pi_c(22)$	2.42
H(N12)...C(242)	2.62		
H(N12)...C(243)	2.60	H(O12)...C(231)	3.19
H(N12)...C(244)	2.60	H(O12)...C(232)	2.99
H(N12)...C(245)	2.61	H(O12)...C(233)	2.93
H(N12)...C(246)	2.64	H(O12)...C(234)	3.07
Mean	2.62(2)	H(O12)...C(235)	3.27
		H(O12)...C(236)	3.32
H(N12)... $\pi_c(24)$	2.22	Mean	3.13(14) _{fv}
H(N13)...O(1)	1.76	H(O12)... $\pi_c(23)$	2.80

Table 54. Selected bond lengths (Å), contacts (Å) and angles (°) for [1-Ad]TBw (with e.s.d.'s in parentheses - continued).

H(O21)...C(141)	2.97		
H(O21)...C(142)	2.97		
H(O21)...C(143)	3.11		
H(O21)...C(144)	3.25		
H(O21)...C(145)	3.25		
H(O21)...C(146)	3.12		
Mean	3.11(12)		
H(O21)... $\pi_c(14)$	2.78		
H(O22)...C(131)	2.47	N(2) - C(21) - C(22)	109.0(6)
H(O22)...C(132)	2.70	N(2) - C(21) - C(22')	108.7(6)
H(O22)...C(133)	2.99	N(2) - C(21) - C(22'')	107.9(6)
H(O22)...C(134)	3.07	Mean	108.5(5)
H(O22)...C(135)	2.87		
H(O22)...C(136)	2.56	C(111) - B(1) - C(121)	103.5(4)
Mean	2.78(2)	C(131) - B(1) - C(141)	104.5(4)
		Mean	103.8(5)
H(O22)... $\pi_c(13)$	2.41		
C(12) - C(11) - C(12')	111.7(7)	C(111) - B(1) - C(131)	112.1(4)
C(12) - C(11) - C(12'')	109.9(6)	C(111) - B(1) - C(141)	111.6(4)
C(12') - C(11) - C(12'')	110.0(6)	C(121) - B(1) - C(131)	112.4(4)
Mean	110.5(8)	C(121) - B(1) - C(141)	113.0(4)
		Mean	112.3(5)
C(22) - C(21) - C(22')	111.6(7)		
C(22) - C(21) - C(22'')	110.1(7)	C(211) - B(2) - C(241)	103.3(5)
C(22') - C(21) - C(22'')	109.5(7)	C(221) - B(2) - C(231)	104.3(5)
Mean	110.4(9)	Mean	104.0(5)
N(1) - C(11) - C(12)	107.4(6)	C(211) - B(2) - C(221)	112.0(5)
N(1) - C(11) - C(12')	110.3(6)	C(211) - B(2) - C(231)	112.4(5)
N(1) - C(11) - C(12'')	107.5(6)	C(221) - B(2) - C(241)	113.4(5)
Mean	108.4(13)	C(231) - B(2) - C(241)	111.7(5)
		Mean	112.4(6)

(1,3-Ad)2TB.MeCN, [C₁₀H₂₀N₂]2TB.MeCN

(1,3-Ad)2TB.MeCN is a solvated 1:2 compound. Reports of tetraphenylborate salts in the cation to anion ratio 1:2 are few. Apart from the complex salts [ML_n]2TB, there are only 5 structural reports of 1:2 TB salts^{163,171-174} in the literature, so far. It is not yet clear what sort of cation favours the formation of a 1:2 product. The size of the cation may be an important factor, however, there is no report of M(TB)₂ salts. The present investigation of organoammonium tetraphenylborates indicates that in addition to some common factors (ionization constant, number of proton acceptor sites, etc.) in the cation, the N...N separation, the conformation of the cation and the solvent, also play important roles in the formation of 1:2 TB compounds. Mixing of an aqueous solution of NaBPh₄, with a dilute acidic (HCl) solution of [H₂N-(CH₂)₂-NH₂] forms a 1:1 product, [H₃N-(CH₂)₂-NH₂]TB ($\psi = 0^\circ$). Similarly [H₂N-(CH₂)₃-NH₂] forms a 1:1 product with respect to TB ratio, [H₃N-(CH₂)₃-NH₃]TBCl ($\psi = 38.1^\circ$) while [H₂N-(CH₂)₄-NH₂] forms solvated 1:2, [H₃N-(CH₂)₄-NH₃]2TB.2MeCN ($\psi = 180^\circ$). Similar situations have also been found in other systems; under the preparative conditions described above, the free base 2,2'-bipyridyl gives a 1:1 product, whereas, the 2,2',2''-tripyridyl base gives a solvated 1:2 product.

The compound (1,3-Ad)2TB.MeCN again is a weak scatterer. The data ($I > 3.0\sigma$) to parameter ratio, after anisotropic refinement of all non-hydrogen atoms, is 3.26. On the other hand, when the eight phenyl rings are constrained to be perfect hexagons (i.e., C - C = 1.395 Å and C - C - C = 120°) the ratio increases to 3.87. Because of the minor improvement of the d/p ratio from the free to constrained refinement, it is sensible to present the results from the free refinement. The use of an arbitrary intensity cut-off value during refinement of a compound like (1,3-Ad)2TB.MeCN (nearly 600

parameters need to be refined) is also matter of concern. The number of reflections between 2σ and 3σ is only 44, so a very minor improvement of the d/p ratio can be expected. The use of 1.5σ intensity data improves the d/p ratio to about 4.13, however, the R factor also increases by about 3%.

The structure consists of the cation, two nonequivalent anions and a solvent MeCN molecule. The cations, the anions and the solvent molecules are arranged in layers in the b direction. Within a layer the anions forms columns generated by the n glide reflection. The phenyl rings are segregated in four layers parallel to (100) at $z = 0, 1/4, 1/2$ and $3/4$. The cations and the solvent molecules are dispersed between the anion columns in such a way that each cation and solvent molecule is surrounded by four anions. Of the four anions, three are close to the cation, two pair of phenyl rings from two anions and one phenyl ring from the third anion are involved in hydrogen bonding whereas the fourth anion is quite far from the cation. The coordinates of the nonhydrogen atoms are given in Table 55. Selected bond lengths and angles are given in Table 56. Two types of hydrogen bonding (E and F) are observed in this compound; two H(N)'s of one NH_3^+ are involved in normal hydrogen bonding to two phenyl groups of the same anion, while the third H(N) forms a hydrogen bond with the solvent molecule. All the hydrogen atoms of the other NH_3^+ are bonded to three phenyl rings, two from the same anion and the third from a neighbouring anion.

The cations fit poorly in the rigid body model, regardless of whether the nitrogen atom is excluded from or included in the TLS analysis (first number, N excluded; second number, N included): $R(U_{ij}) = 14.4\%, 13.9\%$; $R_w(U_{ij}) = 14.4\%, 14.9\%$; $\text{rms}(U_{ij}) = 0.0068, 0.0071$; mean librational amplitude about L_1 , $3.8^\circ, 2.7^\circ$; about L_2 , $5.9^\circ, 4.2^\circ$; about L_3 , $6.2^\circ, 6.0^\circ$.

Table 55. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for [1,3-Ad]2TB.MeCN (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	Ueq
B(1)	0.0192(10)	0.2418(5)	-0.0463(11)	0.0446
C(111)	0.1386(8)	0.2427(4)	-0.0417(10)	0.0381
C(112)	0.1747(9)	0.2655(4)	-0.1132(9)	0.0555
C(113)	0.2772(12)	0.2624(5)	-0.1107(11)	0.0695
C(114)	0.3504(10)	0.2367(6)	-0.0349(15)	0.0786
C(115)	0.3168(10)	0.2151(5)	0.0368(10)	0.0693
C(116)	0.2162(10)	0.2182(4)	0.0340(9)	0.0540
C(121)	-0.0452(9)	0.2905(4)	-0.0972(8)	0.0476
C(122)	0.0019(8)	0.3350(5)	-0.0921(9)	0.0573
C(123)	-0.0510(11)	0.3775(5)	-0.1333(11)	0.0780
C(124)	-0.1570(12)	0.3763(5)	-0.1854(10)	0.0779
C(125)	-0.2085(8)	0.3332(6)	-0.1908(9)	0.0629
C(126)	-0.1544(10)	0.2912(5)	-0.1510(9)	0.0551
C(131)	-0.0292(9)	0.1921(5)	-0.1112(11)	0.0541
C(132)	-0.0868(10)	0.1920(5)	-0.2148(12)	0.0705
C(133)	-0.1233(12)	0.1483(8)	-0.2682(13)	0.1049
C(134)	-0.1037(16)	0.1052(8)	-0.2187(19)	0.1078
C(135)	-0.0436(13)	0.1041(6)	-0.1177(18)	0.0939
C(136)	-0.0089(9)	0.1473(7)	-0.0664(10)	0.0664
C(141)	0.0093(9)	0.2400(4)	0.0654(8)	0.0434
C(142)	0.0784(8)	0.2653(5)	0.1462(11)	0.0561
C(143)	0.0713(10)	0.2670(5)	0.2456(10)	0.0690
C(144)	-0.0075(12)	0.2405(6)	0.2640(10)	0.0774
C(145)	-0.0764(11)	0.2141(5)	0.1856(13)	0.0665
C(146)	-0.0670(9)	0.2148(4)	0.0909(9)	0.0496
B(2)	0.2248(10)	-0.0450(5)	0.7957(12)	0.0607
C(211)	0.0976(9)	-0.0473(5)	0.7563(10)	0.0600
C(212)	0.0416(10)	-0.0169(4)	0.6784(10)	0.0652
C(213)	-0.0650(11)	-0.0111(5)	0.6468(10)	0.0705
C(214)	-0.1203(10)	-0.0366(6)	0.6947(12)	0.0836
C(215)	-0.0696(11)	-0.0682(5)	0.7711(12)	0.0881
C(216)	0.0385(11)	-0.0733(5)	0.8026(9)	0.0747
C(221)	0.2818(9)	-0.0909(5)	0.8700(10)	0.0499
C(222)	0.3460(10)	-0.1260(5)	0.8441(9)	0.0582
C(223)	0.3934(10)	-0.1632(5)	0.9096(12)	0.0731
C(224)	0.3776(11)	-0.1680(5)	1.0037(11)	0.0771
C(225)	0.3143(11)	-0.1360(6)	1.0300(10)	0.0738
C(226)	0.2681(9)	-0.0990(5)	0.9646(12)	0.0631
C(231)	0.2685(9)	0.0024(4)	0.8659(9)	0.0517
C(232)	0.3714(9)	0.0177(5)	0.8953(9)	0.0666

Table 55. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for [1,3-Ad]2TB.MeCN (with e.s.d.'s in parentheses - continued).

Atom	x/a	y/b	z/c	Ueq
C(233)	0.4107(10)	0.0564(5)	0.9628(11)	0.0820
C(234)	0.3476(13)	0.0798(5)	1.0068(11)	0.0860
C(235)	0.2463(11)	0.0651(5)	0.9827(10)	0.0711
C(236)	0.2064(9)	0.0274(4)	0.9118(10)	0.0579
C(241)	0.2562(9)	-0.0481(5)	0.6907(9)	0.0541
C(242)	0.2221(9)	-0.0876(5)	0.6245(11)	0.0712
C(243)	0.2462(11)	-0.0922(6)	0.5347(12)	0.0823
C(244)	0.3053(11)	-0.0570(7)	0.5079(12)	0.0843
C(245)	0.3387(11)	-0.0179(5)	0.5702(13)	0.0771
C(246)	0.3143(10)	-0.0140(5)	0.6598(10)	0.0619
N(1)	0.3786(6)	0.1626(3)	0.5855(6)	0.0642
N(2)	0.1745(6)	0.1510(3)	0.8166(7)	0.0489
C(11)	0.2715(8)	0.1564(4)	0.5925(9)	0.0498
C(21)	0.2804(8)	0.1562(4)	0.7042(8)	0.0562
C(31)	0.1707(9)	0.1502(5)	0.7064(8)	0.0437
C(41)	0.1009(8)	0.1914(4)	0.6503(9)	0.0680
C(22)	0.2045(9)	0.1974(4)	0.5324(8)	0.0679
C(32)	0.0973(9)	0.1913(5)	0.5395(10)	0.0482
C(42)	0.0508(9)	0.1433(6)	0.4912(10)	0.0839
C(23)	0.2305(9)	0.1074(4)	0.5448(8)	0.0607
C(33)	0.1210(11)	0.1017(5)	0.5495(11)	0.0579
C(43)	0.1268(8)	0.1013(5)	0.6624(10)	0.0613
N(3)	0.0179(9)	0.4126(5)	0.2023(10)	0.1056
C(1)	0.0658(11)	0.4415(6)	0.2470(13)	0.0858
C(2)	0.1274(12)	0.4822(5)	0.3068(12)	0.1285

Table 56. Selected bond lengths (Å), contacts (Å) and angles (°) for [1,3-Ad]2TB.MeCN (with e.s.d.'s in parentheses).

N(1) - C(11)	1.52(1)	N(1)...C(141)	3.31(1)
N(2) - C(31)	1.52(1)	N(1)...C(142)	3.27(1)
		N(1)...C(143)	3.43(2)
C(11) - C(21)	1.52(1)	N(1)...C(144)	3.64(2)
C(11) - C(22)	1.52(1)	N(1)...C(145)	3.67(2)
C(11) - C(23)	1.53(1)	N(1)...C(146)	3.48(1)
Mean	1.52(1)	Mean	3.47(15)
C(31) - C(41)	1.53(1)	N(1)... $\pi_c(14)$	3.17
C(31) - C(43)	1.53(1)		
C(31) - C(21)	1.53(1)	N(2)...C(111)	3.36(1)
Mean	1.53(0)	N(2)...C(112)	3.32(1)
		N(2)...C(113)	3.41(2)
B(1) - C(111)	1.62(1)	N(2)...C(114)	3.52(2)
B(1) - C(121)	1.64(2)	N(2)...C(115)	3.51(1)
B(1) - C(131)	1.66(2)	N(2)...C(116)	3.44(1)
B(1) - C(141)	1.61(2)	Mean	3.43(7)
Mean	1.63(2)		
		N(2)... $\pi_c(11)$	3.13
B(2) - C(211)	1.65(2)		
B(2) - C(221)	1.66(2)	N(2)...C(131)	3.47(1)
B(2) - C(231)	1.63(2)	N(2)...C(132)	3.65(1)
B(2) - C(241)	1.66(2)	N(2)...C(133)	3.85(2)
Mean	1.65(1)	N(2)...C(134)	3.89(2)
		N(2)...C(135)	3.65(2)
N(1)...N(3)	2.92(1)	N(2)...C(136)	3.43(1)
		Mean	3.66(17)
N(1)...C(121)	3.33(1)		
N(1)...C(122)	3.44(1)	N(2)... $\pi_c(13)$	3.39
N(1)...C(123)	3.67(2)		
N(1)...C(124)	3.80(2)	N(2)...C(231)	4.30(2)
N(1)...C(125)	3.63(1)	N(2)...C(232)	4.49(2)
N(1)...C(126)	3.42(1)	N(2)...C(233)	4.13(2)
Mean	3.55(16)	N(2)...C(234)	3.51(2)
		N(2)...C(235)	3.23(2)
N(1)... $\pi_c(12)$	3.27	N(2)...C(236)	3.65(2)
		Mean	3.89(45)
		N(2)... $\pi_c(23)$	3.65

Table 56. Selected bond lengths (Å), contacts (Å) and angles (°) for [1,3-Ad]2TB.MeCN (with e.s.d.'s in parentheses - continued).

H(N11)...C(121)	2.48	H(N22)...C(131)	2.70
H(N11)...C(122)	2.61	H(N22)...C(132)	2.83
H(N11)...C(123)	2.81	H(N22)...C(133)	2.93
H(N11)...C(124)	2.87	H(N22)...C(134)	2.90
H(N11)...C(125)	2.66	H(N22)...C(135)	2.68
H(N11)...C(126)	2.48	H(N22)...C(136)	2.56
Mean	2.65(16)	Mean	2.77(14)
H(N11)... $\pi_c(12)$	2.26	H(N22)... $\pi_c(13)$	2.40
H(N12)...C(141)	2.58	H(N23)...C(231)	3.47
H(N12)...C(142)	2.48	H(N23)...C(232)	3.54
H(N12)...C(143)	2.52	H(N23)...C(233)	3.12
H(N12)...C(144)	2.64	H(N23)...C(234)	2.53
H(N12)...C(145)	2.71	H(N23)...C(235)	2.37
H(N12)...C(146)	2.64	H(N23)...C(236)	2.87
Mean	2.60(8)	Mean	2.98(48)
H(N12)... $\pi_c(14)$	2.19	H(N23)... $\pi_c(23)$	2.67
H(N13)...N(3)	1.91		
H(N21)...C(111)	2.55		
H(N21)...C(112)	2.36		
H(N21)...C(113)	2.42		
H(N21)...C(114)	2.64		
H(N21)...C(115)	2.74		
H(N21)...C(116)	2.70		
Mean	2.57(15)		
H(N21)... $\pi_c(11)$	2.16		
C(22) - C(11) - C(23)	111.1(9)	N(1) - C(11) - C(22)	107.3(9)
C(22) - C(11) - C(21)	112.9(9)	N(1) - C(11) - C(23)	107.2(9)
C(23) - C(11) - C(21)	109.4(9)	N(1) - C(11) - C(21)	108.8(9)
Mean	111.1(14)	Mean	107.8(7)
C(41) - C(31) - C(43)	111.0(10)	N(2) - C(31) - C(41)	108.0(9)
C(41) - C(31) - C(21)	111.2(9)	N(2) - C(31) - C(43)	107.0(10)
C(43) - C(31) - C(21)	110.3(9)	N(2) - C(31) - C(21)	109.0(10)
Mean	110.8(4)	Mean	108.0(8)

Table 56. Selected bond lengths (Å), contacts (Å) and angles (°) for [1,3-Ad]2TB.MeCN (with e.s.d.'s in parentheses - continued).

C(111) - B(1) - C(131)	104.3(9)	C(211) - B(2) - C(241)	105.0(10)
C(121) - B(1) - C(141)	103.5(9)	C(221) - B(2) - C(231)	104.0(10)
Mean	103.9(4)	Mean	104.5(5)
C(111) - B(1) - C(121)	113.0(10)	C(211) - B(2) - C(221)	114.0(10)
C(111) - B(1) - C(141)	112.0(10)	C(211) - B(2) - C(231)	111.0(10)
C(121) - B(1) - C(131)	113.0(10)	C(221) - B(2) - C(241)	108.0(10)
C(131) - B(1) - C(141)	111.0(10)	C(231) - B(2) - C(241)	115.0(10)
Mean	112.3(8)	Mean	112.0(27)

LiTBw, [Li(H₂O)₄]TB

Other alkali metal tetraphenylborates^{123,178,179} (Na, K, Rb and Cs) are unsolvated and crystallize in the tetragonal system with space group $I4_2m$ ($Z = 2$). Lithium tetraphenylborate is solvated and crystallizes in the same crystal system but with a different space group, $I4_1/a$ ($Z = 16$). Each Li⁺ ion is coordinated to four water molecules which in turn are bonded to phenyl groups of the anions through O - H... π hydrogen bonds. This compound appears to be the first example of such an exhaustive O - H... π bonding network and can be described as a three dimensional H-bonded polymer. The crystal data of LiTBw are given in Table 57 and the atomic positions, the interatomic distances and bond lengths are given in Table 58.

Each crystal consists of [Li(H₂O)₄]⁺ and TB⁻ ions. The [Li(H₂O)₄]⁺ cation geometry is approximately D_{2d}. The quasi-S₄ axis bisects the O - Li - O angles resulting into $\alpha_1 = 120.4(21)^\circ$ and $\alpha_2 = 104.3(10)^\circ$. The mean Li - O distance, 1.933(7) Å, is comparable to the corresponding distance in the LiO₄ unit of [Li(H₂O)₄](UO₂)(AsO₄)¹⁷⁵.

The [Li(H₂O)₄]⁺ cation is surrounded by four pairs of phenyl groups, each pair from

a different anion. Since the structure was obtained from an x-diffraction study, the problem was accurate location of the hydrogen atoms. Evidence of at least six strong peaks between the oxygens and the nearest phenyl ring atoms has been found in the Fourier difference map. Those positions could be assigned to the positions of H₂O hydrogens but in the presence of the high U_{11} values for the O atoms, this assignment might not necessarily be correct.

On the other hand, as in the case of N - H... π bonds in TB salts of secondary or tertiary organoammonium cation, the hydrogen atom(s) or the water molecule cannot be placed geometrically. Under these circumstances, evidence of the presence of O - H... π bonding in LiTBw is circumstantial though still compelling. The O... π_c distances and the π_c ...O... π_c angles range from 3.27 to 4.13 Å and 86 to 125°, respectively. With the exception of the two longest distances, 4.03 and 4.13 Å, this range coincides with the value observed for O - H... π in other TB compounds. The two exceptions involve the oxygen atoms O(3) and O(4), the U_{11} values of which are very large. It is noticeable that the pair of phenyl rings nearest O(1) belongs to one anion, and as do the rings closest to O(2). The two rings nearest O(3) and O(4) each belong to a different anion. Further, the corresponding π_c ...O... π_c angles at O(1) and O(2) are 86° and 90°, respectively, but those at O(3) and O(4) are 123° and 125° indicating the existence of strongly bent or bifurcated O - H... π bonds.

The involvement of the phenyl groups in the hydrogen bonding is not uniform. Rings 1 and 4 are each bonded from both sides, while rings 2 and 3 are bonded from one side only. Also, the O... π_c distances are remarkably varied. The shortest distance O... π_c (2) = 3.27 Å whereas the longest O... π_c (1) = 4.13 Å, an indication of the unbalanced H...phenyl interaction. The anisotropic thermal parameters, particularly

$U_{22}[\text{O}(3)]$ and $U_{11}[\text{O}(4)]$, are noticeably large. A TLS analysis indicates that the motion of the LiO_4 tetrahedron is consistent with a rigid body model ($R(U_{ij}) = 6.2\%$, $R_w(U_{ij}) = 6.3\%$ and $\text{rms}(U_{ij}) = 0.0048$), and the large U_{ii} values of O are satisfactorily explained in terms of large-amplitude libration about the principle libration axis L_3 which is practically $\parallel c$ (Fig. 65). The mean amplitudes about the three principal axes of libration are L_1 , 2.2° , L_2 , 6.0° , and L_3 , 9.1° .

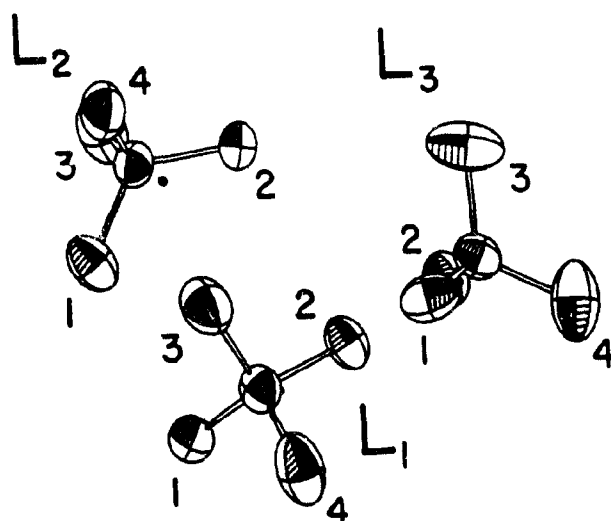


Fig. 65. Projections of the LiO_4 tetrahedron down its principal axes of libration $L_1 - L_3$.

Table 57. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for LiTBw (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	Ueq
B	0.6140(3)	0.4000(3)	0.1284(9)	0.0364
C(11)	0.6178(3)	0.3524(3)	0.0474(5)	0.0400
C(12)	0.6603(3)	0.3440(3)	-0.0127(6)	0.0519
C(13)	0.6653(3)	0.3058(3)	-0.0870(7)	0.0632
C(14)	0.6261(4)	0.2748(3)	-0.1060(7)	0.0671
C(15)	0.5831(3)	0.2829(3)	-0.0512(7)	0.0628
C(16)	0.5791(3)	0.3214(3)	0.0226(6)	0.0478
C(r1)	0.6085(3)	0.4461(3)	0.0438(5)	0.0361
C(22)	0.6482(3)	0.4721(3)	0.0060(7)	0.0523
C(23)	0.6446(3)	0.5078(3)	-0.0751(7)	0.0639
C(24)	0.6001(3)	0.5186(3)	-0.1209(7)	0.0572
C(25)	0.5599(3)	0.4935(3)	-0.0856(6)	0.0471
C(26)	0.5644(2)	0.4584(3)	-0.0056(6)	0.0395
C(31)	0.6608(3)	0.4064(3)	0.2098(5)	0.0389
C(32)	0.6929(3)	0.3680(3)	0.2355(7)	0.0470
C(33)	0.7294(3)	0.3737(3)	0.3137(7)	0.0562
C(34)	0.7354(3)	0.4172(3)	0.3680(7)	0.0600
C(35)	0.7052(3)	0.4555(3)	0.3442(6)	0.0547
C(36)	0.6683(3)	0.4497(3)	0.2662(6)	0.0463
C(41)	0.5667(2)	0.3969(3)	0.2123(5)	0.0345
C(42)	0.5411(3)	0.4388(3)	0.2460(6)	0.0467
C(43)	0.5021(3)	0.4363(3)	0.3183(7)	0.0569
C(44)	0.4873(3)	0.3927(4)	0.3621(7)	0.0624
C(45)	0.5130(3)	0.3513(3)	0.3362(7)	0.0599
C(46)	0.5521(3)	0.3536(3)	0.2631(6)	0.0464
Li	0.1311(5)	0.1598(5)	0.375(1)	0.0688
O(1)	0.1546(2)	0.1328(2)	0.5119(5)	0.0886
O(2)	0.1475(2)	0.1324(2)	0.2355(5)	0.0785
O(3)	0.0616(2)	0.1546(3)	0.3865(5)	0.1290
O(4)	0.1595(3)	0.2242(2)	0.3677(5)	0.1241

Table 58. Selected bond lengths (Å), contacts (Å) and angles (°) for LiTBw (with e.s.d.'s in parentheses).

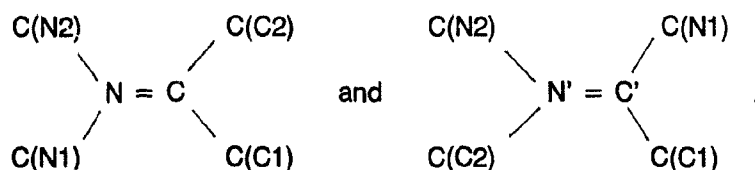
Li - O(1)	1.938(15)	O(1)...O(3)	3.047(9)
Li - O(2)	1.924(15)	O(1)...O(4)	3.078(9)
Li - O(3)	1.928(16)	O(2)...O(3)	3.064(9)
Li - O(4)	1.941(16)	O(2)...O(4)	3.020(9)
Mean	1.933(7)	Mean	3.052(22)
B - C(11)	1.647(11)	O(1)... $\pi_c(2b)$	3.27
B - C(21)	1.647(11)	O(1)... $\pi_c(1b)$	3.57
B - C(31)	1.640(11)	O(2)... $\pi_c(3a)$	3.30
B - C(41)	1.661(11)	O(2)... $\pi_c(4a)$	3.46
Mean	1.649(8)	O(3)... $\pi_c(4c)$	3.53
		O(3)... $\pi_c(1b)$	4.13
O(1)...O(2)	3.386(8)	O(4)... $\pi_c(1d)$	3.34
O(3)...O(4)	3.321(10)	O(4)... $\pi_c(4a)$	4.03
Mean	3.354(33)		
C(11) - B - C(21)	104.1(7)	O(1) - Li - O(2)	122.5(7)
C(31) - B - C(41)	104.4(7)	O(3) - Li - O(4)	118.3(8)
Mean	104.3(2)	Mean	120.4(21)
C(11) - B - C(31)	113.6(6)	O(1) - Li - O(3)	104.0(7)
C(11) - B - C(41)	112.4(6)	O(1) - Li - O(4)	105.0(7)
C(21) - B - C(31)	111.7(6)	O(2) - Li - O(3)	105.4(7)
C(21) - B - C(41)	110.9(6)	O(2) - Li - O(4)	102.8(7)
Mean	112.2(10)	Mean	104.3(10)
C(12) - C(11) - C(16)	115.0(7)	$\pi_c(1b)$ - O(1) - $\pi_c(2b)$	86
C(22) - C(21) - C(26)	114.6(7)	$\pi_c(3a)$ - O(2) - $\pi_c(4a)$	90
C(32) - C(31) - C(36)	116.0(7)	$\pi_c(1b)$ - O(3) - $\pi_c(4c)$	123
C(42) - C(41) - C(46)	115.1(7)	$\pi_c(1c)$ - O(3) - $\pi_c(4c)$	67
Mean	115.2(5)	$\pi_c(1d)$ - O(4) - $\pi_c(4a)$	56
		$\pi_c(1d)$ - O(4) - $\pi_c(4d)$	125

Symmetry code: a $-\frac{1}{4} + y, \frac{3}{4} - x, -\frac{1}{4} + z$
b $-\frac{1}{4} + y, \frac{3}{4} - x, \frac{3}{4} + z$
c $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$
d $-\frac{1}{2} + x, y, \frac{1}{2} - z$

ImBTB, [Me₂C=NMe₂]TB

The structure of ImBTB consists of a discrete iminium cation and a tetraphenylborate anion. The atomic positions are listed in Table 59. Selected bond lengths and angles are given in Table 60.

The iminium cation is planar, with nearly D_{2h} symmetry. In this compound, the cation is perpendicular to the plane (100) and is disordered across a mirror plane parallel to (100). The cation, therefore, appears as a combination of two crystallographically equivalent units:



Attempts were made to resolve the disorder by examining the electron density map of the cation (Fig. 66), but without success. Free refinement of all the non-hydrogen atoms gave some unusual bond distances; N - C(N1) = 1.514(9) Å, N - C(N2) = 1.56(1) Å and C - C(C1) = 1.46(1) Å. Efforts were therefore made to refine the structure by interchanging the positions of N and C but an unreasonable temperature factor for N resulted. This confirmed the validity of the present assignment. The structure was subsequently refined by constraining the N - C and C - C bond lengths to 1.49(2) and 1.52(2) Å, respectively. The distances found between the disordered nitrogens and carbons are 0.883(8) and 0.919(9) Å, respectively. The C = N⁺ bond length is 1.291(8) Å.

An even greater orientational disorder of the cation, [Me₂C = NMe₂], is found in the ClO₄⁻ analogue¹⁷⁶ of ImBTB. This compound crystallizes in the tetragonal crystal system in the space group I4/mmm (Z = 2). In the less constraining environment of nearest

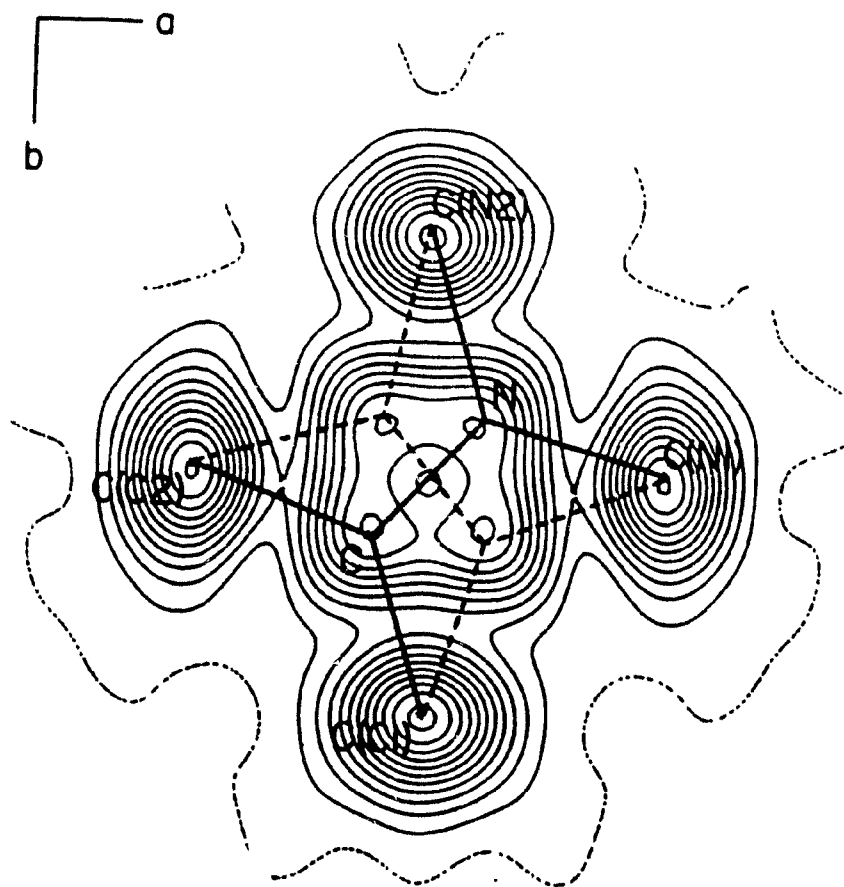


Fig. 66. Electron density map in the plane of the cation, $[\text{Me}_2\text{C}=\text{NMe}_2]^+$. The disorder is across the vertical $m \parallel (100)$.

ClO_4^- neighbours, the cations are situated on mirror planes parallel to (001) and their orientations are distributed over four symmetry equivalent $\text{C}=\text{N}^+$ bond directions (Fig. 67).

The cation does not contain any active hydrogen for hydrogen bonding. The shortest nonbonded contact distance is $3.37(1) \text{ \AA}$.

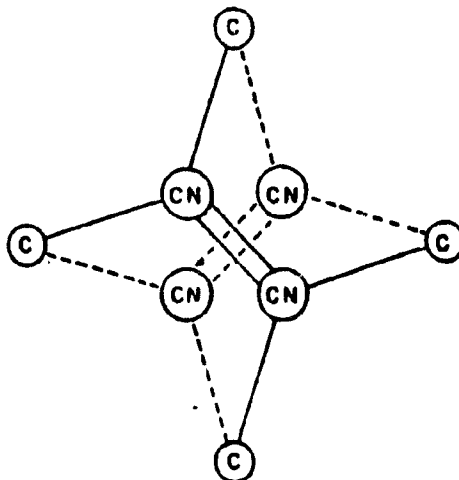


Fig. 67. Disordered $[\text{Me}_2\text{C} = \text{NMe}_2]$ cation: solid line, one bonding arrangement; broken line, the other bonding arrangement.

Table 59. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for ImBTB (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	U _{eq}
B	1/2	0.1647(3)	0.3788(2)	0.0447
C(11)	0.4009(2)	0.0962(1)	0.3777(1)	0.0457
C(12)	0.3557(3)	0.0635(2)	0.3309(1)	0.0590
C(13)	0.2733(3)	0.0031(2)	0.3305(1)	0.0685
C(14)	0.2333(3)	-0.0290(2)	0.3773(1)	0.0665
C(15)	0.2771(3)	-0.0013(2)	0.4243(1)	0.0759
C(16)	0.3595(3)	0.0595(2)	0.4242(1)	0.0652
C(21)	1/2	0.2344(3)	0.4292(2)	0.0532
C(22)	0.4110(3)	0.2713(2)	0.4510(1)	0.0773
C(23)	0.4106(4)	0.3386(2)	0.4909(1)	0.1059
C(24)	1/2	0.3711(4)	0.5110(3)	0.1004
C(31)	1/2	0.2362(3)	0.3264(2)	0.0435
C(32)	0.4110(3)	0.2721(2)	0.3048(1)	0.0630
C(33)	0.4107(3)	0.3376(2)	0.2642(1)	0.0729
C(34)	1/2	0.3708(3)	0.2435(2)	0.0650
N	0.5335(4)	0.2066(4)	0.1417(2)	0.0774
C(N1) = C(C2')	0.6430(2)	0.2307(3)	0.1325(1)	0.1001
C(N2) = C(N2')	1/2	0.1255(4)	0.1752(2)	0.0882
C	0.4652(4)	0.2591(3)	0.1207(2)	0.0498
C(C1) = C(C1')	1/2	0.3410(3)	0.0881(2)	0.0872
C(C2) = C(N1')	0.3570(2)	0.2307(3)	0.1325(1)	0.1001

Table 60. Selected bond lengths (Å) and angles (°) for ImBTB (with e.s.d.'s in parentheses).

C - N	1.291(8)	B - C(11)	1.641(5)
C - C(C1)	1.513(7)	B - C(11)	1.641(5)
C - C(C2)	1.515(7)	B - C(21)	1.620(5)
N - C(N1)	1.505(7)	B - C(31)	1.675(5)
N - C(N2)	1.509(7)	Mean	1.644(20)
C(C1) - C - N	118.0(5)	C(11) - B - C(21)	112.9(3)
C(C2) - C - N	114.7(5)	C(11) - B - C(21)	112.9(3)
C(C1) - C - C(C2)	127.2(5)	C(11) - B - C(31)	111.1(2)
C - N - C(N1)	118.2(5)	C(11) - B - C(31)	111.1(2)
C - N - C(N2)	118.7(5)	Mean	112.0(9)
C(N1) - N - C(N2)	123.1(4)		
		C(12) - C(11) - C(16)	114.0(3)
C(11) - B - C(11)	105.7(2)	C(12) - C(11) - C(16)	114.0(3)
C(21) - B - C(31)	103.3(2)	C(22) - C(21) - C(22)	113.9(3)
Mean	104.5(12)	C(32) - C(31) - C(32)	114.8(3)
		Mean	114.2(4)
B - C(11) - C(12)	123.9(3)		
B - C(11) - C(12)	123.9(3)		
B - C(11) - C(16)	121.9(3)		
B - C(11) - C(16)	121.9(3)		
B - C(21) - C(22)	122.8(3)		
B - C(21) - C(22)	122.8(3)		
B - C(31) - C(32)	122.4(3)		
B - C(31) - C(32)	122.4(3)		
Mean	122.8(7)		

AzPpTB, [C₁₀H₁₉N]TB

To our knowledge, this is the first structural report of a compound containing the 1-azoniapropellane cation. The cation symmetry is very close to C_{3v}, with the unique N - C axis perpendicular to the crystallographic (100) plane. The unique N - C bond length is 1.576(4) Å, longer than the other N - C(n,1) distances (mean 1.515(10) Å). The atomic positions are listed in Table 61 and selected bond lengths and angles are given in Table 62.

The thermal motion of the cation conforms poorly to the rigid body model with $R(U_{1j}) = 12.5\%$, $R_w(U_{1j}) = 11.7\%$, $\text{rms}(U_{1j}) = 0.0059$, $\text{rms}[\text{esd}(U_{1j})] = 0.0028 \text{ Å}^2$. Corrections to the bond lengths, calculated with this model, amount to -0.02 Å; those to the bond angles are within 0.15°. The mean librational amplitudes about the principal axes of libration are 4.6°, 5.7° and 6.6°.

Table 61. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for AzPpTB (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	Ueq
B	0.2165(4)	1.1066(2)	0.7601(3)	0.0360
C(11)	0.1496(3)	1.1564(2)	0.6756(2)	0.0373
C(12)	0.0128(4)	1.1478(2)	0.6447(3)	0.0427
C(13)	-0.0522(4)	1.1891(2)	0.5748(3)	0.0494
C(14)	0.0177(4)	1.2411(2)	0.5329(3)	0.0541
C(15)	0.1513(4)	1.2526(2)	0.5627(3)	0.0497
C(16)	0.2138(4)	1.2115(2)	0.6336(3)	0.0444
C(21)	0.1419(3)	1.1275(2)	0.8613(2)	0.0361
C(22)	0.0421(4)	1.0902(2)	0.9047(3)	0.0447
C(23)	-0.0250(4)	1.1126(2)	0.9871(3)	0.0553
C(24)	0.0067(4)	1.1744(2)	1.0276(3)	0.0577
C(25)	0.1052(4)	1.2132(2)	0.9868(3)	0.0560
C(26)	0.1710(4)	1.1903(2)	0.9049(3)	0.0462
C(31)	0.1933(3)	1.0266(2)	0.7316(2)	0.0352
C(32)	0.2231(4)	0.9753(2)	0.7993(3)	0.0453
C(33)	0.2132(4)	0.9075(2)	0.7760(3)	0.0555
C(34)	0.1719(4)	0.8876(2)	0.6817(4)	0.0623
C(35)	0.1429(4)	0.9364(2)	0.6132(3)	0.0593
C(36)	0.1526(4)	1.0039(2)	0.6372(3)	0.0444
C(41)	0.3820(3)	1.1136(2)	0.7744(3)	0.0398
C(42)	0.4484(4)	1.1077(2)	0.8664(3)	0.0517
C(43)	0.5897(5)	1.1085(2)	0.8791(4)	0.0688
C(44)	0.6688(4)	1.1159(2)	0.8008(5)	0.0768
C(45)	0.6076(5)	1.1222(2)	0.7077(4)	0.0712
C(46)	0.4666(4)	1.1197(2)	0.6957(3)	0.0530
N	0.5981(3)	0.8901(2)	0.7172(2)	0.0522
C(1,1)	0.5319(4)	0.9203(3)	0.6240(3)	0.0722
C(1,2)	0.6431(5)	0.9589(2)	0.5789(3)	0.0678
C(1,3)	0.7671(4)	0.9150(2)	0.5961(3)	0.0671
C(2,1)	0.5841(4)	0.9340(2)	0.8069(3)	0.0679
C(2,2)	0.7202(5)	0.9302(2)	0.8601(3)	0.0687
C(2,3)	0.8177(4)	0.9320(3)	0.7775(3)	0.0709
C(3,1)	0.5537(5)	0.8186(2)	0.7314(4)	0.0774
C(3,2)	0.6604(6)	0.7770(2)	0.6834(4)	0.0843
C(3,3)	0.7902(5)	0.8137(3)	0.7076(4)	0.0779
C	0.7539(3)	0.8879(2)	0.6981(2)	0.0374

Table 62. Selected bond lengths (Å) and angles (°) for AzPpTB (with e.s.d.'s in parentheses).

N - C	1.576(4)	C(1,3) - C	1.502(5)
		C(2,3) - C	1.512(5)
N - C(1,1)	1.528(5)	C(3,3) - C	1.524(6)
N - C(2,1)	1.513(5)	Mean	1.513(9)
N - C(3,1)	1.504(5)		
Mean	1.515(10)	B - C(11)	1.640(5)
		B - C(21)	1.645(5)
C(1,1) - C(1,2)	1.496(6)	B - C(31)	1.651(5)
C(2,1) - C(2,2)	1.506(6)	B - C(41)	1.648(5)
C(3,1) - C(3,2)	1.513(7)	Mean	1.646(4)
Mean	1.505(7)		
C(1,2) - C(1,3)	1.517(6)	C(1,3) - C - N	105.4(3)
C(2,2) - C(2,3)	1.512(6)	C(2,3) - C - N	104.4(3)
C(3,2) - C(3,3)	1.504(7)	C(3,3) - C - N	104.0(3)
Mean	1.511(5)	Mean	104.6(6)
C - N - C(1,1)	105.3(3)	C(1,3) - C - C(2,3)	113.9(4)
C - N - C(2,1)	105.7(3)	C(1,3) - C - C(3,3)	113.5(3)
C - N - C(3,1)	106.8(3)	C(2,3) - C - C(3,3)	114.3(3)
Mean	105.9(6)	Mean	113.9(3)
C(1,1) - N - C(2,1)	113.2(3)	C(11) - B - C(21)	104.6(3)
C(1,1) - N - C(3,1)	111.2(4)	C(31) - B - C(41)	103.8(3)
C(2,1) - N - C(3,1)	113.9(3)	Mean	104.2(4)
Mean	112.8(11)		
N - C(1,1) - C(1,2)	104.2(3)	C(11) - B - C(31)	111.7(3)
N - C(2,1) - C(2,2)	104.5(3)	C(11) - B - C(41)	113.7(3)
N - C(3,1) - C(3,2)	104.4(4)	C(21) - B - C(31)	112.3(3)
Mean	104.4(1)	C(21) - B - C(41)	111.0(3)
		Mean	112.2(10)
C(1,1) - C(1,2) - C(1,3)	104.2(4)	C(12) - C(11) - C(16)	114.8(3)
C(2,1) - C(2,2) - C(2,3)	103.1(3)	C(22) - C(21) - C(26)	115.6(3)
C(3,1) - C(3,2) - C(3,3)	104.2(4)	C(32) - C(31) - C(36)	114.4(3)
Mean	103.8(5)	C(42) - C(41) - C(46)	115.0(3)
		Mean	115.0(4)
C(1,2) - C(1,3) - C	104.5(3)		
C(2,2) - C(2,3) - C	105.0(4)		
C(3,2) - C(3,3) - C	104.8(4)		
Mean	104.8(2)		

2PhITB, [Ph₂I]TB

Each crystal consists of Ph₂I⁺ cations and TB⁻ anions; both the cations and the anions are arranged in layers parallel to the (100) plane. Each layer contains alternating cations and anions. The cation is of C_s symmetry and the angle between the best planes through the ring skeletons is 100.4°. The phenyl rings are planar (the mean deviation from planarity is 0.023 Å) and the iodine atom is 0.113 Å out of the ring planes. The cation geometry is comparable with the reported Ph₂I⁺ cations in diphenyliodonium nitrate¹⁷⁷. The mean I - C distance is 2.069(11) Å in Ph₂ITB and 2.114(8) Å in Ph₂INO₃. The C - I - C angle is 95.1(4)° in Ph₂ITB and 92.0(4)° in Ph₂INO₃. The positions of non-hydrogen atoms are listed in Table 63 and the selected bond lengths and angles are given in Table 64.

The tetraphenylborate anions in all the compounds described above are ordered irrespective of their crystal system, space group and the nature of the cations. However, an exceptional disorder problem has been found in the anion of the compound 2PhITB. The free refinement of 2PhITB was characterized by large temperature factors for the phenyl carbon atoms of both the cation and the anion. A reasonable explanation for this kind of disorder was found when the structural arrangement of the cations and anions was carefully examined.

Ring 3 of the TB anion is perpendicular to a mirror parallel to (010) plane and almost parallel to (001). The cation phenyl rings nearest to ring 3 are 1' and 1'' and the C and H atoms closest to ring 3 are C(4)' and H(4)' of ring 1' (Fig. 68). In fact, the distance H(32)...H(4') is 1.76 Å, the shortest static H(anion)...H(cation) distance in the structure, well below the van der Waals contact of 2.4 Å. All the other distances between the phenyl hydrogens are longer than 2.3 Å. This unusually short

H(anion)...H(cation) distance appears to be the direct cause of the large U_{33} values on C(32) and C(33). To minimize the repulsion between H(32) and H(4') (and between the symmetry-related counterparts of these hydrogens), ring 3 undergoes a large librational motion about its C(31) - C(34) axis, which is approximately parallel to *a*. The directions of the principal libration axes (L_n) and the relative magnitudes of the mean librational amplitudes obtained from a TLS analysis of the thermal parameters of the ring 3 carbon atoms are consistent with the above explanation of the large U_{33} values: $L_1 \parallel c$, $\sim 1^\circ$; $L_2 \parallel b$, $\sim 3^\circ$; $L_3 \parallel a$, $\sim 22^\circ$ (Fig. 68). However, the motion of the ring 3 is not too well accounted for by a rigid body model (the B atom was included during the TLS calculation): $R(U_{ij}) = 13.4\%$, $R_w(U_{ij}) = 9.5\%$, $\text{rms}(U_{ij}) = 0.0087$, $\text{rms}[\text{esd}(U_{ij})] = 0.0036 \text{ \AA}^2$.

Several attempts have been made to model the separate pivoting motions of the different rings. The best attempt to resolve the disorder was made by splitting the C(32) and C(33) positions of ring 3 of the TB anion and all six cation carbons of the cation. This significantly lowered the U_{ii} values of those atoms (Table 65). However, the U_{ii} values of both cationic and anionic carbon atoms remain high which indicates that the complexity of the dynamic disorder in this crystal resists a simple treatment.

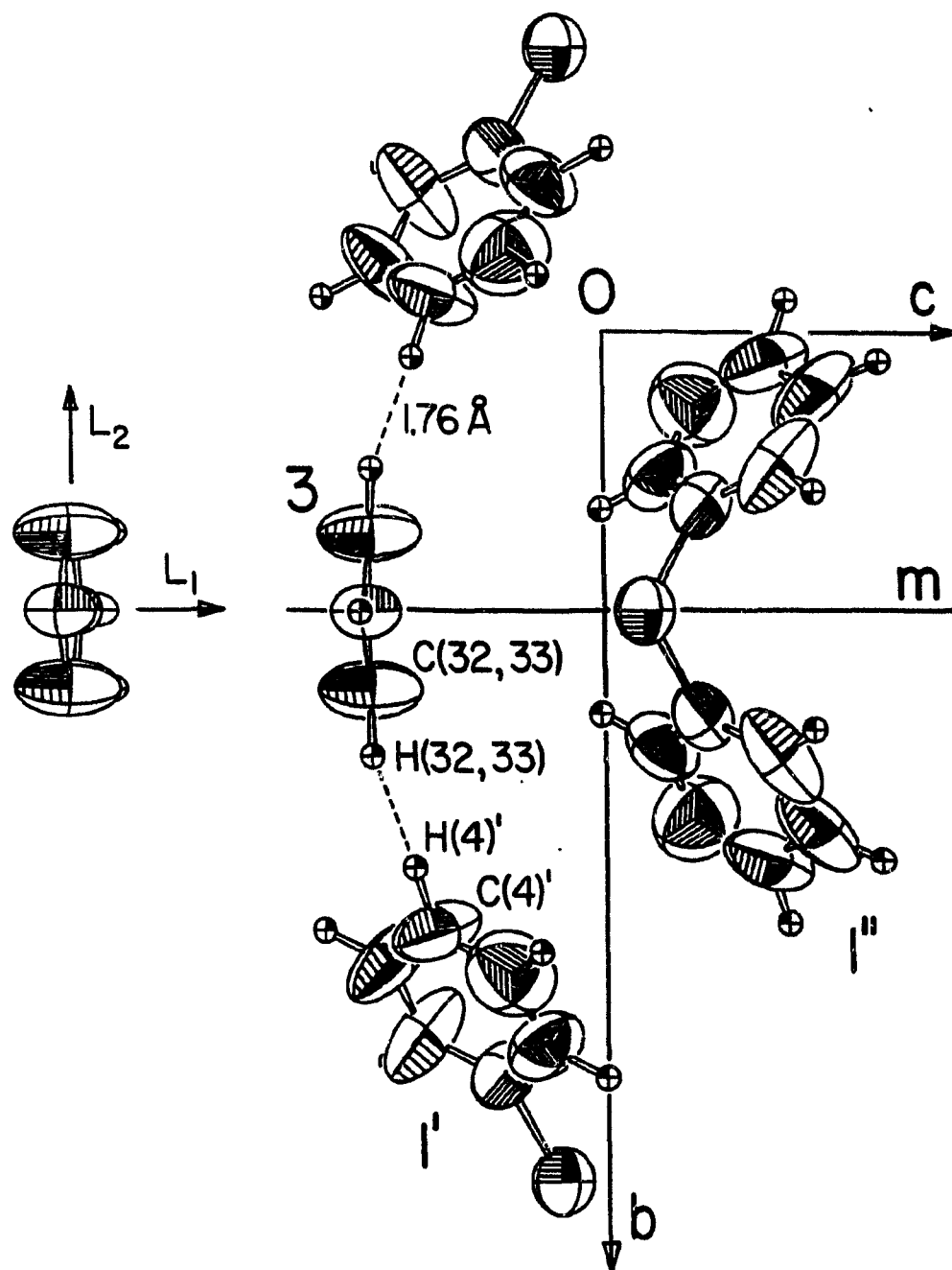


Fig. 68. Thermal motion in 2PhITB (projection on (100); 50% probability ellipsoids). The H(cation)...H(anion) distance of 1.76 Å is between H(32) and H(4'). Inset(left): projection of ring 3 down its principal libration axis L_3 , as obtained from a TLS analysis.

Table 63. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for 2PhITB (free refinement) (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	Ueq
B	0.3738(8)	1/4	0.6686(14)	0.0432
C(11)	0.3364(4)	0.1708(4)	0.5913(7)	0.0445
C(12)	0.3647(5)	0.1421(5)	0.4696(8)	0.0621
C(13)	0.3321(6)	0.0772(5)	0.3997(9)	0.0764
C(14)	0.2672(5)	0.0408(6)	0.4475(10)	0.0759
C(15)	0.2364(5)	0.0675(5)	0.5667(10)	0.0728
C(16)	0.2714(4)	0.1316(5)	0.6340(9)	0.0581
C(21)	0.3572(7)	1/4	0.8287(11)	0.0469
C(22)	0.3507(6)	0.1787(5)	0.9047(8)	0.0757
C(23)	0.3370(7)	0.1773(6)	1.0407(9)	0.1001
C(24)	0.3302(9)	1/4	1.1084(14)	0.0872
C(31)	0.4670(7)	1/4	0.6556(12)	0.0496
C(32)	0.5092(5)	0.1801(6)	0.6525(15)	0.1250
C(33)	0.5869(6)	0.1807(7)	0.6500(16)	0.1348
C(34)	0.6280(9)	1/4	0.6441(16)	0.0827
I	0.1650(7)	1/4	0.4360(13)	0.0932
C(1)	0.1040(6)	0.3432(7)	0.3474(10)	0.0903
C(2)	0.0415(7)	0.3693(8)	0.4109(14)	0.1292
C(3)	-0.0021(9)	0.4327(9)	0.3597(15)	0.1703
C(4)	0.0255(9)	0.4696(7)	0.2485(15)	0.1492
C(5)	0.0848(8)	0.4433(8)	0.1746(14)	0.1540
C(6)	0.1259(7)	0.3782(9)	0.2298(13)	0.1499

Table 64. Selected bond lengths (Å) and angles (°) for 2PhlTB (free refinement) (with e.s.d.'s in parentheses).

I - C(1)	2.069(11)	B - C(11)	1.648(12)
		B - C(11)	1.648(12)
		B - C(21)	1.625(12)
		B - C(31)	1.657(12)
		Mean	1.645(12)
C(1) - I - C(1)'	95.1(4)	C(11) - B - C(21)	112.8(7)
I - C(1) - C(2)	117.7(9)	C(11) - B - C(21)	112.8(7)
I - C(1) - C(6)	121.9(9)	C(11) - B - C(31)	111.4(7)
C(2) - C(1) - C(6)	120.4(12)	C(11) - B - C(31)	111.4(7)
		Mean	112.1(7)
C(11) - B - C(11)	103.8(6)	C(12) - C(11) - C(16)	114.2(8)
C(21) - B - C(31)	104.9(7)	C(12) - C(11) - C(16)	114.2(8)
Mean	104.4(6)	C(22) - C(21) - C(22)	113.4(8)
		C(32) - C(31) - C(32)	113.7(9)
		Mean	113.9(3)

Table 65. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for 2PhITB (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	Ueq
B	0.3743(8)	1/4	0.6686(13)	0.0440
C(11)	0.3362(4)	0.1706(4)	0.5914(7)	0.0462
C(12)	0.3648(5)	0.1424(4)	0.4691(8)	0.0632
C(13)	0.3319(6)	0.0771(5)	0.3990(8)	0.0780
C(14)	0.2674(5)	0.0412(5)	0.4484(10)	0.0782
C(15)	0.2365(5)	0.0672(5)	0.5663(10)	0.0732
C(16)	0.2711(4)	0.1318(5)	0.6352(9)	0.0589
C(21)	0.3572(6)	1/4	0.8287(11)	0.0488
C(22)	0.3504(6)	0.1783(5)	0.9043(8)	0.0770
C(23)	0.3366(7)	0.1784(6)	1.0420(9)	0.0996
C(24)	0.3299(9)	1/4	1.1094(13)	0.0881
C(31)	0.4683(6)	1/4	0.6568(10)	0.0485
C(32)	0.5069(4)	0.1788(6)	0.6931(16)	0.0635
C(32*)	0.5106(7)	0.1819(7)	0.6157(15)	0.0716
C(33)	0.5850(4)	0.1829(7)	0.6879(16)	0.0674
C(33*)	0.5891(7)	0.1783(8)	0.6111(18)	0.0906
C(34)	0.6266(7)	1/4	0.6448(14)	0.0776
I	0.1649(1)	1/4	0.4359(1)	0.0961
C(1)	0.1009(8)	0.3520(8)	0.3655(13)	0.0546
C(1*)	0.1067(9)	0.3335(10)	0.3292(13)	0.0750
C(2)	0.0308(9)	0.3645(12)	0.4237(18)	0.1005
C(2*)	0.0514(10)	0.3765(12)	0.3963(17)	0.1029
C(3)	-0.0124(11)	0.4306(12)	0.3811(17)	0.1215
C(3*)	0.0123(12)	0.4371(13)	0.3278(17)	0.1366
C(4)	0.0123(9)	0.4758(10)	0.2718(16)	0.0802
C(4*)	0.0382(10)	0.4616(11)	0.2028(17)	0.0937
C(5)	0.0783(8)	0.4591(8)	0.2016(15)	0.0630
C(5*)	0.0969(11)	0.4194(12)	0.1426(18)	0.1143
C(6)	0.1221(9)	0.3966(9)	0.2534(14)	0.0720
C(6*)	0.1329(10)	0.3541(12)	0.2031(15)	0.0998

3.5. Role of small cations in Tetraphenylborates

It was reported in the previous section that the size of the cation plays a significant role in determining the crystal packing, as well as the stereochemistry, of small organic ammonium tetraphenylborates. This is evident when the crystal packing in ImATB, ImBTB and ImDTB is compared with that in the alkali, ammonium and tetramethylammonium tetraphenylborates. Sodium¹⁷⁸, potassium¹²³, rubidium¹⁷⁹, cesium¹⁷⁸ and ammonium¹²³ tetraphenylborates belong to the tetragonal system ($I\bar{4}2m$, $Z = 2$) whereas tetramethylammonium tetraphenylborate (4MTB) is orthorhombic with space group $Cmcm$ ($Z = 4$). In all the cases the structures consist of columns in which cations alternate with anions. In the tetragonal tetraphenylborates the axes of the columns coincide with the 4-fold axes and the quasi-spherical cation occupies the tetrahedral cavity formed by four phenyl rings from two neighbouring anions in the same cation-anion column (Fig. 69). However, in the case of 4MTB, the ion packing is slightly different because of the larger size of the Me_4N^+ cation. The environment of the cation is still tetrahedral but this time only two of the rings belong to a neighbouring anion in the same cation-anion column while the other two come, one each, from anions in the neighbouring cation-anion columns. The axis of the column in 4MTB is parallel to the b -axis. The similarity of the ion packing between the two systems, $I\bar{4}2m$ and $Cmcm$, becomes apparent when the crystal structures belonging to the body centred ($I\bar{4}2m$, $Z = 2$) tetragonal system are described in terms of the corresponding face centred lattice ($F\bar{4}m2$, $Z = 4$). It is clear from the above discussions that an increase in the effective size of the cation can bring about a change in the space group symmetry of a TB salt consistent with the transition from homo-column to partial hetero-column coordination (i.e. from $I\bar{4}2m$ to perhaps $Cmcm$ or a subgroup). However, the cation

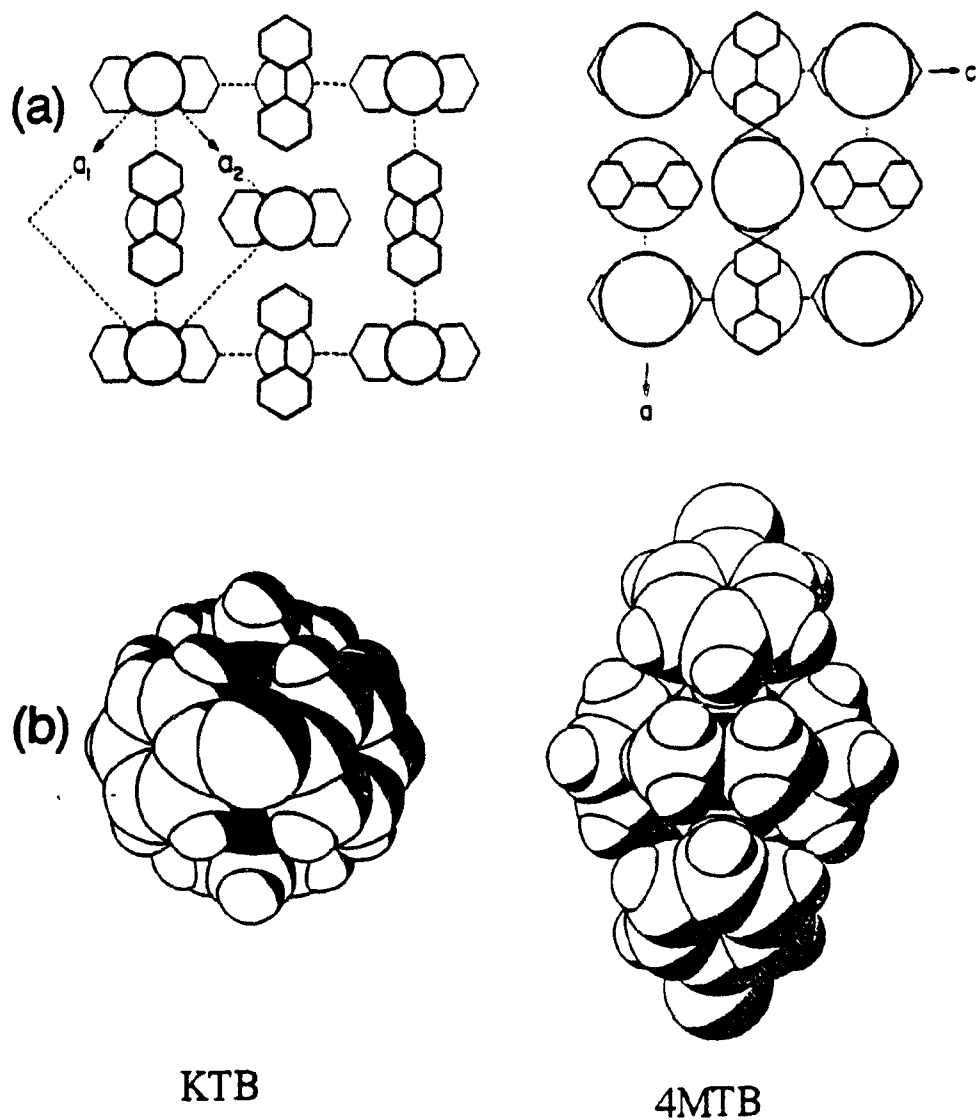


Fig. 69. (a) Schematic representation of the ion packing and anion orientation. left: KTB, and, right: 4MTB. (b) The quasi-tetrahedral enclosure of the cation by the phenyl rings in KTB (left) and 4MTB (right). The cation is inside the heavy outline, with the K and N atoms shown in black.

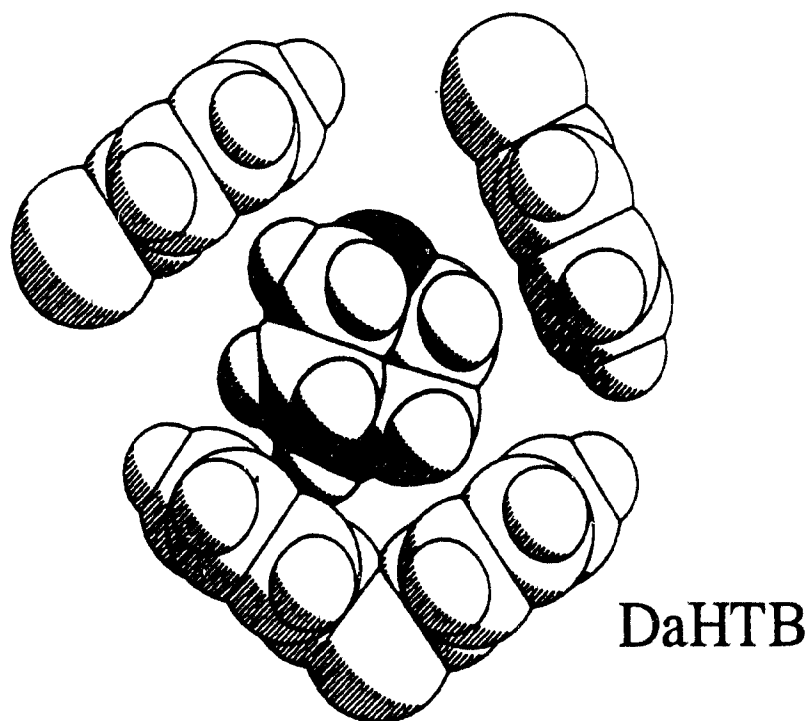
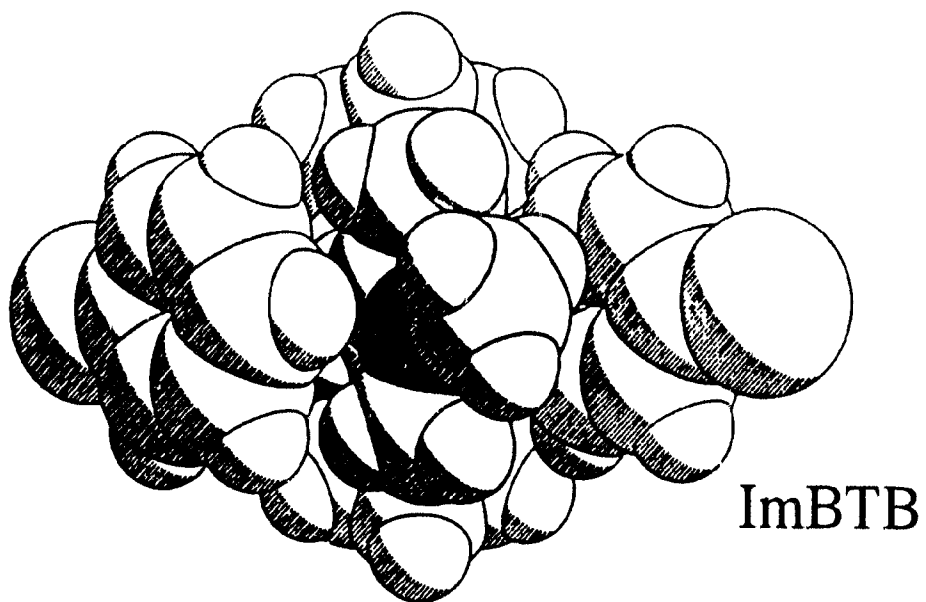


Fig. 70. The quasi-tetrahedral enclosure of the cation by the phenyl rings in ImBTB (upper diagram) and DaHTB (lower diagram).

coordination remains tetrahedral.

The compounds ImATB, ImBTB and ImDTB are all orthorhombic and their space group relationship can be represented as $Cmc2_1$ (ImDTB) $\subset$ [$Cmcm$ (ImATB), $Cmca$ (ImBTB)] $\subset Fmmm \subset Fm3m$. Since the effective sizes of these cations are of the same order as Me_4N^+ , the ion packing in all three compounds is of the same type as found in 4MTB (i.e. the cation is surrounded by four phenyl rings, one pair from an anion in the same column and the other two one each from neighbouring columns). In each case the columns of alternating ions are parallel to b . However, a difference is seen in compound ImBTB where one of the two phenyl rings coming from the neighbouring cation-anion columns points downwards, in the other compounds both point up. This occurs because of the presence of a glide mirror plane in ImBTB which opens the tetrahedral coordination cage on one side (Fig. 70).

Similar tetrahedral coordination about the cation is also observed in the case of QTB and DaHTB. The compounds QTB and DaHTB are isostructural, belonging to orthorhombic, space group $Pnma$, a primitive subgroup of $Cmcm$. The ions are arranged in columns with alternating cation and anions, parallel to c . The cation is enclosed in a tetrahedral cage formed by four phenyl rings, one pair from one anion and the other two, one each from the neighbouring anions. In contrast to the iminium TB salts, in this case, all four phenyl rings approach the cation horizontally and the cage is open on both sides (Fig. 70).

Even in the case of monoclinic space group $P2_1/n$ ($\subset Cmcm$), the coordination by the phenyl rings about the cation remains the same. The compounds ImCTB and 2PiTB are isostructural; in both cases, the cations form an approximate fc arrangement and the anions are arranged in columns of quasi- 2_1 symmetry parallel to c . The cation is

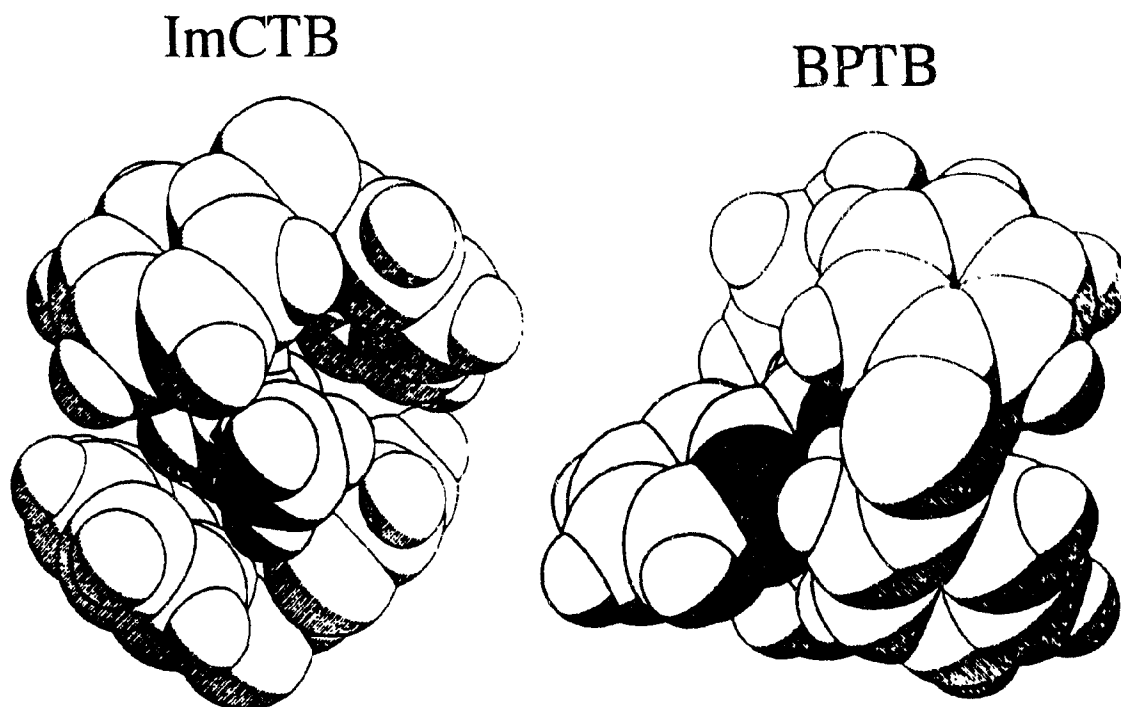


Fig. 71. The asymmetric enclosure of the cation by two pairs of phenyl rings, each pair from a different anion. left, ImCTB; right, BPTB.

enclosed by two pair of phenyl rings from two neighbouring anions. However, the cavity formed by the four phenyl rings is not symmetric compared with that in ImATB, ImBTB, or QTB (Fig. 71). In the compound BPTB (monoclinic, $P2_1/n$), the structure consists of columns of alternating BP^+ and TB^- ions, parallel to c and the cation is surrounded by two pair of phenyl rings from the same column (rings 3 and 4 from the anion above and 1 and 2 from the anion below). The tetrahedral cavity is even less symmetric in this case, and because of its large size, the BP^+ cation does not fit inside the cavity (Fig. 71).

In spite of the small size of the $[Me_2NH_2]^+$ cation (2M), the crystal packing of the

compound 2MTB.MeCN is different from other TB compounds with small cations because of the presence of solvent. The cations, the anions and the solvent molecules in this structure are arranged in layers along *b*, each layer containing three component species in alternating arrangement. The cavity which encloses both the cation and the solvent molecule, formed by the six phenyl rings, two pairs from the anions above and

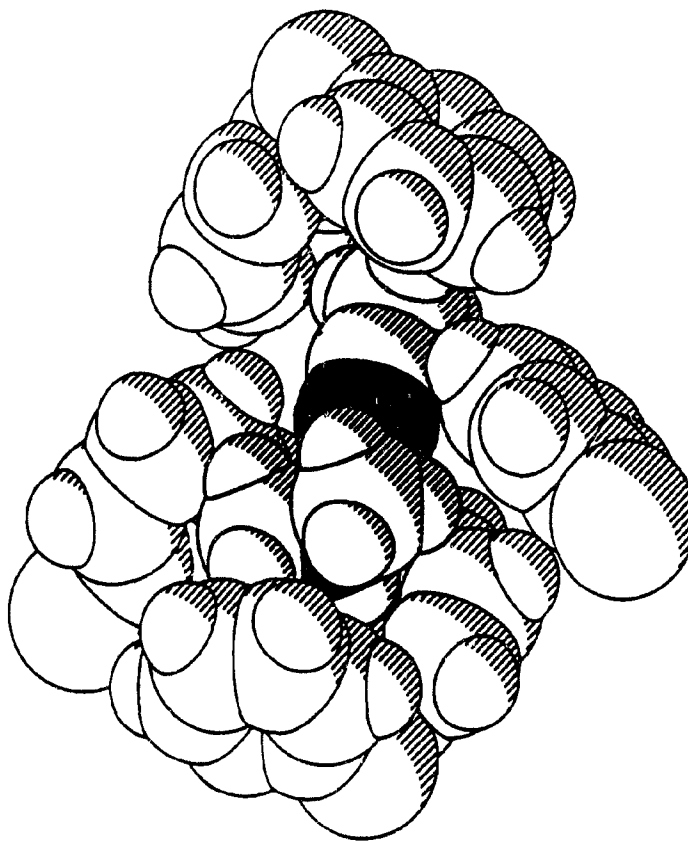


Fig. 72. The enclosure of the cation and solvent molecule by six phenyl rings in 2MTB.MeCN.

below, and the other two, one each, from the two a glide related counterparts (Fig. 72).

There is another interesting feature, related to the size of the cations that is worth noting. The Me_4N^+ cation is completely ordered in 4MTB, whereas the cations

$[\text{Me}_2\text{C}=\text{NHMe}]^+$ in ImATB, $[\text{Me}_2\text{C}=\text{NMe}_2]^+$ in ImBTB, $[\text{Me}_2\text{C}=\text{NHEt}]^+$ in ImCTB and $[\text{MeEtC}=\text{NHMe}]^+$ in ImDTB are disordered. The regularly shaped tetrahedral Me_4N^+ cation, in a symmetric orientation, fits into the phenyl ring coordination cage with little freedom of movement. As a result, its structure is completely ordered. In contrast, the cation of ImBTB is rectangular and those of ImATB and ImDTB are even less regular. Introduction of a cation less "tetrahedral" than Me_4N^+ into the symmetric, wedge-shaped space inside the pair of phenyl rings of TB results in orientational disorder (For details, see individual structures).

It is clear from the above discussion that the crystal packing in the TB compounds is dominated by the cation geometry. For unsolvated TB compounds containing a small cation, the cation is enclosed in a tetrahedral cavity formed by four phenyl rings. If the cation geometry is other than tetrahedral, a disorder problem arises. As the size of the cation increases, the cation coordination may be tetrahedral, but to accommodate a relatively large cation, the cavity loses its regular tetrahedral symmetry. For a structure containing solvent molecule the situation is more complicated; in this case, not only the size and shape of the cation but also the solvent molecule plays a significant role in crystal packing.

3.6. Tetraphenylborate Anion

The highest possible symmetry of the tetraphenylborate anion, D_{2d} , is found only in unsolvated alkali and ammonium salts. Among the 19 (1-16, 26-28) crystal structures reported here, containing 21 distinct tetraphenylborate anions, the anion symmetry is C_{2v} in all compounds except in compounds 3, 5-6, 11 where it is C_s and in compound 23 where it is C_1 . All three symmetries belong to the five subgroups of D_{2d} .

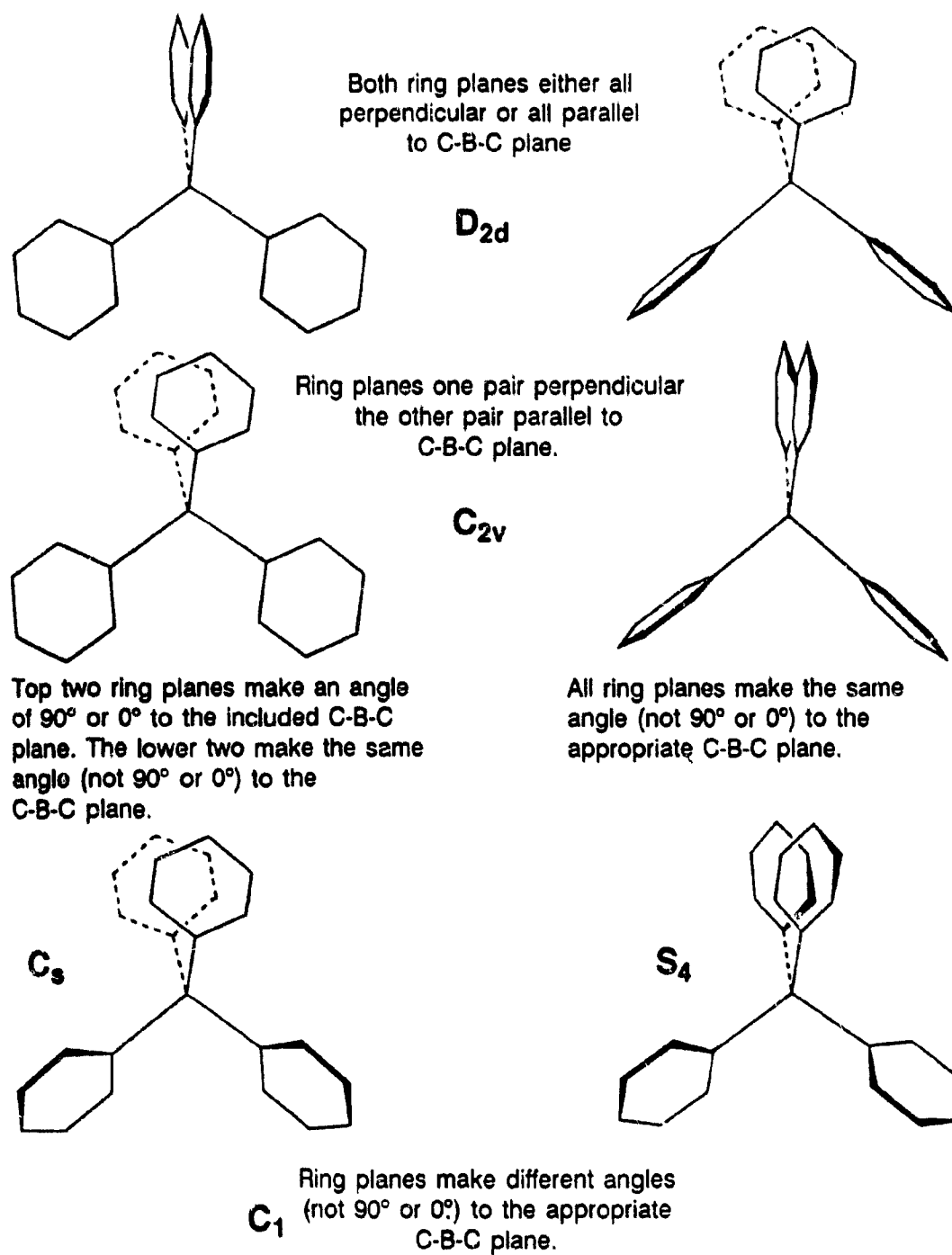


Fig. 73. Conformation of the tetraphenylborate anion (TB) in the five subgroups of D_{2d} .

In TB anions having D_{2d} symmetry, the planes of each of the four phenyl rings are perpendicular to one or the other of the two mirror planes whose line of intersection coincides with the S_4 axis. The C - B - C valence angles α , in the D_{2d} conformation would be bisected by S_4 axis, in subgroups other than S_4 , thus there are two angles C(1) - B - C(3) (α_1) and C(2) - B - C(4) (α_2). In the S_4 conformation, the phenyl rings are each tipped about their own B - C(1) - C(4) axis through the same constant angle (neither 90° nor 0°). Fig. 73 shows the conformations of the TB anion in the five subgroups of D_{2d} .

In spite of the conformational diversity of the tetraphenylborate anion in the 19 TB salts, the skeletal symmetry of the anion is not very far from D_{2d} . The mean α_1 , and α_2 angles in 19 TB compounds are $104.4(17)^\circ$ and $112.1(12)^\circ$, respectively. The mean of the difference between α_1 and α_2 is small, only 2.1° .

The overall mean C - C bond length and C - C - C bond angle, are $1.391(10)$ Å and $119.2(29)^\circ$, respectively. An electropositive substituent on the benzene ring decreases the angle at the ipso carbon atom C(α) and increases the endocyclic angle at the C(β) atom. This also causes lengthening of the *a* bonds with respect to the *b* bonds. Similar effects are visible in the case of TB^- anion. The mean endocyclic C - C - C angles are $114.8(7)^\circ$ at the C(α) atom, $122.9(9)^\circ$ at C(β), $120.3(9)^\circ$ at C(γ) and $118.9(10)^\circ$ at C(δ) and the mean uncorrected C - C bond lengths are $a = 1.401(10)$ Å, $b = 1.395(10)$ Å, $c = 1.377(11)$ Å. Because of the inherently low electronegativity of boron which is further lowered by the negative charge, the anionic $-BPh_3^-$ group was found to be a powerful contractor of the ipso C - C - C phenyl internal angle¹⁵. The geometry definitions for a substituted ring is shown in Fig. 74.

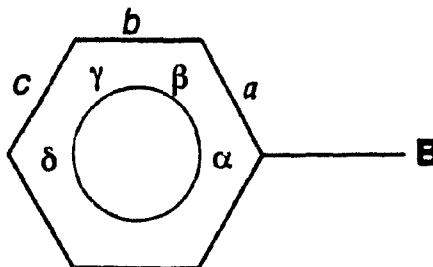


Fig. 74. Geometry definitions for a substituted phenyl ring.

The phenyl rings are planar, the mean of the deviation of the C atoms from the respective best plane through the 34 rings being 0.006 Å. The boron atoms are not coplanar with their phenyl rings, the mean deviation for the sixty-eight rings is 0.12(4) Å. The mean B - C distance is 1.648(18) Å.

3.7. Summary

Formation of hydrogen bonds to an aromatic π systems has been reported in the past. However, the presence of such bonds has not always been noticed, even when a published crystal-structure determination contains evidence of X - H... π bond formation. The present goal-oriented, systematic study indicates that hydrogen bonding to aromatic π systems in crystals occurs much more widely than had commonly been believed.

The present report contains x-ray crystal structures of 16 tetraphenylborate compounds of mostly organoammonium cations, both solvated and unsolvated. Examination of these plus a few literature structures reveals a large variety of H(X)... π

bonding interactions on which to base a classification of bond types and geometries. Such a classification has been made. Examples of normal N - H... π bonds (types A - J) bifurcated N - H...2 π bonds (homodesmic (K, L) and heterodesmic (G)), as well as trifurcated N - H...3 π bonds (homodesmic (H and J)) and heterodesmic (K)), are found in the organo-animonium tetraphenylborates. However, in cases where the cation is too bulky, the crystal is solvated and the solvent molecule acts either as an acceptor or as an intermediary hydrogen bond recipient from the alkylammonium protons (type H and J).

Since description of the directionality and length of the H(X)... π bond poses problems, the distance $d(\text{H(X)}\dots\pi_c)$ of the H(X) atom to the centre of the associated phenyl ring has been adopted as one of the relevant measures. The $d(\text{H(X)}\dots\pi_c)$ distance ranges from ca. 2.1 Å to ca. 2.7 Å in normal and from ca. 2.3 Å to ca. 3.7 Å in branched (i.e. bifurcated and trifurcated) H-bonds. The angle X - H... π_c ranges from ca. 165° to ca. 170° in normal and from ca. 2.3 Å to ca. 3.7 Å in branched (i.e. bifurcated and trifurcated) bonds.

When the H(N) atoms(s) is replaced by an alkyl group(s) or by an atom X containing high local electron density (lone electron pairs, L), the cation orients itself in such a way that the repulsion between the alkyl group or lone pair and the phenyl groups is minimal. The strength of the ring avoiding tendency decreases in the order $L > (\text{CH}_3, \text{CH}_2) > \text{H(N)}$. This observation demonstrates that the orientation of the N(H) containing cation to form a hydrogen bond(s) is a manifestation of a positive hydrogen-bonding tendency (reinforced by ion charge interaction) rather than a passive response to overall packing requirements in the crystal.

Appendix 1

Table 65. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for nonhydrogen atoms of 3-[(*p*-nitrophenoxy)methyl]-3-chlorodiazirine from multiple refinement (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	Ueq
CL(1)	0.02972(17)	0.28577(14)	0.44315(13)	0.0479(3)
O(1)	0.29167(34)	0.15117(31)	0.15794(19)	0.0451(3)
O(2)	0.55850(15)	0.36611(14)	-0.35597(7)	0.0680(2)
O(3)	0.86059(14)	0.44932(13)	-0.20829(8)	0.0667(1)
N(1)	0.14493(53)	-0.03364(40)	0.34996(38)	0.0402(8)
N(2)	0.26646(50)	0.02377(40)	0.46546(37)	0.0380(8)
N(3)	0.67340(52)	0.38198(37)	-0.24097(34)	0.0352(7)
C(1)	0.22409(55)	0.14033(43)	0.38417(40)	0.0291(8)
C(2)	0.39620(57)	0.18607(49)	0.30221(41)	0.0335(9)
C(3)	0.40029(56)	0.20520(44)	0.06673(40)	0.0300(9)
C(4)	0.27410(58)	0.18757(47)	-0.06663(41)	0.0345(9)
C(5)	0.36335(61)	0.24451(47)	-0.16833(41)	0.0359(10)
C(6)	0.57873(58)	0.31664(43)	-0.13775(42)	0.0291(8)
C(7)	0.70786(56)	0.33217(45)	-0.00666(41)	0.0321(9)
C(8)	0.61752(59)	0.27718(46)	0.09671(41)	0.0339(9)

Table 67. Positional parameters and isotropic temperature factors ($\text{\AA}^2$) for hydrogen atoms of 3-[(*p*-nitrophenoxy)methyl]-3-chlorodiazirine from multiple refinement (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	U_{iso}
H(21)	0.5371	0.1135	0.3067	0.058(18)
H(22)	0.4487	0.3141	0.3469	0.067(19)
H(41)	0.1081	0.1275	-0.0910	0.026(14)
H(51)	0.2661	0.2335	-0.2712	0.039(17)
H(71)	0.8768	0.3871	0.0159	0.035(14)
H(81)	0.7155	0.2874	0.2000	0.042(17)

Table 68. Scale factor, extinction and kappa of 3-[(*p*-nitrophenoxy)methyl]-3-chlorodiazirine from multiple refinement (with e.s.d.'s in parentheses).

Scale Factor		Extinction	
1.7614(33)		0.000	
K'		K''	
1.011(5)		0.718(18)	Cl(1)
0.960(4)		0.472(17)	O(1)
0.945(3)		0.400(9)	O(2), O(3)
0.976(4)		0.544(11)	N(1), N(2)
0.946(5)		0.515(10)	N(3)
0.959(4)		0.880(15)	C(1), C(2)
0.990(4)		0.813(12)	C(3) - C(8)
1.000		1.000	H(21) - H(81)

Table 69. Multipole parameters from monopole to 8-PX²-Y² of 3-[(p-nitrophenoxy) methyl]-3-chlorodiazirine (e.s.d.'s are in parentheses).

Atom	Monopol	Dipol X	Dipol Y	Dipol Z	4-Pol Z ²	4-Pol ZX	4-Pol ZY	4-PX ² -Y ²	4-Pol XY	8-PolZ ³	8-PolXZ ²	8-PolYZ ²	8-PX ² -Y ²									
CL(1)	7.51(9)	-0.07(4)	0.26(5)	0.11(6)	0.07(7)	0.44(5)	-0.16(6)	0.44(5)	-0.18(5)	0.10(8)	0.06(6)	-0.09(7)	0.10(7)									
O(1)	6.30(8)	0.02(8)	0.30(12)	-0.14(14)	-0.26(12)	-0.27(9)	-0.23(12)	-0.25(9)	0.35(8)	0.20(12)	-0.14(11)	-0.08(14)	0.30(11)									
O(2)	6.53(11)	0.34(28)	-0.11(35)	0.10(10)	0.35(12)	0.59(23)	-0.45(26)	-0.05(14)	-0.03(14)	0.45(16)	0.38(18)	-0.60(19)	-0.05(16)									
O(3)	6.25(11)	0.28(28)	-0.12(35)	0.37(10)	-0.10(11)	0.51(22)	-0.29(26)	0.12(14)	0.02(14)	-0.36(14)	0.31(17)	0.11(18)	0.06(14)									
N(1)	5.11(7)	0.26(17)	0.10(6)	0.33(5)	0.40(6)	0.12(15)	0.34(5)	-0.07(4)	-0.05(7)	0.13(6)	0.15(11)	0.11(8)	-0.14(6)									
N(2)	from N(1)																					
N(3)	4.98(18)	-0.13(26)	-0.25(22)	0.67(29)	-0.15(21)	-0.45(13)	-0.10(19)	-0.39(14)	-0.68(23)	1.11(21)	0.26(17)	0.41(32)	0.44(15)									
C(1)	3.98(20)	0.16(6)	-0.21(7)	0.00	0.23(6)	0.00	0.00	0.11(6)	0.17(6)	0.00	-0.14(7)	0.18(7)	0.00									
C(2)	3.97(21)	-0.09(5)	-0.29(8)	-0.02(7)	-0.18(7)	0.10(6)	0.11(6)	0.00(6)	-0.17(6)	0.46(8)	0.00(8)	-0.04(6)	-0.02(7)									
C(3)	3.95(24)	0.08(6)	0.01(8)	0.34(9)	0.27(8)	-0.16(6)	0.15(8)	0.11(6)	-0.16(7)	0.22(9)	-0.05(8)	0.21(15)	0.40(8)									
C(4)	4.00(18)	0.13(7)	0.16(9)	-0.27(10)	-0.11(9)	-0.30(7)	-0.02(9)	-0.13(7)	0.05(6)	0.47(10)	-0.06(9)	-0.26(15)	0.35(9)									
C(5)	4.12(18)	-0.11(7)	0.07(8)	-0.33(10)	-0.13(9)	-0.21(7)	-0.21(9)	-0.27(7)	-0.16(6)	0.50(10)	-0.14(9)	-0.16(14)	0.28(9)									
C(6)	3.76(24)	-0.33(8)	0.35(9)	0.22(7)	-0.10(6)	-0.10(7)	0.22(6)	-0.26(7)	-0.32(8)	-0.08(8)	-0.10(8)	-0.12(8)	0.09(11)									
C(7)	3.87(15)	0.05(7)	0.22(8)	-0.38(9)	-0.24(9)	0.20(7)	-0.18(8)	-0.26(6)	0.07(6)	0.23(9)	-0.02(9)	-0.08(14)	0.44(8)									
C(8)	4.03(12)	-0.10(6)	-0.16(8)	0.46(9)	0.33(8)	-0.02(7)	0.31(8)	0.06(6)	-0.03(6)	0.67(8)	0.06(8)	0.02(14)	0.19(8)									
H(21)	0.83(7)	-0.04(5)	-0.06(4)	0.08(6)																		
H(22)	from H(21)																					
H(41)	from H(71)																					
H(51)	from H(71)																					
H(71)	0.72(4)	-0.01(3)	-0.06(5)	0.31(3)																		
H(81)	from H(71)																					

Table 69. Multipole parameters from 8-POLXYZ to 16-P X^3Y of 3-[(p-nitrophenoxy) methyl]-3-chlorodiazirine (e.s.d.'s are in parentheses - continued).

Atom	8-POLXYZ	8-PolX ³	8-PolY ³	16-PolZ ⁴	16-PoXZ ³	16-PoYZ ³	16PX ² -Y ²	16-PXYZ ²	16-PX ³ Z	16-PY ³ Z	16PX ⁴ +Y ⁴	16-polX ³ Y
CL(1)	0.03(6)	-0.17(6)	-0.10(7)	-0.22(9)	-0.05(5)	-0.03(6)	0.42(8)	0.13(7)	0.10(7)	-0.09(8)	-0.09(7)	-0.78(7)
O(1)	-0.13(11)	-0.23(9)	0.14(9)									
O(2)	-0.08(15)	-0.21(10)	-0.03(10)									
O(3)	0.49(15)	-0.21(10)	-0.35(10)									
N(1)	0.07(10)	-0.06(6)	0.11(5)									
N(3)	-0.25(22)	0.20(13)	0.55(17)									
C(1)	0.00(6)	0.23(8)	-0.16(7)									
C(2)	0.03(7)	-0.04(7)	0.25(7)									
C(3)	0.03(9)	0.04(7)	-0.24(8)									
C(4)	-0.07(9)	-0.05(7)	0.07(8)									
C(5)	0.01(9)	0.08(7)	0.19(8)									
C(6)	-0.18(8)	0.41(9)	-0.06(13)									
C(7)	-0.12(9)	-0.09(7)	0.11(7)									
C(8)	0.07(9)	0.06(7)	0.09(7)									

Table 70. Positional parameters and equivalent isotropic temperature factors ($\text{\AA}^2$) for nonhydrogen atoms of monochloropentaaziridinotricyclophosphazene from multiple refinement (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	Ueq
CL(1)	0.71351(9)	0.05319(5)	0.08818(10)	0.0562(2)
P(1)	0.80507(6)	0.34590(3)	0.14299(5)	0.0192(1)
P(2)	0.81159(6)	0.16534(3)	-0.00603(6)	0.0219(1)
P(3)	1.11207(6)	0.24731(3)	0.23291(5)	0.0191(1)
N(1)	0.71240(20)	0.25879(11)	0.00682(19)	0.0257(3)
N(2)	1.00874(19)	0.16070(11)	0.10185(18)	0.0238(3)
N(3)	1.00163(19)	0.33200(11)	0.26560(17)	0.0218(3)
N(4)	0.78053(21)	0.44959(11)	0.03284(18)	0.0250(3)
N(5)	0.69110(22)	0.37064(13)	0.26543(19)	0.0307(4)
N(6)	0.76563(24)	0.14056(12)	-0.22491(20)	0.0375(4)
N(7)	1.25183(21)	0.29360(12)	0.15954(21)	0.0292(4)
N(8)	1.24444(21)	0.19900(12)	0.42915(19)	0.0292(3)
C(1)	0.79770(31)	0.44905(16)	-0.14386(24)	0.0362(5)
C(2)	0.62957(30)	0.46224(16)	-0.13947(26)	0.0374(5)
C(3)	0.76828(34)	0.41892(20)	0.44526(27)	0.0484(7)
C(4)	0.71282(35)	0.31917(20)	0.43242(28)	0.0470(7)
C(5)	0.61721(35)	0.08456(19)	-0.34526(34)	0.0669(7)
C(6)	0.78890(36)	0.04480(17)	-0.29295(31)	0.0552(7)
C(7)	1.19646(34)	0.30489(17)	-0.04179(27)	0.0401(6)
C(8)	1.32173(30)	0.23098(18)	0.05498(30)	0.0407(6)
C(9)	1.29731(32)	0.25672(18)	0.59985(25)	0.0442(6)
C(10)	1.17973(34)	0.17552(19)	0.56914(26)	0.0468(7)

Table 71. Positional parameters and isotropic temperature factors ($\text{\AA}^2$) for hydrogen atoms of monochloropentaaziridinotricyclophosphazene from multiple refinement (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	U_{iso}
H(1)	0.8575	0.5071	-0.1781	0.043
H(2)	0.8267	0.3845	-0.1971	0.043
H(3)	0.5383	0.4070	-0.1886	0.044
H(4)	0.5690	0.5297	-0.1697	0.044
H(5)	0.8983	0.4362	0.5001	0.056
H(6)	0.7015	0.4736	0.4820	0.056
H(7)	0.6065	0.3008	0.4601	0.057
H(8)	0.8031	0.2636	0.4778	0.057
H(9)	0.5337	0.0556	-0.2913	0.078
H(10)	0.5466	0.1061	-0.4820	0.078
H(11)	0.8419	0.0378	-0.3923	0.067
H(12)	0.8065	-0.0125	-0.2013	0.067
H(13)	1.0725	0.2845	-0.1306	0.049
H(14)	1.2327	0.3663	-0.0939	0.049
H(15)	1.4490	0.2392	0.0725	0.049
H(16)	1.2887	0.1575	0.0353	0.049
H(17)	1.4222	0.2512	0.6998	0.054
H(18)	1.2540	0.3280	0.5974	0.054
H(19)	1.0519	0.1893	0.5439	0.057
H(20)	1.2188	0.1124	0.6469	0.057

Table 72. Scale factor, extinction and kappa of monochloropentaaziridinotricyclophosphazene from multiple refinement (with e.s.d.'s in parentheses).

Scale Factor	Extinction	
1.5157(0)	0.000(0)	
K'	K'	
0.988(8)	1.300(18)	Cl(1)
1.066(6)	1.107(14)	P(1) - P(3)
0.938(6)	1.055(18)	N(1) - N(3)
0.970(8)	0.560(16)	N(4) - N(8)
0.999(5)	0.606(19)	C(1) - C(10)
1.000	1.000	H(1) - H(20)

Table 73. Multipole parameters from monopole to 8-PX²-Y² of monochloropentaaziridinotricyclophosphazene (e.s.d.'s are in parentheses).

Atom	Monopol	Dipol X	Dipol Y	Dipol Z	4-Pol Z ²	4-Pol ZX	4-Pol ZY	4-Px ² -Y ²	4-Pol XY	8-Pol Z ³	8-PolXZ ²	8-PolYZ ²	8-Px ² -Y ²									
CL(1)	7.59(12)	-0.09(2)	0.01(2)	0.06(2)	0.20(4)	-0.15(4)	0.01(3)	0.17(3)	0.00(3)	-0.13(6)	0.05(5)	0.25(5)	-0.03(6)									
P(1)	3.60(30)	0.03(4)	0.00(4)	0.02(3)	-0.12(3)	-0.07(3)	0.13(2)	-0.01(3)	-0.12(3)	0.32(4)	0.01(3)	0.11(2)	0.08(3)									
P(2)	3.65(24)	-0.05(5)	0.11(5)	0.00(0)	0.15(4)	0.00(0)	0.00(0)	0.05(4)	0.25(4)	0.00(0)	0.10(4)	0.33(5)	0.00(0)									
P(3)	from P(1)																					
N(1)	from N(2)																					
N(2)	6.10(11)	-0.05(2)	-0.01(2)	0.04(2)	0.02(2)	0.01(2)	0.00(2)	-0.01(2)	-0.05(2)	0.09(3)	-0.01(3)	0.02(2)	0.11(3)									
N(3)	6.28(11)	0.10(3)	0.05(3)	0.00(0)	-0.01(3)	0.00(0)	0.00(0)	0.10(3)	-0.02(3)	0.00(0)	0.18(5)	0.19(4)	0.00(0)									
N(4)	5.53(14)	-0.12(13)	0.26(16)	0.00(0)	0.39(14)	0.00(0)	0.00(0)	0.04(9)	0.32(9)	0.00(0)	0.29(14)	-0.83(14)	0.00(0)									
N(5)	5.58(15)	-0.25(12)	0.08(15)	0.00(0)	-0.14(13)	0.00(0)	0.00(0)	-0.06(9)	0.26(10)	0.00(0)	0.05(12)	-0.25(12)	0.00(0)									
N(6)	5.81(15)	0.22(12)	0.22(16)	0.00(0)	-0.02(13)	0.00(0)	0.00(0)	0.00(9)	-0.06(10)	0.00(0)	-0.04(12)	-0.39(11)	0.00(0)									
N(7)	5.55(15)	-0.06(13)	-0.20(15)	0.00(0)	-0.15(14)	0.00(0)	0.00(0)	0.02(10)	0.05(9)	0.00(0)	0.00(13)	-0.40(12)	0.00(0)									
N(8)	5.81(15)	-0.13(13)	0.29(14)	0.00(0)	0.14(14)	0.00(0)	0.00(0)	-0.12(9)	0.17(10)	0.00(0)	0.44(14)	-0.61(13)	0.00(0)									
C(1)	4.22(22)	0.15(11)	0.14(10)	-0.19(9)	-0.04(5)	0.12(7)	0.49(7)	-0.03(7)	0.07(10)	0.29(6)	0.02(7)	-0.04(7)	-0.02(7)									
C(2)	from C(1)																					
C(3)	4.40(23)	0.00(13)	-0.10(9)	-0.06(9)	-0.19(5)	-0.15(8)	0.19(6)	0.11(7)	0.23(12)	0.25(7)	0.10(8)	-0.10(7)	-0.33(7)									
C(4)	from C(3)																					
C(5)	3.94(21)	-0.38(14)	-0.19(9)	-0.06(9)	-0.17(5)	-0.02(8)	0.36(6)	-0.09(8)	-0.11(11)	0.20(7)	-0.17(8)	-0.19(7)	-0.05(7)									
C(6)	from C(5)																					
C(7)	4.13(22)	0.22(12)	-0.14(9)	0.03(9)	-0.22(5)	0.01(7)	0.14(6)	-0.07(7)	0.37(10)	0.26(7)	0.02(7)	-0.05(7)	-0.22(7)									
C(8)	from C(7)																					
C(9)	3.97(22)	0.16(12)	0.23(10)	-0.12(9)	-0.15(5)	-0.03(7)	0.42(7)	-0.09(7)	0.10(11)	0.24(6)	-0.10(7)	0.00(7)	-0.21(7)									
C(10)	from C(9)																					
H(1)	0.76(11)	0.01(1)	-0.09(1)	0.13(2)																		
H(2)	from H(1)																					
H(3)	from H(1)																					
H(4)	from H(1)																					
H(5)	from H(1)																					
H(6)	from H(1)																					
H(7)	from H(1)																					
H(8)	from H(1)																					
H(9)	from H(1)																					
H(10)	from H(1)																					
H(11)	from H(1)																					
H(12)	from H(1)																					
H(13)	from H(1)																					
H(14)	from H(1)																					
H(15)	from H(1)																					
H(16)	from H(1)																					

Table 73. Multipole parameters from monopole to $8\text{-PX}^2\text{-Y}^2$ of monochloropentaaziridinotricyclophosphazene (e.s.d.'s are in parentheses - continued).

Atom	Monopol	Dipol X	Dipol Y	Dipol Z	4-Pol Z^2	4-Pol ZX	4-Pol ZY	4-PX ² -Y ²	4-Pol XY	8-PolZ ³	8-PolXZ ²	8-PolYZ ²	8-PX ² -Y ²
H(17)	from	H(1)											
H(18)	from	H(1)											
H(19)	from	H(1)											
H(20)	from	H(1)											

Table 73. Multipole parameters from from 8-POLXYZ to 16-P X³Y of monochloropentaaziridinotricyclophosphazene (e.s.d.'s are in parentheses - continued).

Atom	8-POLXYZ	8-POLX ³	8-POLY ³	16-POLZ ⁴	16-POXZ ³	16-POYZ ³	16PX ² -Y ²	16-PXYZ ²	16-PX ³ Z	16-PY ³ Z	16PX ⁴ +Y ⁴	16-PX ³ Y
CL(1)	-0.21(6)	0.44(6)	-0.57(6)	-0.16(10)	0.02(6)	0.03(7)	0.00(10)-0.06(10)-0.31(11)	0.34(11)	0.11(11)-0.13(10)			
P(1)	0.01(3)	0.03(3)	0.22(3)	0.02(3)	0.03(2)	-0.07(2)	-0.01(3)-0.08(3)-0.09(3)-0.13(3)-0.15(3)	0.08(3)				
P(2)	0.00(0)	-0.08(4)	0.09(4)	-0.10(6)	0.00(0)	0.00(0)	-0.22(5)	0.02(5)	0.00(0)	0.00(0)	0.02(4)-0.13(4)	
N(2)	0.02(3)	0.07(3)	0.01(3)									
N(3)	0.00(0)	-0.10(4)	-0.03(3)									
N(4)	0.00(0)	-0.18(8)	0.09(11)									
N(5)	0.00(0)	0.06(8)	0.24(12)									
N(6)	0.00(0)	-0.14(10)	0.45(12)									
N(7)	0.00(0)	-0.32(9)	0.20(12)									
N(8)	0.00(0)	0.10(8)	-0.02(12)									
C(1)	0.14(8)	-0.13(9)	0.16(6)									
C(3)	-0.05(9)	-0.14(9)	0.00(6)									
C(5)	-0.06(9)	0.04(10)	0.35(6)									
C(7)	0.11(8)	-0.17(9)	0.32(6)									
C(9)	0.03(8)	-0.15(9)	0.25(6)									

Table 74. Positional parameters and isotropic temperature factors ($\text{\AA}^2$) for nonhydrogen atoms of DaHTB from multiple refinement (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	U_{iso}
B(1)	0.67145(24)	0.75000	0.07799(45)	0.0129(11)
C(11)	0.63460(14)	0.65300(21)	0.15728(26)	0.0138(6)
C(12)	0.56358(15)	0.61775(24)	0.12386(27)	0.0190(7)
C(13)	0.52772(16)	0.54343(24)	0.20167(30)	0.0233(8)
C(14)	0.56051(17)	0.50641(25)	0.31722(29)	0.0258(8)
C(15)	0.62965(16)	0.54053(24)	0.35528(28)	0.0249(8)
C(16)	0.66532(17)	0.61319(26)	0.27660(27)	0.0244(8)
C(21)	0.76254(21)	0.75000	0.09129(38)	0.0152(10)
C(22)	0.80453(15)	0.66063(25)	0.09478(27)	0.0203(7)
C(23)	0.88059(16)	0.65985(26)	0.10501(28)	0.0237(7)
C(24)	0.91972(23)	0.75000	0.11379(42)	0.0280(14)
C(31)	0.65107(21)	0.75000	-0.08143(38)	0.0151(10)
C(32)	0.64228(15)	0.66029(26)	-0.15558(28)	0.0244(7)
C(33)	0.62092(17)	0.66034(30)	-0.29126(30)	0.0321(9)
C(34)	0.61067(25)	0.75000	-0.35973(48)	0.0359(16)
N(1)	-0.70484(19)	0.75000	-0.17034(34)	0.0221(10)
C(1)	-0.63894(24)	0.75000	-0.26094(43)	0.0264(11)
C(2)	-0.56972(24)	0.75000	-0.16632(46)	0.0263(12)
C(3)	-0.70359(17)	0.84207(28)	-0.08437(31)	0.0354(9)
C(4)	-0.63353(17)	0.84043(31)	0.00130(35)	0.0418(9)
N(2)	-0.58953(20)	0.75000	-0.02816(38)	0.0319(11)

Table 75. Positional parameters and isotropic temperature factors ($\text{\AA}^2$) for nonhydrogen atoms of DaHTB from multiple refinement (with e.s.d.'s in parentheses).

Atom	x/a	y/b	z/c	U_{iso}
H(12)	0.5365	0.6457	0.0346	0.049
H(13)	0.4738	0.5175	0.1710	0.059
H(14)	0.5316	0.4518	0.3782	0.059
H(15)	0.6562	0.5130	0.4452	0.062
H(16)	0.7193	0.6399	0.3059	0.052
H(22)	0.7743	0.5904	0.0887	0.050
H(23)	0.9088	0.5880	0.1084	0.057
H(24)	0.9791	0.7500	0.1236	0.053
H(32)	0.6505	0.5893	-0.1042	0.056
H(33)	0.6148	0.5889	-0.3424	0.074
H(34)	0.5969	0.7500	-0.4652	0.073
H(C11)	-0.6401	0.6840	-0.3213	0.066
H(C12)	-0.6401	0.8160	-0.3212	0.066
H(C21)	-0.5388	0.8156	-0.1902	0.065
H(C22)	-0.5388	0.6844	-0.1902	0.065
H(C31)	-0.7045	0.9077	-0.1454	0.080
H(C32)	-0.7507	0.8442	-0.0214	0.080
H(C41)	-0.6489	0.8395	0.1040	0.091
H(C42)	-0.6016	0.9055	-0.0210	0.091
H(N1)	-0.7547	0.7500	-0.2179	0.050

Table 76. Scale factor, extinction and kappa of monochloropentaaziridino-tricyclopophosphazene from multiple refinement (with e.s.d.'s in parentheses).

Scale Factor	Extinction	
0.4547(0)	0.000(0)	
K'	K''	
1.002(8)	0.821(12)	N(1), N(2)
1.016(11)	1.066(24)	C(1), C(2)
0.983(8)	1.031(23)	C(3), C(4)
0.974(3)	0.912(25)	C(11) - C(16), C(22), C(23), C(32), C(33)
1.001(8)	0.945(29)	C(21), C(24), C(31), C(34)
1.088(10)	1.148(24)	B(1)
1.000	1.000	H(12) - H(16) H(22), H(23) H(32), H(33)
1.000	1.000	H(24), H(34)
1.000	1.000	H(C11), H(C12) H(C21), H(C22)
1.000	1.000	H(C31), H(C32) H(C41), H(C42)
1.000	1.000	H(N1)

Table 77. Multipole parameters from monopole to $8\text{-}p\text{-}x^2\text{-}y^2$ of DaHTB (e.s.d.'s are in parentheses)

Atom	Monopol	Dipol X	Dipol Y	Dipol Z	4-Pol Z^2	4-Pol ZX	4-Pol ZY	4-Pol X^2-Y^2	4-Pol XY	8-Pol Z^3	8-Pol XZ^2	8-Pol YZ^2	8-Pol X^2Y^2				
N(1)	2.54(0)-0.13(10)-0.02(4)	0.00(0)	0.11(9)	0.00(0)	0.00(0)-0.05(7)-0.05(10)	0.00(0)-0.11(8)	0.06(11)	0.00(0)	-2.60(0) 0.05(12)-0.08(4)	0.00(0)-0.04(15)	0.00(0)	0.00(0)-0.12(9)-0.09(15)	0.00(0)				
N(2)	2.20(0)-0.07(8)-0.14(4)	0.00(0)	0.10(9)	0.00(0)	0.00(0)-0.07(6)-0.13(9)	0.00(0)-0.13(7)-0.06(11)	0.00(0)	0.00(0)	2.20(0)-0.07(8)-0.14(4)	0.00(0)-0.10(9)	0.00(0)	0.00(0)-0.13(7)-0.06(11)	0.00(0)				
C(1)	2.24(0)-0.13(8)-0.20(5)	0.00(0)	0.09(9)	0.00(0)	0.00(0) 0.05(6) 0.22(11)	0.00(0) 0.05(7)-0.13(11)	0.00(0)	0.00(0)	4.43(0)-0.40(6)-0.20(6)	0.00(0) 0.16(7) 0.00(0)	0.00(0)-0.06(8)	0.00(0)-0.13(9) 0.50(9)	0.00(0)				
C(2)	4.36(0) 0.03(6) 0.06(7)	0.06(6)-0.15(8)-0.20(6)	0.00(0)	0.02(8)-0.03(9)-0.06(9)-0.03(11)-0.10(9)-0.02(9)-0.03(11)	0.01(15)-0.11(11)	0.46(9)-0.01(12)			4.36(0) 0.03(6) 0.06(7)	0.06(6)-0.15(8)-0.20(6)	0.00(0)	0.02(8) 0.22(12)-0.29(10)-0.09(11)	0.04(11)				
C(3)	4.39(0) 0.15(6)-0.01(8)	0.01(8) 0.24(8) 0.03(8)-0.01(9)-0.15(7)-0.06(7)	0.01(15)-0.11(11)	0.46(9)-0.01(12)					4.54(0) 0.05(7) 0.08(8)	0.16(7)-0.18(7)-0.02(7)	0.02(8)-0.03(9)-0.06(9)-0.03(11)-0.10(9)-0.02(9)-0.03(11)						
C(4)	4.46(0)-0.04(8)	0.00(8) 0.07(7)-0.18(7)-0.07(8)	0.09(9)-0.02(10)	0.05(9) 0.02(11)-0.09(10)-0.14(10)-0.04(12)					4.61(0)-0.07(8)-0.29(7)	0.01(10)	0.17(9)-0.01(10)	0.00(12)	0.00(8)-0.02(7)-0.01(15)	0.01(13)			
C(15)	0.00(0)-0.02(13)	0.03(14)	0.04(11)-0.16(11)-0.06(12)	0.09(12)-0.01(18)	0.05(14)	0.06(16)-0.06(14)-0.11(16)-0.08(17)			0.00(0) 0.03(11)	0.04(14)	0.11(10)-0.21(11)-0.05(10)-0.02(11)	0.00(16)	0.05(14)	0.06(16)-0.06(14)-0.11(16)-0.08(17)			
C(16)	2.04(0) 0.11(5)-0.08(5)	0.00(0)	0.24(6)	0.00(0)	0.00(0) 0.03(4)	0.15(5)	0.00(0)-0.01(8)	0.28(6)	0.00(0)	4.26(0)-0.09(7)-0.02(7)	0.01(7)-0.32(6)-0.16(8)	0.19(9)	0.02(9)	0.19(9) 0.07(10)-0.21(9)	0.19(9) 0.04(13)		
C(22)	4.63(0)-0.06(8)-0.07(8)	0.19(8)-0.11(7)	0.00(9)	0.07(9)	0.02(9)	0.19(9)-0.07(10)-0.21(9)	0.19(9)	0.04(13)	2.32(0)-0.03(5)-0.04(5)	0.00(0)	0.13(8)	0.00(0)	0.00(0)-0.07(5)	0.13(5)	0.00(0)-0.02(10)	0.18(7)	0.00(0)
C(23)	2.00(0) 0.01(4)-0.10(5)	0.00(0)	0.11(6)	0.00(0)	0.00(0) 0.07(5)-0.02(5)	0.00(0)	0.01(8)-0.02(6)	0.00(0)	4.78(0)-0.02(7)-0.16(8)	0.02(7)-0.05(7)-0.03(8)-0.01(8)	0.11(8)-0.17(9)	0.00(10)-0.22(9)-0.03(9)	0.11(12)				
C(31)	4.55(0) 0.01(8)-0.03(8)	0.07(8)-0.30(7)-0.33(10)-0.09(9)-0.09(10)	0.16(10)-0.03(11)-0.02(10)-0.13(10)-0.06(15)						2.06(0) 0.02(6)	0.02(6)	0.00(0)-0.06(8)	0.00(0)	0.00(0)-0.19(5)-0.14(6)	0.00(0)	0.00(0)	0.15(8)	0.00(0)
C(34)	1.29(0)-0.01(4)	0.03(4)	0.00(0)-0.04(5)	0.00(0)	0.00(0)-0.02(5)-0.03(5)	0.00(0)-0.09(7)-0.06(7)	0.00(0)		N(12)	0.62(0)	0.24(12)	0.25(12)	0.20(18)				
H(1)	from	H(12)							H(13)	from	H(12)						
H(13)	from	H(12)							H(14)	from	H(12)						
H(14)	from	H(12)							H(15)	0.00(0)	0.26(57)	0.22(59)	0.10(59)				
H(15)	from	H(12)							H(16)	from	H(12)						
H(16)	from	H(12)							H(22)	from	H(12)						
H(22)	from	H(12)							H(23)	from	H(12)						
H(23)	from	H(12)							H(24)	0.20(0)	0.25(24)	0.48(37)					
H(24)	from	H(12)							H(32)	from	H(12)						
H(32)	from	H(12)							H(33)	from	H(12)						
H(33)	from	H(12)							H(34)	0.17(0)	0.23(32)	0.12(26)					
H(34)	from	H(12)							H(C11)	0.29(0)	0.04(33)-0.38(42)						
H(C11)	from	H(C11)							H(C12)	from	H(C11)						
H(C12)	from	H(C11)							H(C21)	from	H(C11)						

Table 77. Multipole parameters from monopole to $8\text{-PX}^2\text{-Y}^2$ of DaHTB (e.s.d.'s are in parentheses - continued)

Atom	Monopol	Dipol X	Dipol Y	Dipol Z	4-Pol Z^2	4-Pol ZX	4-Pol ZY	4-Pol $\text{PX}^2\text{-Y}^2$	4-Pol XY	8-Pol Z^3	8-Pol XZ^2	8-Pol YZ^2	8-Pol $\text{PX}^2\text{-Y}^2$
H(C22) from		H(C11)											
H(C31)	0.56(0)	0.16(17)	0.54(17)	-0.11(39)									
H(C32) from		H(C31)											
H(C41) from		H(C31)											
H(C42) from		H(31)											
H(N1)	0.29(0)	0.12(42)	0.72(44)										

Table 77. Multipole parameters from 8-POLXYZ to 16-P X^3Y of DaHTB (e.s.d.'s are in parentheses - continued)

Atom	8-POLXYZ	8-POLX ³	8-POLY ³	16-POLZ ⁴	16-POXZ ³	16-POYZ ³	16PX ² -Y ²	16-PXYZ ²	16-P X ³ Z	16-P Y ³ Z	16PX ⁴ +Y ⁴	16-P X ³ Y
N(1)	0.00(0)	0.11(13)	-0.06(9)									
N(2)	0.00(0)	0.32(15)	-0.14(12)									
C(1)	0.00(0)	0.11(15)	0.06(10)									
C(2)	0.00(0)	-0.04(15)	0.07(10)									
C(3)	0.00(0)	-0.07(12)	0.38(10)									
C(4)	0.16(10)	0.08(13)	0.31(11)									
C(11)	0.01(11)	0.07(9)	-0.10(9)									
C(12)	-0.08(11)	0.00(13)	0.28(9)									
C(13)	-0.05(12)	0.13(14)	0.27(9)									
C(14)	-0.01(12)	0.08(9)	-0.17(9)									
C(15)	-0.04(17)	0.09(22)	0.27(14)									
C(16)	-0.04(15)	0.02(20)	0.29(13)									
C(21)	0.00(0)	-0.09(7)	-0.10(6)									
C(22)	0.05(13)	0.16(13)	0.21(8)									
C(23)	0.03(14)	-0.03(15)	0.36(9)									
C(24)	0.00(0)	0.01(6)	-0.14(6)									
C(31)	0.00(0)	-0.03(7)	-0.06(6)									
C(32)	-0.04(12)	0.23(14)	0.36(9)									
C(33)	-0.05(14)	-0.41(16)	0.30(9)									
C(34)	0.00(0)	0.02(7)	-0.09(6)									
B(1)	0.00(0)	0.06(7)	0.05(6)									

Appendix 2

Table 78. Anisotropic temperature factors ($\text{\AA}^2$) for 3-[(*p*-nitrophenoxy) methyl]-3-chlorodiazirine from conventional refinement (It) (with e.s.d's in parentheses).

Atom	U11	U22	U33	U12	U13	U23
Cl(1)	0.0458(7)	0.0530(7)	0.0618(8)	0.0175(6)	0.0160(6)	0.0254(6)
O(1)	0.038(2)	0.055(2)	0.030(2)	-0.010(1)	0.004(1)	0.017(1)
O(2)	0.063(2)	0.069(2)	0.038(2)	-0.006(2)	0.005(2)	0.027(2)
O(3)	0.050(2)	0.062(2)	0.049(2)	-0.017(2)	0.008(2)	0.022(2)
N(1)	0.042(2)	0.040(2)	0.045(2)	-0.004(2)	0.012(2)	0.012(2)
N(2)	0.038(2)	0.047(2)	0.043(2)	0.004(2)	0.012(2)	0.024(2)
N(3)	0.048(2)	0.036(2)	0.033(2)	0.002(2)	0.009(2)	0.012(2)
C(1)	0.032(2)	0.040(2)	0.034(2)	0.002(2)	0.007(2)	0.016(2)
C(2)	0.034(2)	0.050(3)	0.030(2)	-0.002(2)	0.006(2)	0.017(2)
C(3)	0.037(2)	0.039(2)	0.028(2)	0.003(2)	0.008(2)	0.013(2)
C(4)	0.035(2)	0.050(3)	0.028(2)	-0.002(2)	0.006(2)	0.011(2)
C(5)	0.040(2)	0.047(3)	0.026(2)	0.002(2)	0.003(2)	0.011(2)
C(6)	0.037(2)	0.034(2)	0.027(2)	0.003(2)	0.009(2)	0.011(2)
C(7)	0.029(2)	0.042(2)	0.033(2)	0.001(2)	0.005(2)	0.011(2)
C(8)	0.032(2)	0.044(3)	0.031(2)	0.002(2)	-0.001(2)	0.016(2)

Table 79. Anisotropic temperature factors ($\text{\AA}^2$) for monochloropentaaziridino-tricyclopophosphazene from conventional refinement (rt) (with e.s.d's in parentheses).

Atom	U11	U22	U33	U12	U13	U23
Cl(1)	0.0637(8)	0.0496(7)	0.128(1)	-0.0098(6)	0.0434(9)	0.0266(8)
P(1)	0.0265(5)	0.0291(5)	0.0301(5)	0.0048(4)	0.0101(4)	0.0013(4)
P(2)	0.0252(5)	0.0242(5)	0.0411(6)	-0.0018(4)	0.0062(4)	0.0009(4)
P(3)	0.0229(5)	0.0294(5)	0.0308(5)	0.0018(4)	0.0072(4)	-0.0014(4)
N(1)	0.021(2)	0.030(2)	0.049(2)	0.002(1)	0.005(1)	-0.003(1)
N(2)	0.025(2)	0.028(2)	0.041(2)	0.002(1)	0.007(1)	-0.007(1)
N(3)	0.028(2)	0.031(2)	0.030(2)	0.005(1)	0.007(1)	-0.003(1)
N(4)	0.038(2)	0.030(2)	0.032(2)	0.004(1)	0.008(1)	0.003(1)
N(5)	0.042(2)	0.054(2)	0.046(2)	0.015(2)	0.025(2)	0.006(2)
N(6)	0.048(2)	0.040(2)	0.042(2)	0.011(2)	-0.003(2)	-0.011(2)
N(7)	0.036(2)	0.045(2)	0.049(2)	-0.008(1)	0.023(2)	-0.009(2)
N(8)	0.034(2)	0.044(2)	0.034(2)	0.009(1)	0.003(1)	0.000(2)
C(1)	0.068(3)	0.046(2)	0.034(2)	0.000(2)	0.018(2)	0.009(2)
C(2)	0.046(3)	0.044(2)	0.047(3)	0.009(2)	-0.000(2)	0.009(2)
C(3)	0.072(3)	0.085(4)	0.041(3)	0.012(3)	0.028(3)	-0.007(3)
C(4)	0.065(3)	0.090(4)	0.058(3)	0.018(3)	0.038(3)	0.027(3)
C(5)	0.061(3)	0.068(4)	0.078(4)	0.012(3)	-0.018(3)	-0.034(3)
C(6)	0.072(3)	0.058(3)	0.063(3)	0.023(3)	0.002(3)	-0.024(3)
C(7)	0.070(3)	0.054(3)	0.052(3)	-0.006(2)	0.040(3)	-0.004(2)
C(8)	0.046(3)	0.060(3)	0.069(3)	-0.004(2)	0.038(2)	-0.017(2)
C(9)	0.064(3)	0.067(3)	0.034(3)	0.023(3)	-0.006(2)	-0.008(2)
C(10)	0.064(3)	0.080(4)	0.043(3)	0.012(3)	0.012(3)	0.022(3)

Table 80. Hydrogen atom positional parameters for ImATB.

Atom	x/a	y/b	z/c	U_{iso}
H(12)	0.302(0)	0.241(0)	0.641(0)	0.069(4)
H(13)	0.302(0)	0.348(0)	0.509(0)	0.096(4)
H(14)	1/2	0.401(2)	0.440(3)	0.077(4)
H(22)	0.365(0)	0.093(0)	0.593(0)	0.075(4)
H(23)	0.199(0)	-0.015(0)	0.593(0)	0.114(4)
H(24)	0.105(5)	-0.061(3)	3/4	0.111(4)
H(N)	1/2	0.046(14)	0.234(4)	0.096(4)
H(C11)	1/2	0.284(4)	0.324(0)	0.082(4)
H(C12)	0.418(0)	0.268(4)	0.205(0)	0.106(4)
H(CN1)	1/2	0.066(4)	0.085(4)	0.098(4)
H(CN2)	0.582(0)	0.168(4)	0.093(4)	0.134(4)

Table 81. Anisotropic temperature factors ($\text{\AA}^2$) for ImATB (with e.s.d's in parentheses).

Atom	U11	U22	U33	U23	U13	U12
B	0.028(3)	0.037(2)	0.036(3)	0	0	0
C(11)	0.035(2)	0.041(2)	0.036(2)	-0.004(2)	0	0
C(12)	0.039(2)	0.048(1)	0.048(1)	0.002(1)	-0.002(2)	0.006(2)
C(13)	0.053(2)	0.048(1)	0.051(2)	0.002(1)	-0.005(2)	0.010(2)
C(14)	0.073(3)	0.045(2)	0.046(2)	0.006(2)	0	0
C(21)	0.035(2)	0.042(2)	0.037(2)	0	0	0.001(2)
C(22)	0.053(2)	0.049(1)	0.052(2)	-0.000(1)	-0.008(2)	-0.009(2)
C(23)	0.071(2)	0.058(2)	0.083(2)	-0.004(2)	-0.023(2)	-0.015(2)
C(24)	0.049(3)	0.066(2)	0.104(3)	0	0	-0.017(2)
N	0.105(4)	0.051(3)	0.054(4)	-0.003(3)	0	0
C(N)	0.139(4)	0.086(3)	0.050(3)	0.005(3)	0	0
C	0.048(4)	0.061(3)	0.056(4)	0.003(3)	0	0
C(C1)=C(C1')	0.194(5)	0.069(3)	0.070(4)	0	0	0
C(C2)=C(N')	0.139(4)	0.086(3)	0.050(3)	-0.005(3)	0	0

Table 82. Hydrogen atom positional parameters for ImCTB.

Atom	x/a	y/b	z/c	U _{iso}
H(12)	0.929	-0.021	0.292	0.065
H(13)	0.754	-0.091	0.328	0.085
H(14)	0.588	0.006	0.329	0.088
H(15)	0.596	0.176	0.289	0.082
H(16)	0.770	0.246	0.251	0.061
H(22)	1.216	0.149	0.323	0.059
H(23)	1.353	0.037	0.273	0.078
H(24)	1.301	-0.082	0.151	0.087
H(25)	1.107	-0.086	0.074	0.078
H(26)	0.971	0.026	0.123	0.060
H(32)	0.827	0.171	0.086	0.059
H(33)	0.816	0.266	-0.060	0.077
H(34)	0.950	0.394	-0.076	0.084
H(35)	1.096	0.424	0.054	0.076
H(36)	1.108	0.329	0.199	0.061
H(42)	1.087	0.122	0.432	0.059
H(43)	1.131	0.214	0.578	0.072
H(44)	1.080	0.383	0.582	0.084
H(45)	0.983	0.456	0.439	0.081
H(46)	0.945	0.365	0.293	0.062
H(N)	0.770	0.206	0.440	0.079
H(N11)	0.690	0.329	0.575	0.102
H(N12)	0.814	0.375	0.540	0.102
H(N21)	0.655	0.439	0.446	0.163
H(N22)	0.737	0.369	0.377	0.163
H(N23)	0.613	0.323	0.412	0.163
H(C11)	0.908	0.159	0.711	0.103
H(C12)	0.920	0.275	0.668	0.103
H(C13)	0.792	0.235	0.700	0.103
H(C21)	0.787	0.045	0.524	0.104
H(C22)	0.916	0.083	0.491	0.104
H(C23)	0.905	0.049	0.609	0.104

Table 83. Anisotropic temperature factors ($\text{\AA}^2$) for ImCTB (with e.s.d's in parentheses).

Atom	U11	U22	U33	U12	U13	U23
B	0.035(3)	0.039(3)	0.037(3)	-0.003(2)	0.003(2)	-0.002(2)
C(11)	0.043(2)	0.041(2)	0.034(2)	-0.001(2)	-0.000(2)	-0.005(2)
C(12)	0.050(3)	0.052(3)	0.061(3)	-0.006(2)	0.011(2)	-0.003(2)
C(13)	0.082(3)	0.061(3)	0.074(3)	-0.019(3)	0.026(3)	-0.004(3)
C(14)	0.061(3)	0.090(4)	0.074(3)	-0.033(3)	0.023(3)	-0.019(3)
C(15)	0.041(3)	0.098(4)	0.067(3)	-0.007(3)	0.016(2)	-0.009(3)
C(16)	0.047(3)	0.060(3)	0.048(3)	-0.002(2)	0.011(2)	0.000(2)
C(21)	0.041(2)	0.037(2)	0.033(2)	-0.003(2)	0.003(2)	0.004(2)
C(22)	0.043(3)	0.065(3)	0.041(3)	0.003(2)	0.007(2)	-0.003(2)
C(23)	0.050(3)	0.089(3)	0.056(3)	0.016(3)	0.010(2)	0.005(3)
C(24)	0.077(4)	0.074(3)	0.071(3)	0.038(3)	0.030(3)	0.011(3)
C(25)	0.086(4)	0.055(3)	0.058(3)	0.015(3)	0.023(3)	-0.004(2)
C(26)	0.047(3)	0.048(3)	0.057(3)	0.003(2)	0.008(2)	-0.010(2)
C(31)	0.032(2)	0.036(2)	0.040(2)	0.006(2)	0.005(2)	-0.004(2)
C(32)	0.050(3)	0.051(3)	0.046(2)	-0.001(2)	0.006(2)	0.004(2)
C(33)	0.063(3)	0.080(3)	0.047(3)	0.013(3)	-0.000(2)	0.009(3)
C(34)	0.079(4)	0.074(4)	0.060(3)	0.020(3)	0.022(3)	0.027(3)
C(35)	0.058(3)	0.057(3)	0.078(3)	0.002(2)	0.024(3)	0.015(3)
C(36)	0.046(3)	0.052(3)	0.055(3)	0.001(2)	0.008(2)	0.005(2)
C(41)	0.032(2)	0.041(3)	0.040(2)	-0.000(2)	0.006(2)	-0.002(2)
C(42)	0.051(3)	0.054(3)	0.045(3)	0.005(2)	0.009(2)	-0.004(2)
C(43)	0.056(3)	0.085(4)	0.038(3)	0.005(3)	-0.001(2)	-0.005(3)
C(44)	0.075(3)	0.080(4)	0.053(3)	-0.013(3)	0.004(3)	-0.029(3)
C(45)	0.087(4)	0.051(3)	0.066(3)	-0.001(3)	0.014(3)	-0.019(3)
C(46)	0.058(3)	0.049(3)	0.046(3)	0.005(2)	0.004(2)	-0.010(2)
N	0.071(3)	0.073(3)	0.054(2)	0.012(2)	0.008(2)	0.004(2)
C(N12)	0.180(6)	0.132(5)	0.088(4)	0.100(5)	-0.014(4)	0.010(4)
C(N11)	0.101(4)	0.072(3)	0.086(4)	0.034(3)	0.026(3)	-0.002(3)
C	0.057(3)	0.073(3)	0.054(3)	0.005(3)	0.014(2)	0.016(3)
C(C1)	0.091(4)	0.110(4)	0.057(3)	0.011(3)	0.014(3)	0.004(3)
C(C2)	0.103(4)	0.073(3)	0.086(4)	0.005(3)	0.021(3)	0.011(3)

Table 84. Hydrogen atom positional parameters for ImDTB (It).

Atom	x/a	y/b	z/c	U _{iso}
H(12)	0.195	0.258	-0.019	0.035
H(13)	0.195	0.155	-0.154	0.048
H(14)	0.000	0.086	-0.209	0.066
H(22)	0.191	0.263	0.198	0.038
H(23)	0.193	0.152	0.327	0.037
H(24)	0.000	0.109	0.404	0.043
H(32)	0.131	0.410	-0.072	0.046
H(33)	0.301	0.514	-0.067	0.074
H(34)	0.382	0.569	0.092	0.061
H(35)	0.293	0.518	0.249	0.051
H(36)	0.136	0.407	0.245	0.042
H(N)	0.011	0.455	-0.431	0.095
H(N1)	0.021	0.310	-0.573	0.075
H(N2)	0.046	0.418	-0.604	0.075
H(N3)	-0.098	0.385	-0.561	0.075
H(C11)	0.018	0.309	-0.223	0.062
H(C12)	-0.041	0.410	-0.255	0.062
H(C13)	0.118	0.392	-0.258	0.062
H(C211)	0.087	0.250	-0.487	0.047
H(C212)	0.119	0.222	-0.362	0.047
H(C221)	-0.042	0.130	-0.438	0.069
H(C222)	-0.130	0.222	-0.464	0.069
H(C223)	-0.098	0.193	-0.339	0.069

Table 85. Anisotropic temperature factors ($\text{\AA}^2$) for ImDTB (with e.s.d's in parentheses).

Atom	U11	U22	U33	U23	U13	U12
B	0.023(2)	0.037(2)	0.030(2)	0.001(4)	0.000(0)	0.000(0)
C(11)	0.038(3)	0.026(3)	0.014(3)	0.010(2)	0.000(0)	0.000(0)
C(12)	0.025(3)	0.034(2)	0.048(3)	0.004(2)	0.011(2)	0.021(2)
C(13)	0.051(3)	0.055(3)	0.045(3)	-0.018(2)	0.014(3)	0.032(3)
C(14)	0.074(4)	0.043(3)	0.064(4)	-0.003(3)	0.000(0)	0.000(0)
C(21)	0.013(3)	0.035(3)	0.052(4)	0.008(3)	0.000(0)	0.000(0)
C(22)	0.033(3)	0.051(3)	0.034(3)	0.002(2)	0.012(3)	-0.016(3)
C(23)	0.032(3)	0.040(3)	0.044(3)	-0.010(2)	0.004(3)	-0.007(2)
C(24)	0.049(3)	0.029(3)	0.022(3)	-0.002(2)	0.000(0)	0.000(0)
C(31)	0.026(2)	0.039(2)	0.038(2)	-0.018(3)	-0.003(3)	0.001(1)
C(32)	0.059(3)	0.043(3)	0.043(3)	0.021(2)	-0.002(3)	-0.008(3)
C(33)	0.081(4)	0.052(3)	0.094(4)	0.019(3)	0.041(3)	-0.029(3)
C(34)	0.055(2)	0.058(2)	0.078(3)	-0.008(4)	0.002(4)	-0.027(2)
C(35)	0.042(3)	0.059(3)	0.058(3)	0.011(3)	0.004(3)	-0.009(3)
C(36)	0.031(3)	0.044(3)	0.054(3)	0.019(2)	-0.007(3)	-0.007(3)
N	0.034(4)	0.032(3)	0.086(4)	0.005(3)	-0.006(3)	-0.008(3)
C(N)	0.105(4)	0.088(4)	0.013(3)	0.000(3)	0.001(4)	0.022(4)
C	0.040(4)	0.054(3)	0.053(4)	0.003(3)	0.002(3)	-0.028(3)
C(C1)	0.072(4)	0.057(4)	0.067(4)	0.009(3)	0.006(4)	-0.042(3)
C(C21)	0.042(3)	0.046(3)	0.058(3)	-0.017(4)	0.003(4)	0.007(3)
C(C22)	0.058(3)	0.072(4)	0.085(4)	-0.030(4)	0.048(4)	-0.033(3)

Table 86. Hydrogen atom positional parameters for ImETBw.

Atom	x/a	y/b	z/c	U _{iso}
H(12)	0.1021	-0.1995	0.0345	0.051
H(13)	0.0443	-0.3139	0.0868	0.060
H(14)	0.0107	-0.2064	0.1800	0.059
H(15)	0.0373	0.0189	0.2217	0.058
H(16)	0.0957	0.1341	0.1691	0.047
H(22)	0.1925	0.0941	0.1964	0.051
H(23)	0.2502	-0.0370	0.2646	0.061
H(24)	0.2824	-0.2391	0.2141	0.065
H(25)	0.2531	-0.3131	0.0993	0.057
H(26)	0.1962	-0.1820	0.0308	0.048
H(32)	0.2184	0.2278	0.0994	0.049
H(33)	0.2212	0.4748	0.1046	0.054
H(34)	0.1531	0.6116	0.0845	0.054
H(35)	0.0820	0.4930	0.0586	0.053
H(36)	0.0799	0.2468	0.0510	0.041
H(42)	0.0724	0.0292	-0.0335	0.052
H(43)	0.0657	0.0273	-0.1604	0.063
H(44)	0.1321	0.0206	-0.2164	0.068
H(45)	0.2042	0.0216	-0.1484	0.063
H(46)	0.2118	0.0345	-0.0246	0.047
H(N)	0.1498	0.4192	-0.2252	0.095
H(N11)	0.1279	0.7122	-0.2238	0.051
H(N12)	0.1385	0.6161	-0.2953	0.051
H(N21)	0.0593	0.6498	-0.2987	0.058
H(N22)	0.0721	0.4767	-0.2842	0.058
H(N4)	0.0606	0.3686	-0.1794	0.058
H(N5)	0.0297	0.3800	-0.0713	0.081
H(N6)	0.0080	0.6010	-0.0255	0.088
H(N7)	0.0105	0.8075	-0.0975	0.080
H(N8)	0.0419	0.7927	-0.2041	0.061
H(C11)	0.1580	0.3133	-0.1080	0.068
H(C12)	0.2097	0.3762	-0.1232	0.068
H(C13)	0.1879	0.4210	-0.0478	0.068
H(C21)	0.1626	0.6227	-0.0422	0.056
H(C22)	0.1652	0.7291	-0.1135	0.056
H(C23)	0.1147	0.6577	-0.0983	0.056
H(O1)	0.6347	0.2408	0.1754	0.093
H(O2)	0.6820	0.2086	0.2141	0.104

Table 87. Anisotropic temperature factors ($\text{\AA}^2$) for ImETBw (with e.s.d's in parentheses).

Atom	U11	U22	U33	U12	U13	U23
B	0.030(5)	0.034(6)	0.033(5)	0.001(4)	0.001(4)	-0.002(5)
C(11)	0.030(4)	0.036(5)	0.045(5)	0.001(4)	-0.005(3)	-0.003(5)
C(12)	0.052(6)	0.049(7)	0.065(6)	-0.004(5)	0.016(5)	0.000(5)
C(13)	0.058(6)	0.055(6)	0.081(8)	-0.022(5)	0.021(5)	-0.008(6)
C(14)	0.044(5)	0.069(8)	0.078(8)	-0.015(5)	0.014(5)	0.001(6)
C(15)	0.059(6)	0.071(7)	0.057(6)	-0.009(6)	0.020(4)	-0.004(6)
C(16)	0.052(5)	0.053(6)	0.043(5)	-0.016(5)	0.010(4)	-0.006(5)
C(21)	0.035(4)	0.044(6)	0.039(5)	-0.011(4)	0.007(3)	0.001(5)
C(22)	0.038(4)	0.073(7)	0.050(6)	-0.004(5)	0.004(4)	0.009(5)
C(23)	0.043(5)	0.098(9)	0.052(6)	-0.007(5)	-0.007(4)	0.012(6)
C(24)	0.031(5)	0.068(8)	0.103(9)	-0.000(5)	-0.009(5)	0.031(7)
C(25)	0.042(5)	0.045(6)	0.091(8)	0.002(5)	-0.003(5)	0.012(6)
C(26)	0.045(5)	0.041(6)	0.064(6)	-0.005(5)	0.001(4)	-0.002(5)
C(31)	0.039(4)	0.044(5)	0.034(5)	-0.002(5)	0.003(3)	-0.003(5)
C(32)	0.042(5)	0.044(6)	0.067(7)	-0.003(5)	0.003(4)	-0.001(5)
C(33)	0.057(6)	0.061(7)	0.053(6)	-0.010(5)	-0.003(4)	0.001(5)
C(34)	0.085(6)	0.038(6)	0.046(5)	-0.008(6)	0.006(5)	-0.005(5)
C(35)	0.069(6)	0.047(7)	0.051(6)	0.006(5)	0.005(4)	-0.005(5)
C(36)	0.046(5)	0.042(6)	0.040(5)	-0.007(5)	0.000(4)	-0.002(5)
C(41)	0.041(4)	0.033(5)	0.040(5)	0.010(4)	0.004(4)	0.007(4)
C(42)	0.051(5)	0.076(7)	0.039(5)	0.006(5)	0.005(4)	0.002(5)
C(43)	0.066(6)	0.089(8)	0.042(6)	-0.007(6)	-0.001(4)	-0.001(6)
C(44)	0.102(8)	0.060(7)	0.045(6)	-0.005(7)	-0.003(5)	0.011(6)
C(45)	0.068(6)	0.071(8)	0.062(6)	0.013(6)	0.019(5)	0.014(6)
C(46)	0.052(5)	0.058(6)	0.042(5)	0.002(5)	0.013(4)	0.001(5)
N	0.039(4)	0.052(5)	0.055(5)	-0.003(4)	0.003(3)	0.002(4)
C(N1)	0.055(5)	0.062(7)	0.046(6)	-0.001(5)	0.007(4)	0.002(5)
C(N2)	0.053(6)	0.071(7)	0.058(6)	-0.003(5)	-0.006(4)	0.007(5)
C(N3)	0.033(5)	0.081(8)	0.042(6)	-0.011(5)	-0.001(4)	0.001(6)
C(N4)	0.052(6)	0.088(9)	0.058(6)	-0.023(5)	0.011(5)	0.006(7)
C(N5)	0.059(7)	0.100(10)	0.090(10)	-0.051(7)	-0.001(6)	0.021(8)
C(N6)	0.072(7)	0.140(10)	0.066(8)	-0.027(9)	0.018(6)	-0.01(1)
C(N7)	0.050(6)	0.110(10)	0.090(10)	0.007(7)	0.007(6)	-0.022(8)
C(N8)	0.062(6)	0.079(8)	0.057(7)	0.009(6)	0.016(5)	-0.005(6)
C	0.044(5)	0.064(7)	0.056(6)	-0.001(5)	0.005(4)	0.004(6)
C(C1)	0.068(6)	0.074(8)	0.076(7)	0.013(6)	0.003(5)	0.018(6)
C(C2)	0.058(5)	0.076(7)	0.048(5)	-0.010(5)	0.005(4)	-0.000(6)
O(1)	0.098(5)	0.071(5)	0.070(4)	-0.010(4)	0.022(3)	0.017(4)

Table 88. Hydrogen atom positional parameters for QTB.

Atom	x/a	y/b	z/c	U_{iso}
H(12)	0.9599	0.3589	0.0311	0.0657
H(13)	1.0214	0.4862	0.1662	0.0714
H(14)	0.9666	0.5455	0.3772	0.0737
H(15)	0.8461	0.4819	0.4408	0.0781
H(16)	0.7835	0.3566	0.3057	0.0705
H(22)	0.8504	0.4096	-0.1073	0.0727
H(23)	0.8875	0.4111	-0.3434	0.0926
H(24)	0.9125	1/4	-0.4586	0.1033
H(32)	0.7274	0.4098	0.0853	0.0670
H(33)	0.5953	0.4107	0.1075	0.0718
H(34)	0.5278	1/4	0.1253	0.0761
H(N)	0.7506	3/4	0.2327	0.0769
H(1,11)	0.7929	0.5908	0.1476	0.0975
H(1,12)	0.7399	0.6549	0.0281	0.0975
H(1,21)	0.8861	0.5904	0.0058	0.1096
H(1,22)	0.8335	0.6557	-0.1130	0.1096
H(2,11)	0.8636	0.6839	0.3100	0.0901
H(2,21)	0.9602	0.6839	0.1711	0.0875
H(3)	0.9446	3/4	-0.0582	0.0875

Table 89. Anisotropic temperature factors ($\text{\AA}^2$) for QTB (with e.s.d's in parentheses).

Atom	U11	U22	U33	U23	U13	U12
B	0.045(6)	0.035(7)	0.055(6)	0	0.002(5)	0
C(11)	0.049(3)	0.038(4)	0.051(3)	0.006(3)	0.001(3)	0.003(3)
C(12)	0.052(3)	0.051(4)	0.061(4)	-0.001(3)	0.001(3)	-0.009(3)
C(13)	0.058(4)	0.051(4)	0.070(4)	-0.010(3)	-0.006(3)	-0.007(4)
C(14)	0.074(4)	0.055(5)	0.055(4)	-0.007(3)	-0.009(3)	-0.010(3)
C(15)	0.084(5)	0.061(5)	0.051(4)	-0.005(4)	0.006(4)	-0.007(4)
C(16)	0.065(4)	0.062(4)	0.048(4)	-0.011(3)	0.007(3)	-0.010(3)
C(21)	0.043(5)	0.050(6)	0.046(5)	0	-0.005(4)	0
C(22)	0.071(4)	0.061(4)	0.050(3)	-0.017(4)	-0.009(3)	0.006(3)
C(23)	0.074(4)	0.096(6)	0.061(4)	-0.028(4)	-0.012(4)	0.020(4)
C(24)	0.055(6)	0.150(10)	0.055(7)	0	0.001(5)	0
C(31)	0.048(5)	0.039(6)	0.049(5)	0	-0.007(4)	0
C(32)	0.051(4)	0.051(4)	0.066(4)	0.002(3)	0.003(3)	0.009(4)
C(33)	0.052(4)	0.057(5)	0.070(4)	0.013(3)	0.003(3)	0.006(4)
C(34)	0.046(6)	0.090(9)	0.053(5)	0	-0.004(4)	0
N	0.054(5)	0.075(6)	0.065(5)	0	0.010(4)	0
C(1,1)	0.093(5)	0.073(5)	0.077(5)	-0.019(4)	0.002(4)	-0.028(4)
C(1,2)	0.072(4)	0.111(6)	0.090(5)	0.002(5)	0.008(4)	-0.037(5)
C(2,1)	0.095(8)	0.079(8)	0.054(5)	0	-0.005(6)	0
C(2,2)	0.065(6)	0.062(7)	0.079(6)	0	-0.011(5)	0
C(3)	0.058(6)	0.097(9)	0.061(6)	0	0.011(5)	0

Table 90. Hydrogen atom positional parameters for DaHTB.

Atom	x/a	y/b	z/c	U _{iso}
H(12)	0.5372	0.6449	0.0370	0.0486
H(13)	0.4750	0.5181	0.1717	0.0585
H(14)	0.5319	0.4525	0.3775	0.0594
H(15)	0.6556	0.5137	0.4431	0.0617
H(16)	0.7187	0.6396	0.3056	0.0517
H(22)	0.7742	0.5903	0.0887	0.0499
H(23)	0.9083	0.5895	0.1083	0.0574
H(24)	0.9768	3/4	0.1232	0.0528
H(32)	0.6504	0.5901	-0.1047	0.0562
H(33)	0.6149	0.5900	-0.3415	0.0740
H(34)	0.5973	3/4	-0.4623	0.0726
H(N1)	-0.7546	3/4	-0.2178	0.0503
H(N11)	-0.6401	0.6837	-0.3215	0.0656
H(N12)	-0.6401	0.8163	-0.3215	0.0656
H(N21)	-0.5385	0.6837	-0.1904	0.0654
H(N22)	-0.5385	0.8163	-0.1904	0.0654
H(N31)	-0.7046	0.9090	-0.1466	0.0796
H(N32)	-0.7522	0.8442	-0.0194	0.0796
H(N41)	-0.6491	0.8394	0.1055	0.0909
H(N42)	-0.6017	0.9054	-0.0210	0.0909

Table 91. Anisotropic temperature factors ($\text{\AA}^2$) for DaHTB (with e.s.d's in parentheses).

Atom	U11	U22	U33	U23	U13	U12
B	0.034(3)	0.034(3)	0.030(3)	0	0.000(2)	0
C(11)	0.035(2)	0.034(2)	0.033(1)	0.003(1)	0.002(1)	-0.004(1)
C(12)	0.038(2)	0.046(2)	0.041(2)	-0.002(2)	-0.000(1)	0.007(2)
C(13)	0.040(2)	0.053(2)	0.058(2)	-0.007(2)	0.005(2)	0.005(2)
C(14)	0.058(2)	0.045(2)	0.049(2)	-0.004(2)	0.015(2)	0.008(2)
C(15)	0.064(2)	0.051(2)	0.040(2)	-0.003(2)	-0.001(2)	0.009(2)
C(16)	0.046(2)	0.047(2)	0.039(2)	-0.010(2)	-0.005(1)	0.003(2)
C(21)	0.037(2)	0.043(3)	0.026(2)	0	-0.001(2)	0
C(22)	0.040(2)	0.044(2)	0.043(2)	0.004(2)	-0.000(2)	-0.005(2)
C(23)	0.043(2)	0.058(2)	0.046(2)	0.013(2)	-0.005(2)	-0.004(2)
C(24)	0.035(3)	0.074(4)	0.040(3)	0	-0.003(2)	0
C(31)	0.027(2)	0.046(3)	0.034(2)	0	0.002(2)	0
C(32)	0.046(2)	0.057(2)	0.041(2)	-0.013(2)	0.009(2)	-0.007(2)
C(33)	0.052(2)	0.094(3)	0.043(2)	-0.026(2)	0.010(2)	-0.020(2)
C(34)	0.039(3)	0.139(6)	0.034(3)	0	0.001(2)	0
N(1)	0.038(2)	0.062(3)	0.042(2)	0	-0.008(2)	0
C(1)	0.059(3)	0.072(4)	0.036(3)	0	0.008(3)	0
C(2)	0.040(3)	0.066(4)	0.063(4)	0	0.006(3)	0
C(3)	0.062(2)	0.078(3)	0.064(2)	0.017(2)	-0.004(2)	-0.025(2)
C(4)	0.062(2)	0.103(3)	0.063(2)	-0.002(3)	-0.003(2)	-0.036(3)
N(2)	0.042(2)	0.093(4)	0.051(3)	0	-0.008(2)	0

Table 92. Hydrogen atom positional parameters for 1MPzBTB.Me₂CO

Atom	x/a	y/b	z/c	U _{iso}
H(112)	0.194	0.761	0.092	0.053
H(113)	0.191	0.697	0.003	0.063
H(114)	0.282	0.757	-0.077	0.060
H(115)	0.378	0.886	-0.066	0.054
H(116)	0.387	0.949	0.024	0.045
H(122)	0.485	0.831	0.210	0.045
H(123)	0.725	0.854	0.241	0.052
H(124)	0.850	0.958	0.203	0.056
H(125)	0.737	1.036	0.127	0.057
H(126)	0.497	1.012	0.094	0.051
H(132)	0.355	1.056	0.171	0.050
H(133)	0.232	1.175	0.151	0.064
H(134)	0.021	1.178	0.087	0.058
H(135)	-0.062	1.061	0.041	0.051
H(136)	0.068	0.943	0.056	0.044
H(142)	0.098	0.955	0.193	0.047
H(143)	0.002	0.896	0.271	0.055
H(144)	0.056	0.763	0.296	0.058
H(145)	0.220	0.694	0.244	0.056
H(146)	0.327	0.755	0.168	0.048
H(N1)	0.678	0.865	0.100	0.060
H(CN11)	0.784	0.947	0.041	0.062
H(CN12)	0.619	0.919	0.014	0.062
H(CN13)	0.764	0.877	-0.011	0.062
H(C1,1)	0.917	0.797	0.053	0.047
H(C1,2)	0.923	0.864	0.107	0.047
H(C2,1)	0.533	0.791	0.040	0.047
H(C2,2)	0.675	0.753	0.010	0.047
H(C3,1)	0.822	0.772	0.165	0.043
H(C3,2)	0.974	0.736	0.142	0.043
H(C4,1)	0.589	0.662	0.073	0.046
H(C4,2)	0.604	0.729	0.127	0.046

Table 92. Hydrogen atom positional parameters for 1MPzBTB.Me₂CO (continued).

Atom	x/a	y/b	z/c	U _{iso}
H(N2)	0.828	0.672	0.068	0.054
H(212)	0.938	0.667	0.245	0.060
H(213)	0.842	0.714	0.328	0.078
H(214)	0.597	0.699	0.338	0.084
H(215)	0.446	0.644	0.262	0.082
H(216)	0.538	0.600	0.178	0.064
H(222)	0.693	0.479	0.186	0.066
H(223)	0.589	0.367	0.140	0.084
H(224)	0.560	0.360	0.039	0.068
H(225)	0.637	0.465	-0.016	0.063
H(226)	0.746	0.577	0.030	0.053
H(232)	0.947	0.519	0.225	0.050
H(233)	1.183	0.475	0.238	0.065
H(234)	1.348	0.516	0.174	0.064
H(235)	1.273	0.598	0.095	0.061
H(236)	1.035	0.642	0.082	0.045
H(C12,1)	0.693	0.131	0.642	0.186
H(C12,2)	0.727	0.222	0.617	0.186
H(C12,3)	0.818	0.144	0.595	0.186
H(C13,1)	0.510	0.072	0.605	0.171
H(C13,2)	0.515	0.047	0.535	0.171
H(C13,3)	0.404	0.119	0.553	0.171

Table 93. Anisotropic temperature factors ($\text{\AA}^2$) for 1MPzBTB.Me₂CO (with e.s.d's in parentheses).

Atom	U11	U22	U33	U23	U13	U12
B(1)	0.046(3)	0.035(3)	0.042(3)	0.014(3)	0.000(3)	-0.004(3)
C(111)	0.032(3)	0.038(3)	0.050(3)	-0.001(3)	0.002(2)	0.002(2)
C(112)	0.070(3)	0.061(3)	0.038(3)	-0.010(3)	0.014(3)	-0.015(3)
C(113)	0.077(3)	0.054(3)	0.068(3)	-0.014(3)	0.005(3)	-0.025(3)
C(114)	0.073(3)	0.069(3)	0.047(3)	-0.008(3)	-0.001(3)	0.005(3)
C(115)	0.071(3)	0.067(3)	0.034(3)	0.011(3)	0.002(3)	0.015(3)
C(116)	0.049(3)	0.042(3)	0.048(3)	0.014(3)	-0.006(3)	0.002(3)
C(121)	0.039(3)	0.037(3)	0.045(3)	-0.005(3)	0.004(2)	0.002(2)
C(122)	0.045(3)	0.047(3)	0.051(3)	0.000(3)	0.012(2)	-0.003(3)
C(123)	0.046(3)	0.064(3)	0.052(3)	-0.001(3)	-0.005(3)	0.009(3)
C(124)	0.041(3)	0.068(3)	0.069(3)	-0.012(3)	-0.004(3)	-0.004(3)
C(125)	0.053(3)	0.054(3)	0.073(3)	0.005(3)	0.006(3)	-0.005(3)
C(126)	0.043(3)	0.054(3)	0.062(3)	-0.002(3)	-0.006(3)	0.002(3)
C(131)	0.043(3)	0.047(3)	0.040(3)	0.002(3)	0.016(2)	0.001(3)
C(132)	0.065(3)	0.043(3)	0.051(3)	-0.009(3)	0.000(3)	0.006(3)
C(133)	0.091(3)	0.047(3)	0.064(3)	-0.019(3)	0.009(3)	0.009(3)
C(134)	0.070(3)	0.054(3)	0.062(3)	0.005(3)	0.014(3)	0.027(3)
C(135)	0.042(3)	0.066(3)	0.054(3)	0.003(3)	0.008(3)	0.010(3)
C(136)	0.041(3)	0.049(3)	0.049(3)	0.008(3)	0.001(2)	0.001(3)
C(141)	0.030(3)	0.049(3)	0.045(3)	-0.001(3)	-0.005(2)	-0.002(3)
C(142)	0.039(3)	0.056(3)	0.053(3)	0.009(3)	-0.006(3)	-0.004(3)
C(143)	0.052(3)	0.070(3)	0.051(3)	-0.008(3)	0.006(3)	-0.007(3)
C(144)	0.057(3)	0.087(3)	0.041(3)	0.002(3)	0.005(3)	-0.029(3)
C(145)	0.069(3)	0.058(3)	0.049(3)	0.019(3)	-0.008(3)	-0.023(3)
C(146)	0.049(3)	0.046(3)	0.055(3)	0.003(3)	-0.003(3)	0.001(3)

Table 93. Anisotropic temperature factors ($\text{\AA}^2$) for 1MPzBTB.Me₂CO (with e.s.d's in parentheses - continued).

Atom	U11	U22	U33	U23	U13	U12
N(1)	0.058(3)	0.038(2)	0.051(2)	0.006(2)	0.020(2)	0.012(2)
C(N1)	0.074(3)	0.059(3)	0.068(3)	0.026(3)	0.024(3)	0.014(3)
C(1)	0.044(3)	0.046(3)	0.059(3)	0.000(3)	0.007(2)	0.003(2)
C(2)	0.046(3)	0.048(3)	0.052(3)	0.001(3)	0.002(2)	0.009(2)
C(3)	0.044(3)	0.043(3)	0.048(3)	-0.001(3)	-0.003(2)	-0.002(2)
C(4)	0.036(3)	0.047(3)	0.062(3)	0.001(3)	0.004(2)	-0.001(2)
N(2)	0.033(2)	0.045(2)	0.044(2)	-0.002(2)	0.004(2)	0.006(2)
B(2)	0.044(3)	0.042(3)	0.043(3)	-0.003(3)	0.006(3)	-0.004(3)
C(211)	0.052(3)	0.038(3)	0.049(3)	0.004(3)	0.013(2)	0.002(3)
C(212)	0.071(3)	0.065(3)	0.056(3)	-0.006(3)	0.023(3)	-0.010(3)
C(213)	0.108(3)	0.090(3)	0.054(3)	-0.019(3)	0.028(3)	-0.025(3)
C(214)	0.103(3)	0.104(3)	0.068(3)	-0.011(3)	0.052(3)	-0.001(3)
C(215)	0.063(3)	0.131(4)	0.072(3)	0.003(3)	0.026(3)	0.004(3)
C(216)	0.051(3)	0.089(3)	0.066(3)	-0.004(3)	0.017(3)	-0.001(3)
C(221)	0.031(3)	0.048(3)	0.053(3)	0.009(3)	-0.002(2)	0.008(2)
C(222)	0.101(3)	0.054(3)	0.055(3)	-0.004(3)	0.003(3)	-0.021(3)
C(223)	0.125(3)	0.058(3)	0.088(3)	0.001(3)	0.028(3)	-0.032(3)
C(224)	0.073(3)	0.057(3)	0.086(3)	-0.017(3)	-0.001(3)	-0.015(3)
C(225)	0.067(3)	0.072(3)	0.057(3)	-0.012(3)	-0.004(3)	-0.001(3)
C(226)	0.060(3)	0.059(3)	0.049(3)	0.000(3)	0.000(3)	-0.010(3)
C(231)	0.044(3)	0.040(3)	0.042(3)	-0.006(3)	0.003(2)	0.002(2)
C(232)	0.043(3)	0.058(3)	0.056(3)	0.011(3)	0.001(3)	0.008(3)
C(233)	0.058(3)	0.071(3)	0.074(3)	0.011(3)	-0.010(3)	0.005(3)
C(234)	0.049(3)	0.060(3)	0.091(3)	-0.009(3)	-0.012(3)	0.017(3)
C(235)	0.053(3)	0.056(3)	0.086(3)	-0.005(3)	0.023(3)	0.000(3)
C(236)	0.038(3)	0.055(3)	0.049(3)	0.006(3)	0.002(2)	0.006(3)
O(1)	0.110(3)	0.067(3)	0.066(2)	0.008(2)	0.017(2)	0.000(2)
C(11)	0.075(3)	0.047(3)	0.076(3)	0.014(3)	0.003(3)	0.006(3)
C(12)	0.313(4)	0.109(4)	0.146(4)	0.038(3)	-0.103(4)	-0.050(4)
C(13)	0.101(3)	0.183(4)	0.259(4)	0.153(3)	0.005(3)	-0.021(3)

Table 94. Hydrogen atom positional parameters for BPTB.

Atom	x/a	y/b	z/c	U_{iso}
H(N2')	0.2709	0.6917	0.5420	0.073
H(12)	0.0244	0.5550	0.9216	0.057
H(13)	-0.1353	0.4344	0.9650	0.074
H(14)	-0.3987	0.4607	0.9640	0.083
H(15)	-0.5000	0.6109	0.9209	0.082
H(16)	-0.3395	0.7338	0.8783	0.063
H(22)	0.2140	0.6841	0.9496	0.058
H(23)	0.2929	0.7280	1.0627	0.071
H(24)	0.1687	0.8554	1.1205	0.070
H(25)	-0.0378	0.9379	1.0648	0.064
H(26)	-0.1247	0.8891	0.9533	0.055
H(32)	-0.2450	0.7131	0.7689	0.057
H(33)	-0.3558	0.8250	0.6883	0.072
H(34)	-0.2879	0.9938	0.6918	0.079
H(35)	-0.1120	1.0497	0.7774	0.072
H(36)	-0.0000	0.9390	0.8584	0.058
H(42)	0.0213	0.5609	0.8017	0.074
H(43)	0.2271	0.5153	0.7348	0.106
H(44)	0.4259	0.6295	0.7202	0.129
H(45)	0.4207	0.7855	0.7730	0.117
H(46)	0.2211	0.8285	0.8420	0.080
H(3)	0.2203	0.4258	0.5213	0.084
H(4)	0.0293	0.3391	0.5742	0.085
H(5)	-0.1359	0.4253	0.6450	0.087
H(6)	-0.0972	0.5978	0.6643	0.077
H(3')	0.3580	0.8494	0.5440	0.090
H(4')	0.2469	0.9645	0.6181	0.097
H(5')	0.0536	0.9093	0.6883	0.094
H(6')	-0.0314	0.7446	0.6822	0.078

Table 95. Anisotropic temperature factors ($\text{\AA}^2$) for BPTB (with e.s.d's in parentheses).

Atom	U11	U22	U33	U23	U13	U12
B	0.036(2)	0.035(3)	0.042(3)	-0.003(2)	-0.004(2)	-0.002(2)
C(11)	0.044(3)	0.038(2)	0.037(2)	-0.004(2)	-0.006(2)	-0.003(2)
C(12)	0.057(3)	0.039(3)	0.045(3)	-0.008(2)	-0.013(2)	0.005(2)
C(13)	0.090(4)	0.043(3)	0.051(3)	-0.011(3)	-0.013(3)	0.005(2)
C(14)	0.085(4)	0.063(3)	0.059(3)	-0.033(3)	-0.001(3)	0.011(3)
C(15)	0.054(3)	0.080(4)	0.071(3)	-0.017(3)	0.008(3)	0.007(3)
C(16)	0.049(3)	0.046(3)	0.063(3)	-0.004(2)	0.009(2)	0.005(2)
C(21)	0.041(2)	0.030(2)	0.043(2)	-0.008(2)	0.002(2)	0.004(2)
C(22)	0.048(3)	0.038(2)	0.057(3)	-0.004(2)	-0.010(2)	0.003(2)
C(23)	0.064(3)	0.053(3)	0.057(3)	-0.012(3)	-0.018(2)	0.007(3)
C(24)	0.065(3)	0.064(3)	0.046(3)	-0.024(3)	-0.007(2)	-0.005(3)
C(25)	0.058(3)	0.052(3)	0.050(3)	-0.013(2)	0.008(2)	-0.013(2)
C(26)	0.044(3)	0.045(2)	0.048(3)	-0.009(2)	0.006(2)	-0.002(2)
C(31)	0.034(2)	0.046(3)	0.039(2)	0.001(2)	0.005(2)	0.001(2)
C(32)	0.045(3)	0.054(3)	0.042(2)	0.002(2)	0.000(2)	0.003(2)
C(33)	0.053(3)	0.085(4)	0.042(3)	0.004(3)	-0.002(2)	0.001(3)
C(34)	0.062(3)	0.085(4)	0.050(3)	0.022(3)	0.004(2)	0.023(3)
C(35)	0.064(3)	0.044(3)	0.072(3)	0.007(2)	0.016(3)	0.024(3)
C(36)	0.046(3)	0.041(3)	0.058(3)	-0.003(2)	0.001(2)	0.012(2)
C(41)	0.049(3)	0.049(3)	0.037(2)	0.011(2)	-0.006(2)	-0.001(2)
C(42)	0.074(3)	0.063(3)	0.048(3)	0.024(3)	-0.003(2)	-0.001(2)
C(43)	0.109(5)	0.098(5)	0.057(3)	0.063(4)	-0.004(3)	-0.010(3)
C(44)	0.074(4)	0.170(8)	0.080(4)	0.061(5)	0.016(3)	0.009(5)
C(45)	0.048(3)	0.161(6)	0.084(4)	0.011(4)	0.013(3)	0.004(4)
C(46)	0.044(3)	0.092(4)	0.065(3)	-0.007(3)	0.009(2)	-0.003(3)
C(1)	0.045(3)	0.059(3)	0.049(3)	0.008(3)	0.001(2)	0.005(2)
N(2)	0.056(3)	0.061(3)	0.072(3)	0.008(2)	0.020(2)	-0.006(2)
C(3)	0.071(4)	0.054(3)	0.087(4)	0.007(3)	0.015(3)	-0.003(3)
C(4)	0.062(3)	0.067(3)	0.084(4)	-0.007(3)	0.004(3)	0.009(3)
C(5)	0.055(3)	0.087(4)	0.074(3)	-0.008(3)	0.006(3)	0.012(3)
C(6)	0.045(3)	0.084(4)	0.064(3)	0.002(3)	0.008(2)	0.006(3)
C(1')	0.045(3)	0.064(3)	0.046(3)	0.019(2)	0.008(2)	0.007(2)
N(2')	0.074(3)	0.055(3)	0.056(2)	0.011(2)	0.020(2)	-0.000(2)
C(3')	0.096(4)	0.057(3)	0.073(3)	-0.000(3)	0.023(3)	0.000(3)
C(4')	0.112(5)	0.060(3)	0.069(3)	0.012(3)	0.005(3)	-0.011(3)
C(5')	0.088(4)	0.086(4)	0.062(3)	0.025(4)	0.008(3)	-0.016(3)
C(6')	0.060(3)	0.078(4)	0.056(3)	0.016(3)	0.009(2)	-0.009(3)

Table 96. Hydrogen atom positional parameters for PTB.

Atom	x/a	y/b	z/c	U_{iso}
H(N)	-0.320	-0.018	0.094	0.073
H(12)	-0.187	0.110	0.107	0.054
H(13)	-0.173	0.253	0.031	0.057
H(14)	0.009	0.361	0.074	0.064
H(15)	0.176	0.325	0.193	0.063
H(16)	0.164	0.179	0.268	0.054
H(22)	-0.209	0.165	0.237	0.056
H(23)	-0.397	0.149	0.278	0.075
H(24)	-0.463	-0.010	0.312	0.087
H(25)	-0.330	-0.153	0.311	0.077
H(26)	-0.139	-0.136	0.275	0.061
H(32)	-0.075	-0.001	0.077	0.060
H(33)	-0.060	-0.146	0.002	0.077
H(34)	0.029	-0.298	0.068	0.073
H(35)	0.099	-0.302	0.209	0.062
H(36)	0.085	-0.157	0.282	0.058
H(42)	0.245	0.011	0.277	0.064
H(43)	0.409	0.014	0.402	0.082
H(44)	0.354	0.024	0.522	0.091
H(45)	0.132	0.037	0.516	0.083
H(46)	-0.032	0.036	0.392	0.057
H(2)	-0.392	0.265	0.068	0.089
H(3)	-0.587	0.332	0.079	0.096
H(4)	-0.749	0.224	0.097	0.094
H(5)	-0.814	0.049	0.116	0.109
H(6)	-0.767	-0.121	0.125	0.108
H(7)	-0.613	-0.256	0.124	0.106
H(8)	-0.409	-0.306	0.120	0.108
H(9)	-0.252	-0.182	0.109	0.092

Table 97. Anisotropic temperature factors ($\text{\AA}^2$) for PTB (with e.s.d's in parentheses).

Atom	U11	U22	U33	U23	U13	U12
B	0.034(4)	0.036(4)	0.045(4)	0.004(3)	0.014(3)	-0.002(3)
C(11)	0.037(3)	0.041(4)	0.046(4)	-0.004(3)	0.019(3)	0.000(3)
C(12)	0.047(4)	0.038(4)	0.051(3)	0.000(3)	0.015(3)	0.001(3)
C(13)	0.060(4)	0.042(4)	0.043(3)	0.003(3)	0.020(3)	0.012(3)
C(14)	0.068(4)	0.034(4)	0.068(4)	0.001(3)	0.036(4)	-0.003(3)
C(15)	0.049(4)	0.045(4)	0.068(4)	-0.005(4)	0.024(3)	-0.007(3)
C(16)	0.044(4)	0.038(4)	0.056(4)	0.000(3)	0.019(3)	0.002(3)
C(21)	0.037(3)	0.044(3)	0.038(3)	0.001(3)	0.010(2)	-0.006(3)
C(22)	0.042(3)	0.052(4)	0.044(3)	0.000(3)	0.010(3)	0.002(3)
C(23)	0.048(4)	0.079(5)	0.062(4)	-0.001(4)	0.021(3)	0.016(4)
C(24)	0.054(4)	0.110(6)	0.059(4)	0.006(4)	0.029(3)	-0.008(4)
C(25)	0.059(4)	0.076(5)	0.061(4)	0.013(4)	0.025(3)	-0.012(4)
C(26)	0.046(4)	0.056(4)	0.053(4)	0.005(3)	0.021(3)	-0.005(3)
C(31)	0.033(3)	0.042(4)	0.046(4)	-0.001(3)	0.017(3)	-0.004(3)
C(32)	0.055(4)	0.054(4)	0.042(4)	-0.001(3)	0.018(3)	0.005(3)
C(33)	0.066(4)	0.069(5)	0.057(4)	-0.014(4)	0.017(3)	0.005(4)
C(34)	0.062(4)	0.053(4)	0.075(5)	-0.024(4)	0.031(4)	-0.008(3)
C(35)	0.055(4)	0.038(4)	0.068(4)	-0.001(3)	0.029(3)	-0.003(3)
C(36)	0.050(4)	0.044(4)	0.053(4)	-0.002(3)	0.019(3)	-0.002(3)
C(41)	0.047(4)	0.033(3)	0.050(3)	0.005(3)	0.013(3)	0.003(3)
C(42)	0.043(4)	0.046(4)	0.065(4)	-0.006(3)	0.008(3)	0.002(3)
C(43)	0.051(4)	0.055(4)	0.084(5)	-0.002(4)	-0.004(4)	0.003(3)
C(44)	0.082(5)	0.063(5)	0.058(4)	-0.003(4)	-0.014(4)	-0.008(4)
C(45)	0.086(5)	0.065(5)	0.049(4)	-0.005(4)	0.010(4)	-0.010(4)
C(46)	0.051(4)	0.042(4)	0.044(3)	-0.001(3)	0.005(3)	-0.003(3)
N(1)	0.056(3)	0.060(4)	0.053(3)	0.004(3)	0.006(3)	-0.009(3)
C(2)	0.084(5)	0.057(5)	0.075(5)	-0.002(4)	0.012(4)	-0.013(4)
C(3)	0.087(6)	0.070(5)	0.080(5)	-0.021(4)	0.019(5)	0.003(5)
C(4)	0.068(5)	0.096(6)	0.070(5)	-0.028(5)	0.017(4)	0.011(5)
C(5)	0.062(5)	0.138(8)	0.079(5)	-0.006(6)	0.032(4)	-0.017(6)
C(6)	0.074(6)	0.123(8)	0.080(6)	0.001(6)	0.034(4)	-0.039(6)
C(7)	0.106(7)	0.089(7)	0.062(5)	0.002(5)	0.014(5)	-0.043(6)
C(8)	0.132(7)	0.053(5)	0.065(5)	0.012(4)	0.000(5)	-0.023(6)
C(9)	0.086(5)	0.073(6)	0.059(4)	0.011(4)	0.005(4)	0.011(5)
N(10)	0.062(4)	0.059(4)	0.054(3)	0.008(3)	0.006(3)	-0.010(3)
C(1.1)	0.047(4)	0.067(5)	0.041(4)	-0.001(3)	0.008(3)	-0.010(4)
C(1.2)	0.050(4)	0.067(5)	0.042(4)	-0.004(3)	0.013(3)	-0.012(4)
C(1.3)	0.059(5)	0.088(6)	0.053(4)	-0.016(4)	0.020(4)	-0.013(4)
C(1.4)	0.082(5)	0.072(5)	0.053(4)	0.000(4)	0.020(4)	-0.031(5)

Table 98. Hydrogen atom positional parameters for 2MTB.MeCN.

Atom	x/a	y/b	z/c	U_{15c}
H(12)	0.443(0)	0.048(0)	0.617(0)	0.085(3)
H(13)	0.307(0)	-0.073(0)	0.616(0)	0.106(3)
H(14)	0.324(0)	-0.167(0)	0.766(0)	0.107(3)
H(15)	0.468(0)	-0.130(0)	0.920(0)	0.095(3)
H(16)	0.604(0)	-0.006(0)	0.919(0)	0.073(3)
H(22)	0.779(0)	-0.037(0)	0.856(0)	0.077(3)
H(23)	0.884(0)	-0.151(0)	0.793(0)	0.065(3)
H(24)	0.861(0)	-0.153(0)	0.617(0)	0.096(3)
H(25)	0.734(0)	-0.039(0)	0.505(0)	0.100(3)
H(26)	0.635(0)	0.079(0)	0.569(0)	0.095(3)
H(32)	0.724(0)	0.234(0)	0.662(0)	0.047(3)
H(33)	0.655(0)	0.390(0)	0.568(0)	0.110(3)
H(34)	0.479(1)	0.448(0)	0.549(0)	0.104(3)
H(35)	0.371(0)	0.360(0)	0.629(0)	0.127(3)
H(36)	0.435(0)	0.204(0)	0.716(0)	0.083(3)
H(42)	0.848(0)	0.144(0)	0.851(0)	0.081(3)
H(43)	0.950(0)	0.217(0)	1.010(0)	0.115(3)
H(44)	0.860(1)	0.269(0)	1.125(0)	0.089(3)
H(45)	0.668(0)	0.252(0)	1.076(0)	0.095(3)
H(46)	0.567(0)	0.176(0)	0.916(0)	0.093(3)
H(N11)	0.123(0)	0.131(0)	0.786(0)	0.119(3)
H(N12)	0.125(0)	0.010(0)	0.764(0)	0.108(3)
H(111)	-0.005(1)	0.046(0)	0.833(1)	0.150(3)
H(112)	0.090(1)	0.100(0)	0.936(1)	0.140(3)
H(113)	0.095(1)	-0.028(0)	0.915(1)	0.146(3)
H(121)	0.300(0)	0.077(0)	0.824(0)	0.125(3)
H(122)	0.277(0)	-0.012(0)	0.904(0)	0.134(3)
H(123)	0.272(0)	0.116(0)	0.930(0)	0.143(3)
H(221)	0.023(0)	-0.337(0)	0.655(0)	0.148(3)
H(222)	0.132(0)	-0.323(0)	0.615(0)	0.155(3)
H(223)	0.007(0)	-0.278(0)	0.542(0)	0.148(3)

Table 99. Anisotropic temperature factors ($\text{\AA}^2$) for 2MTB.MeCN (with e.s.d.'s in parentheses).

Atom	U11	U22	U33	U23	U13	U12
B	0.040(2)	0.052(2)	0.039(2)	0.003(2)	0.016(2)	0.000(2)
C(11)	0.049(2)	0.047(2)	0.048(2)	0.005(2)	0.023(2)	0.006(2)
C(12)	0.069(3)	0.065(3)	0.053(2)	0.002(2)	0.016(2)	-0.013(2)
C(13)	0.070(3)	0.073(3)	0.072(3)	0.005(2)	0.012(2)	-0.023(2)
C(14)	0.060(3)	0.059(2)	0.094(3)	0.008(2)	0.030(2)	-0.007(2)
C(15)	0.058(2)	0.065(3)	0.083(3)	0.028(2)	0.026(2)	0.004(2)
C(16)	0.051(2)	0.061(2)	0.059(2)	0.016(2)	0.014(2)	0.000(2)
C(21)	0.041(2)	0.051(2)	0.049(2)	-0.002(2)	0.016(2)	-0.006(2)
C(22)	0.060(2)	0.062(2)	0.054(2)	-0.002(2)	0.016(2)	0.002(2)
C(23)	0.070(3)	0.063(3)	0.075(3)	-0.004(2)	0.016(2)	0.015(2)
C(24)	0.074(3)	0.078(3)	0.087(3)	-0.008(3)	0.039(2)	0.013(2)
C(25)	0.085(3)	0.081(3)	0.065(3)	-0.007(2)	0.041(2)	0.007(3)
C(26)	0.057(2)	0.068(3)	0.055(2)	-0.003(2)	0.026(2)	0.003(2)
C(31)	0.054(2)	0.048(2)	0.048(2)	0.002(2)	0.023(2)	-0.005(2)
C(32)	0.079(3)	0.061(3)	0.061(2)	-0.001(2)	0.039(2)	-0.008(2)
C(33)	0.119(3)	0.067(3)	0.063(3)	0.006(2)	0.047(2)	-0.021(3)
C(34)	0.112(3)	0.070(3)	0.069(3)	0.016(2)	0.016(3)	0.005(3)
C(35)	0.077(3)	0.069(3)	0.108(3)	0.027(3)	0.021(3)	0.011(2)
C(36)	0.061(3)	0.058(2)	0.077(3)	0.012(2)	0.022(2)	0.007(2)
C(41)	0.051(2)	0.046(2)	0.046(2)	0.006(2)	0.018(2)	-0.004(2)
C(42)	0.058(2)	0.068(3)	0.064(3)	-0.011(2)	0.014(2)	-0.012(2)
C(43)	0.078(3)	0.079(3)	0.071(3)	-0.007(3)	0.003(3)	-0.015(3)
C(44)	0.122(3)	0.071(3)	0.051(3)	-0.001(2)	0.011(3)	-0.038(3)
C(45)	0.114(3)	0.075(3)	0.067(3)	-0.009(2)	0.047(2)	-0.031(3)
C(46)	0.078(3)	0.067(3)	0.049(2)	-0.006(2)	0.029(2)	-0.017(2)
N(1)	0.120(3)	0.085(3)	0.076(2)	0.004(2)	0.017(2)	0.002(2)
C(N11)	0.151(3)	0.101(3)	0.145(3)	0.004(3)	0.071(3)	-0.017(3)
C(N12)	0.101(3)	0.112(3)	0.117(3)	-0.034(3)	-0.012(3)	0.023(3)
N(2)	0.096(3)	0.104(3)	0.107(3)	-0.019(3)	0.006(2)	-0.003(3)
C(N21)	0.048(2)	0.095(3)	0.082(3)	0.021(3)	0.015(2)	0.013(2)
C(N22)	0.105(3)	0.074(3)	0.140(3)	0.010(3)	0.024(3)	0.018(3)

Table 100. Hydrogen atom positional parameters for 2PiTB.

Atom	x/a	y/b	z/c	U _{iso}
H(12)	0.2932	0.8424	0.1894	0.058
H(13)	0.1711	0.9707	0.2298	0.065
H(14)	0.2362	1.1111	0.3272	0.071
H(15)	0.4250	1.1265	0.3852	0.071
H(16)	0.5471	1.0008	0.3442	0.063
H(22)	0.4211	0.8863	0.0726	0.068
H(23)	0.3612	0.7922	-0.0675	0.080
H(24)	0.3809	0.6088	-0.0712	0.081
H(25)	0.4602	0.5220	0.0662	0.071
H(26)	0.5181	0.6123	0.2087	0.059
H(32)	0.3942	0.6643	0.2993	0.059
H(33)	0.4079	0.5697	0.4398	0.080
H(34)	0.5500	0.6048	0.5660	0.086
H(35)	0.6821	0.7316	0.5476	0.074
H(36)	0.6690	0.8297	0.4072	0.060
H(42)	0.5712	1.0093	0.1719	0.067
H(43)	0.7400	1.0681	0.1321	0.083
H(44)	0.8990	0.9643	0.1598	0.096
H(45)	0.8862	0.7961	0.2248	0.084
H(46)	0.7182	0.7365	0.2668	0.063
H(N1)	0.1121	0.7819	0.5242	0.063
H(N2)	0.2261	0.7266	0.5621	0.063
H(1)	0.2571	0.7049	0.4047	0.072
H(1,11)	0.0633	0.6115	0.4597	0.090
H(1,12)	0.1338	0.5640	0.3767	0.090
H(1,13)	0.1937	0.5704	0.4911	0.090
H(1,21)	0.1438	0.8397	0.3392	0.093
H(1,22)	0.1055	0.7256	0.2850	0.093
H(1,23)	0.0327	0.7758	0.3653	0.093
H(2)	0.1999	0.9201	0.4642	0.065
H(2,11)	0.1609	0.9281	0.6179	0.082
H(2,12)	0.2816	0.8700	0.6590	0.082
H(2,13)	0.2800	0.9899	0.6101	0.082
H(2,21)	0.3970	0.8122	0.5453	0.098
H(2,22)	0.3905	0.9320	0.4958	0.098
H(2,23)	0.3506	0.8266	0.4285	0.098

Table 101. Anisotropic temperature factors ($\text{\AA}^2$) for 2PITB (with e.s.d.'s in parentheses).

Atom	U11	U22	U33	U23	U13	U12
B	0.042(7)	0.046(8)	0.041(8)	-0.012(7)	0.010(6)	-0.008(8)
C(11)	0.047(7)	0.038(7)	0.038(7)	0.006(6)	0.018(5)	0.005(5)
C(12)	0.035(6)	0.064(8)	0.045(7)	0.003(6)	0.002(5)	0.000(6)
C(13)	0.038(6)	0.061(8)	0.065(8)	0.010(7)	0.011(6)	0.005(7)
C(14)	0.046(8)	0.060(10)	0.080(10)	0.017(7)	0.022(7)	-0.000(7)
C(15)	0.049(7)	0.057(8)	0.069(9)	0.007(7)	0.011(7)	-0.023(7)
C(16)	0.041(6)	0.059(8)	0.059(8)	0.004(7)	0.011(6)	-0.011(6)
C(21)	0.028(6)	0.049(8)	0.058(8)	-0.003(6)	0.017(5)	-0.009(7)
C(22)	0.056(7)	0.057(8)	0.053(8)	-0.007(7)	-0.001(6)	-0.010(8)
C(23)	0.048(7)	0.080(10)	0.060(10)	0.009(8)	-0.006(6)	-0.004(8)
C(24)	0.051(8)	0.100(10)	0.050(10)	-0.017(8)	0.005(7)	-0.028(8)
C(25)	0.057(8)	0.051(8)	0.070(10)	-0.003(7)	0.025(7)	-0.021(8)
C(26)	0.043(7)	0.063(9)	0.044(8)	0.001(7)	0.017(6)	-0.011(7)
C(31)	0.047(6)	0.037(7)	0.038(7)	0.010(6)	0.016(5)	-0.006(6)
C(32)	0.045(6)	0.043(7)	0.063(9)	-0.002(6)	0.013(6)	-0.005(6)
C(33)	0.080(10)	0.055(8)	0.070(10)	-0.006(8)	0.030(8)	0.006(8)
C(34)	0.090(10)	0.060(10)	0.070(10)	0.014(8)	0.024(8)	0.027(8)
C(35)	0.065(8)	0.070(10)	0.042(8)	0.027(7)	0.002(6)	-0.002(7)
C(36)	0.045(7)	0.050(8)	0.051(8)	0.003(6)	0.004(6)	-0.007(7)
C(41)	0.043(6)	0.045(7)	0.026(6)	-0.000(6)	-0.001(5)	-0.005(5)
C(42)	0.053(8)	0.062(8)	0.052(8)	0.001(6)	0.016(6)	-0.001(7)
C(43)	0.090(9)	0.060(9)	0.064(8)	-0.019(8)	0.029(8)	-0.004(6)
C(44)	0.058(9)	0.110(10)	0.080(10)	-0.020(10)	0.018(8)	-0.021(9)
C(45)	0.030(7)	0.110(10)	0.067(9)	0.004(8)	0.007(6)	-0.030(8)
C(46)	0.039(6)	0.064(8)	0.053(7)	0.005(7)	0.003(6)	-0.003(6)
N(1)	0.047(5)	0.059(6)	0.056(6)	0.009(5)	0.008(4)	-0.008(5)
C(N1)	0.062(7)	0.080(10)	0.042(7)	-0.010(7)	0.017(6)	-0.019(7)
C(N11)	0.100(10)	0.058(9)	0.071(9)	-0.016(7)	0.012(7)	-0.012(7)
C(N12)	0.082(8)	0.100(10)	0.047(7)	-0.012(7)	-0.003(6)	0.009(7)
C(N2)	0.072(8)	0.035(7)	0.051(8)	-0.010(6)	-0.005(7)	0.004(6)
C(N21)	0.055(7)	0.054(8)	0.100(10)	-0.015(6)	0.023(7)	-0.027(7)
C(N22)	0.061(8)	0.100(10)	0.090(10)	-0.025(7)	0.046(7)	-0.028(8)

Table 102. Hydrogen atom positional parameters for AC7TB.

Atom	x/a	y/b	z/c	U_{iso}
H(12)	0.071	0.150	0.550	0.050
H(13)	0.187	0.024	0.456	0.060
H(14)	0.440	-0.040	0.305	0.062
H(15)	0.564	0.015	0.856	0.057
H(16)	0.449	0.142	0.950	0.047
H(22)	-0.033	0.097	0.744	0.051
H(23)	-0.310	0.097	0.665	0.072
H(24)	-0.449	1/4	0.637	0.078
H(32)	0.226	0.097	1.014	0.056
H(33)	0.274	0.097	1.275	0.080
H(34)	0.293	1/4	1.403	0.082
H(N1)	-0.096	1/4	0.938	0.052
H(N2)	0.012	1/4	1.113	0.052
H(1,1)	-0.119	0.100	1.020	0.081
H(1,2)	-0.289	0.163	0.988	0.081
H(2,1)	-0.239	0.065	1.183	0.093
H(2,2)	-0.066	0.125	1.277	0.093
H(2*,1)	-0.008	0.143	1.267	0.079
H(2*,2)	-0.170	0.070	1.222	0.079
H(3,1)	-0.385	0.192	1.241	0.089
H(3,2)	-0.212	0.251	1.335	0.089
H(3*,1)	-0.298	0.181	1.325	0.127
H(3*,2)	-0.136	0.254	1.369	0.127

Table 103. Anisotropic temperature factors ($\text{\AA}^2$) for AC7TB (with e.s.d.'s in parentheses).

Atom	U11	U22	U33	U23	U13	U12
B	0.039(1)	0.035(1)	0.041(1)	0.000(0)	0.011(1)	0.000(0)
C(11)	0.041(1)	0.036(1)	0.042(1)	0.003(1)	0.016(1)	-0.004(1)
C(12)	0.059(1)	0.051(1)	0.047(1)	0.003(1)	0.018(1)	0.008(1)
C(13)	0.080(1)	0.055(1)	0.052(1)	-0.011(1)	0.029(1)	-0.001(1)
C(14)	0.068(1)	0.047(1)	0.077(1)	-0.006(1)	0.043(1)	0.002(1)
C(15)	0.048(1)	0.048(1)	0.077(1)	-0.005(1)	0.025(1)	0.006(1)
C(16)	0.040(1)	0.048(1)	0.059(1)	-0.006(1)	0.014(1)	-0.002(1)
C(21)	0.045(1)	0.043(1)	0.035(1)	0.000(0)	0.013(1)	0.000(0)
C(22)	0.050(1)	0.060(1)	0.052(1)	-0.011(1)	0.018(1)	-0.009(1)
C(23)	0.050(1)	0.103(2)	0.063(1)	-0.027(1)	0.018(1)	-0.026(1)
C(24)	0.036(1)	0.127(2)	0.056(1)	0.000(0)	0.009(1)	0.000(0)
C(31)	0.034(1)	0.045(1)	0.049(1)	0.000(0)	0.015(1)	0.000(0)
C(32)	0.061(1)	0.063(1)	0.054(1)	0.016(1)	0.023(1)	0.019(1)
C(33)	0.068(1)	0.116(2)	0.057(1)	0.032(1)	0.025(1)	0.031(1)
C(34)	0.058(2)	0.132(2)	0.041(1)	0.000(0)	0.009(1)	0.000(0)
N	0.053(1)	0.059(1)	0.052(1)	0.000(0)	0.025(1)	0.000(0)
C(1)	0.092(1)	0.071(1)	0.092(1)	-0.023(1)	0.046(1)	-0.026(1)
C(2)	0.098(2)	0.061(2)	0.125(2)	-0.007(2)	0.083(1)	-0.027(2)
C(2*)	0.071(2)	0.030(2)	0.111(2)	0.034(2)	0.047(2)	-0.008(2)
C(3)	0.106(2)	0.080(2)	0.097(2)	-0.009(2)	0.073(1)	-0.016(2)
C(3*)	0.192(2)	0.075(2)	0.106(2)	-0.034(2)	0.052(2)	0.011(2)

Table 104. Hydrogen atom positional parameters for [1-Ad]TBw.

Atom	x/a	y/b	z/c	U_{iso}
H(112)	0.931	0.988	0.885	0.053
H(113)	0.810	1.024	0.738	0.073
H(114)	0.648	0.950	0.703	0.067
H(115)	0.606	0.839	0.815	0.066
H(116)	0.727	0.804	0.962	0.055
H(122)	0.998	1.042	1.087	0.057
H(123)	0.943	1.158	1.184	0.081
H(124)	0.799	1.136	1.263	0.083
H(125)	0.709	0.997	1.245	0.075
H(126)	0.764	0.881	1.149	0.062
H(132)	1.086	0.920	1.175	0.062
H(133)	1.263	0.927	1.161	0.091
H(134)	1.313	0.895	1.005	0.105
H(135)	1.185	0.856	0.864	0.100
H(136)	1.008	0.848	0.879	0.063
H(142)	0.881	0.717	0.943	0.064
H(143)	0.876	0.570	1.008	0.075
H(144)	0.897	0.547	1.184	0.076
H(145)	0.923	0.671	1.294	0.083
H(146)	0.928	0.819	1.229	0.067
H(212)	0.555	1.266	0.613	0.052
H(213)	0.693	1.301	0.747	0.071
H(214)	0.859	1.239	0.751	0.069
H(215)	0.888	1.141	0.621	0.074
H(216)	0.750	1.105	0.487	0.051
H(222)	0.633	1.009	0.526	0.063
H(223)	0.624	0.864	0.452	0.081
H(224)	0.541	0.845	0.283	0.095
H(225)	0.468	0.970	0.187	0.081
H(226)	0.477	1.114	0.261	0.060
H(232)	0.376	1.233	0.335	0.075
H(233)	0.205	1.238	0.369	0.094
H(234)	0.172	1.185	0.525	0.081
H(235)	0.309	1.128	0.647	0.072
H(236)	0.480	1.123	0.613	0.054
H(242)	0.495	1.345	0.433	0.046
H(243)	0.545	1.463	0.336	0.057
H(244)	0.655	1.434	0.219	0.056
H(245)	0.714	1.286	0.199	0.060
H(246)	0.663	1.167	0.296	0.047

Table 104. Hydrogen atom positional parameters for [1-Ad]TBw (continued).

Atom	x/a	y/b	z/c	U _{iso}
H(N11)	0.226	0.806	0.459	0.056
H(N12)	0.263	0.841	0.572	0.056
H(N13)	0.267	0.907	0.479	0.056
H(12,1)	0.174	0.956	0.641	0.067
H(12,2)	0.178	1.018	0.000	0.067
H(12',1)	0.069	0.761	0.508	0.074
H(12',2)	0.109	0.806	0.622	0.074
H(12'',1)	0.068	0.848	0.364	0.058
H(12'',2)	0.115	0.954	0.372	0.058
H(13)	0.033	1.063	0.608	0.089
H(13')	-0.076	0.803	0.583	0.108
H(13'')	-0.070	0.955	0.335	0.080
H(14,1)	0.015	0.923	0.686	0.133
H(14,2)	-0.098	0.960	0.614	0.133
H(14',1)	-0.162	0.893	0.450	0.106
H(14',2)	-0.088	0.814	0.406	0.106
H(14'',1)	0.017	1.068	0.433	0.097
H(14'',2)	-0.099	1.043	0.468	0.097
H(N21)	0.296	0.523	0.083	0.052
H(N22)	0.281	0.535	-0.035	0.052
H(N23)	0.243	0.612	0.032	0.052
H(22,1)	0.472	0.488	0.085	0.069
H(22,2)	0.456	0.511	-0.039	0.069
H(22',1)	0.380	0.648	-0.104	0.069
H(22',2)	0.341	0.725	-0.027	0.069
H(22'',1)	0.365	0.695	0.148	0.065
H(22'',2)	0.419	0.597	0.194	0.065
H(23)	0.633	0.534	0.043	0.082
H(23')	0.502	0.769	-0.070	0.084
H(23'')	0.541	0.716	0.225	0.065
H(24,1)	0.649	0.677	-0.023	0.101
H(24,2)	0.552	0.619	-0.097	0.101
H(24',1)	0.596	0.788	0.091	0.071
H(24',2)	0.468	0.804	0.087	0.071
H(24'',1)	0.672	0.649	0.157	0.076
H(24'',2)	0.599	0.572	0.199	0.076
H(O11)	0.622	0.474	0.630	0.090
H(O12)	0.713	0.529	0.612	0.090
H(O21)	0.896	0.193	0.890	0.071
H(O22)	0.821	0.239	0.945	0.071

Table 105. Anisotropic temperature factors ($\text{\AA}^2$) for [1-Ad]TBw (with e.s.d.'s in parentheses).

Atom	U11	U22	U33	U23	U13	U12
B(1)	0.042(2)	0.039(2)	0.056(2)	0.013(2)	0.007(2)	0.009(2)
C(111)	0.064(2)	0.045(2)	0.051(2)	-0.003(2)	0.009(2)	0.013(2)
C(112)	0.065(2)	0.052(2)	0.052(2)	0.007(2)	0.027(2)	0.006(2)
C(113)	0.092(2)	0.070(2)	0.062(2)	0.017(2)	0.032(2)	0.015(2)
C(114)	0.073(2)	0.090(2)	0.046(2)	-0.004(2)	-0.002(2)	0.016(2)
C(115)	0.066(2)	0.080(2)	0.067(2)	-0.002(2)	0.002(2)	-0.010(2)
C(116)	0.053(2)	0.050(2)	0.068(2)	-0.003(2)	0.013(2)	-0.003(2)
C(121)	0.037(2)	0.063(2)	0.042(2)	0.006(2)	0.003(2)	0.014(2)
C(122)	0.067(2)	0.050(2)	0.067(2)	-0.009(2)	0.014(2)	0.003(2)
C(123)	0.092(3)	0.064(2)	0.093(3)	-0.003(2)	0.008(2)	0.016(2)
C(124)	0.084(2)	0.094(3)	0.082(3)	-0.008(2)	0.014(2)	0.037(2)
C(125)	0.065(2)	0.112(3)	0.047(2)	0.011(2)	0.017(2)	0.032(2)
C(126)	0.055(2)	0.087(2)	0.049(2)	0.010(2)	0.013(2)	0.016(2)
C(131)	0.046(2)	0.042(2)	0.086(2)	0.019(2)	0.019(2)	0.010(2)
C(132)	0.047(2)	0.068(2)	0.082(2)	0.010(2)	-0.009(2)	-0.005(2)
C(133)	0.074(2)	0.056(2)	0.138(3)	0.029(2)	-0.002(2)	-0.013(2)
C(134)	0.086(2)	0.071(2)	0.161(3)	0.048(2)	0.038(2)	0.011(2)
C(135)	0.106(3)	0.088(3)	0.124(3)	0.014(3)	0.063(2)	0.027(2)
C(136)	0.058(2)	0.076(2)	0.071(2)	0.009(2)	0.026(2)	0.021(2)
C(141)	0.034(2)	0.051(2)	0.062(2)	0.007(2)	0.010(2)	0.007(2)
C(142)	0.074(2)	0.048(2)	0.076(2)	0.007(2)	0.027(2)	0.007(2)
C(143)	0.059(2)	0.058(2)	0.110(3)	-0.006(2)	0.023(2)	0.003(2)
C(144)	0.076(2)	0.073(2)	0.091(3)	0.029(2)	0.013(2)	0.003(2)
C(145)	0.097(3)	0.080(2)	0.083(2)	0.032(2)	0.004(2)	-0.005(2)
C(146)	0.088(2)	0.051(2)	0.067(2)	0.024(2)	-0.015(2)	-0.001(2)
B(2)	0.054(2)	0.031(2)	0.044(2)	-0.002(2)	0.008(2)	-0.002(2)
C(211)	0.060(2)	0.039(2)	0.029(2)	0.001(2)	0.002(2)	-0.004(2)
C(212)	0.071(2)	0.054(2)	0.034(2)	-0.004(2)	0.013(2)	-0.015(2)
C(213)	0.084(2)	0.084(2)	0.054(2)	-0.001(2)	0.021(2)	-0.031(2)
C(214)	0.087(2)	0.081(2)	0.043(2)	0.018(2)	-0.015(2)	-0.025(2)
C(215)	0.072(2)	0.068(2)	0.092(2)	0.014(2)	-0.018(2)	0.009(2)
C(216)	0.051(2)	0.048(2)	0.062(2)	0.006(2)	0.006(2)	0.010(2)
C(221)	0.046(2)	0.048(2)	0.049(2)	-0.005(2)	0.026(2)	-0.001(2)
C(222)	0.071(2)	0.056(2)	0.070(2)	0.003(2)	0.027(2)	-0.004(2)
C(223)	0.096(2)	0.055(2)	0.101(2)	0.012(2)	0.045(2)	-0.013(2)
C(224)	0.111(2)	0.088(3)	0.099(3)	-0.030(2)	0.059(2)	-0.017(2)
C(225)	0.102(2)	0.091(3)	0.057(2)	-0.015(2)	0.036(2)	-0.028(2)
C(226)	0.085(2)	0.056(2)	0.049(2)	-0.014(2)	0.030(2)	-0.026(2)

Table 105. Anisotropic temperature factors ($\text{\AA}^2$) for [1-Ad]TBw (with e.s.d.'s in parentheses - continued).

Atom	U11	U22	U33	U23	U13	U12
C(231)	0.054(2)	0.039(2)	0.044(2)	0.000(2)	0.018(2)	-0.004(2)
C(232)	0.048(2)	0.087(2)	0.093(2)	0.022(2)	0.019(2)	0.010(2)
C(233)	0.066(2)	0.110(3)	0.113(3)	0.020(2)	0.035(2)	0.026(2)
C(234)	0.084(2)	0.071(2)	0.103(2)	-0.011(2)	0.017(2)	0.005(2)
C(235)	0.079(2)	0.081(2)	0.071(2)	-0.015(2)	0.033(2)	-0.031(2)
C(236)	0.054(2)	0.073(2)	0.043(2)	-0.010(2)	0.006(2)	-0.018(2)
C(241)	0.040(2)	0.040(2)	0.032(2)	-0.006(2)	-0.001(2)	-0.003(2)
C(242)	0.055(2)	0.043(2)	0.048(2)	0.001(2)	0.001(2)	0.007(2)
C(243)	0.051(2)	0.048(2)	0.076(2)	0.006(2)	-0.002(2)	0.005(2)
C(244)	0.070(2)	0.062(2)	0.051(2)	0.018(2)	-0.005(2)	-0.017(2)
C(245)	0.076(2)	0.069(2)	0.044(2)	0.003(2)	0.012(2)	-0.021(2)
C(246)	0.056(2)	0.053(2)	0.043(2)	-0.008(2)	0.016(2)	-0.013(2)
N(1)	0.061(2)	0.051(2)	0.062(2)	-0.004(2)	0.007(2)	-0.002(2)
C(11)	0.041(2)	0.043(2)	0.048(2)	-0.008(2)	0.007(2)	-0.003(2)
C(12)	0.059(2)	0.078(2)	0.074(2)	-0.032(2)	-0.004(2)	0.012(2)
C(12')	0.080(2)	0.092(2)	0.061(2)	-0.001(2)	0.010(2)	-0.010(2)
C(12'')	0.062(2)	0.072(2)	0.043(2)	-0.002(2)	0.001(2)	0.009(2)
C(13)	0.094(3)	0.100(2)	0.089(3)	-0.046(2)	0.007(2)	0.024(2)
C(13')	0.110(3)	0.116(3)	0.115(3)	-0.003(3)	0.048(2)	-0.031(3)
C(13'')	0.084(2)	0.093(2)	0.082(2)	-0.023(2)	-0.018(2)	0.030(2)
C(14)	0.108(3)	0.179(3)	0.125(3)	-0.029(3)	0.039(3)	0.023(3)
C(14')	0.076(3)	0.134(3)	0.122(3)	-0.011(3)	-0.004(2)	0.009(3)
C(14'')	0.078(2)	0.121(3)	0.106(3)	-0.015(3)	0.003(2)	0.033(2)
N(2)	0.055(2)	0.060(2)	0.051(2)	-0.005(2)	0.011(2)	-0.013(2)
C(21)	0.060(2)	0.048(2)	0.027(2)	-0.008(2)	0.005(2)	-0.009(2)
C(22)	0.067(2)	0.059(2)	0.092(2)	-0.017(2)	0.013(2)	0.003(2)
C(22')	0.082(2)	0.072(2)	0.067(2)	0.021(2)	-0.008(2)	-0.027(2)
C(22'')	0.074(2)	0.072(2)	0.063(2)	-0.012(2)	0.011(2)	-0.008(2)
C(23)	0.066(2)	0.087(2)	0.109(3)	-0.019(2)	0.027(2)	0.003(2)
C(23')	0.086(2)	0.090(2)	0.084(2)	0.036(2)	0.000(2)	-0.051(2)
C(23'')	0.086(2)	0.063(2)	0.049(2)	-0.007(2)	-0.006(2)	0.000(2)
C(24)	0.093(3)	0.142(3)	0.079(2)	-0.029(2)	0.032(2)	-0.041(3)
C(24')	0.082(2)	0.065(2)	0.079(2)	-0.007(2)	-0.006(2)	-0.021(2)
C(24'')	0.080(2)	0.078(2)	0.086(2)	-0.009(2)	-0.017(2)	0.003(2)
O(1)	0.102(2)	0.078(2)	0.120(2)	0.002(2)	0.059(2)	0.012(2)
O(2)	0.072(2)	0.080(2)	0.077(2)	0.007(2)	0.018(2)	-0.024(2)

Table 106. Hydrogen atom positional parameters for TMTB.MeCN.

Atom	x/a	y/b	z/c	U _{iso}
H(12)	0.4954	-0.0511	-0.3484	0.058
H(13)	0.5478	-0.0679	-0.4484	0.073
H(14)	0.6337	0.1100	-0.4877	0.076
H(15)	0.6666	0.3022	-0.4259	0.073
H(16)	0.6114	0.3220	-0.3265	0.054
H(22)	0.4249	0.3285	-0.1897	0.049
H(23)	0.4992	0.4960	-0.1214	0.064
H(24)	0.6715	0.5325	-0.1105	0.068
H(25)	0.7685	0.3943	-0.1661	0.060
H(26)	0.6948	0.2266	-0.2339	0.050
H(32)	0.4243	0.0470	-0.1651	0.049
H(33)	0.4712	-0.1286	-0.0952	0.063
H(34)	0.6099	-0.2612	-0.1073	0.074
H(35)	0.6982	-0.2135	-0.1918	0.070
H(36)	0.6517	-0.0383	-0.2616	0.051
H(42)	0.3976	0.3597	-0.3084	0.052
H(43)	0.2267	0.3841	-0.3429	0.067
H(44)	0.1197	0.2028	-0.3394	0.074
H(45)	0.1838	-0.0046	-0.3034	0.071
H(46)	0.3531	-0.0293	-0.2668	0.057
H(1)	0.6683	0.0546	-0.1307	0.052
H(2,1)	0.5484	0.1006	-0.0844	0.074
H(2,2)	0.5591	0.2182	-0.0256	0.074
H(4,1)	0.9544	0.2532	0.0492	0.074
H(4,2)	0.8518	0.2771	0.0833	0.074
H(7,1)	0.9052	0.0348	-0.2470	0.071
H(7,2)	1.0261	0.0577	-0.2120	0.071
H(62)	1.0827	0.2435	-0.1978	0.070
H(63)	1.2548	0.2647	-0.1947	0.078
H(64)	1.3637	0.1878	-0.1060	0.079
H(65)	1.3027	0.0973	-0.0177	0.077
H(66)	1.1297	0.0739	-0.0197	0.066
H(91)	0.7578	0.0560	0.4650	0.101
H(92)	0.8339	-0.0272	0.4235	0.101
H(93)	0.8274	-0.0696	0.4998	0.101

Table 107. Anisotropic temperature factors ($\text{\AA}^2$) for TMTB.MeCN (with e.s.d.'s in parentheses).

Atom	U11	U22	U33	U23	U13	U12
B	0.039(4)	0.030(4)	0.039(4)	-0.001(4)	0.008(4)	0.005(3)
C(11)	0.028(4)	0.043(4)	0.036(4)	0.008(3)	-0.002(3)	0.003(3)
C(12)	0.059(5)	0.040(4)	0.045(4)	0.007(4)	0.003(4)	-0.003(3)
C(13)	0.080(6)	0.063(5)	0.039(4)	0.024(5)	0.001(4)	-0.012(4)
C(14)	0.056(5)	0.099(7)	0.034(4)	0.019(5)	0.008(4)	0.001(5)
C(15)	0.050(5)	0.090(6)	0.043(4)	-0.006(4)	0.010(4)	0.010(4)
C(16)	0.044(4)	0.054(5)	0.037(4)	-0.002(4)	0.006(3)	-0.000(3)
C(21)	0.045(4)	0.031(4)	0.029(3)	-0.002(3)	0.009(3)	0.007(3)
C(22)	0.047(4)	0.042(4)	0.036(4)	-0.005(3)	0.010(3)	0.003(3)
C(23)	0.070(5)	0.050(5)	0.042(4)	-0.005(4)	0.018(4)	-0.005(4)
C(24)	0.087(6)	0.044(5)	0.039(4)	-0.017(4)	0.002(4)	-0.002(3)
C(25)	0.051(4)	0.053(5)	0.044(4)	-0.014(4)	0.001(4)	0.008(4)
C(26)	0.035(4)	0.050(4)	0.040(4)	-0.006(3)	0.005(3)	0.001(3)
C(31)	0.033(3)	0.031(4)	0.039(4)	-0.001(3)	0.001(3)	-0.003(3)
C(32)	0.037(4)	0.042(4)	0.042(4)	-0.002(3)	0.008(3)	0.004(3)
C(33)	0.059(5)	0.049(5)	0.050(4)	-0.013(4)	0.009(4)	0.010(4)
C(34)	0.077(6)	0.045(5)	0.061(5)	0.009(4)	0.001(4)	0.014(4)
C(35)	0.058(5)	0.051(5)	0.063(5)	0.020(4)	-0.002(4)	0.001(4)
C(36)	0.040(4)	0.047(4)	0.040(4)	0.005(4)	0.008(3)	-0.002(3)
C(41)	0.035(4)	0.038(4)	0.034(3)	0.001(3)	0.008(3)	-0.004(3)
C(42)	0.045(4)	0.041(4)	0.041(4)	0.002(3)	0.003(3)	0.006(3)
C(43)	0.057(5)	0.060(5)	0.050(4)	0.023(4)	0.003(4)	0.005(4)
C(44)	0.038(4)	0.074(6)	0.069(5)	0.007(5)	-0.007(4)	-0.005(4)
C(45)	0.037(4)	0.060(5)	0.075(5)	-0.006(4)	-0.005(4)	-0.004(4)
C(46)	0.041(4)	0.040(4)	0.058(4)	-0.001(4)	-0.004(3)	-0.002(3)
N(1)	0.045(3)	0.047(4)	0.040(3)	-0.007(3)	0.002(3)	-0.013(3)
C(2)	0.044(4)	0.041(4)	0.048(4)	0.002(4)	0.002(4)	0.003(4)
N(2)	0.043(4)	0.077(4)	0.063(4)	-0.004(3)	0.003(3)	-0.025(3)
N(3)	0.039(3)	0.053(4)	0.038(3)	-0.005(3)	0.001(3)	-0.007(3)
C(4)	0.050(5)	0.045(4)	0.035(4)	-0.004(4)	0.004(3)	-0.002(3)
N(4)	0.046(3)	0.096(5)	0.038(3)	-0.012(3)	0.007(3)	-0.022(3)
N(5)	0.044(3)	0.048(4)	0.040(3)	-0.007(3)	0.006(3)	-0.004(3)
C(6)	0.054(5)	0.036(4)	0.038(4)	-0.002(4)	0.007(3)	-0.003(3)
C(7)	0.064(5)	0.034(4)	0.038(4)	0.004(4)	0.007(4)	-0.002(3)
N(7)	0.064(4)	0.070(4)	0.042(3)	-0.007(3)	0.010(3)	-0.023(3)
N(8)	0.052(4)	0.045(4)	0.043(3)	-0.003(3)	0.008(3)	-0.012(3)
C(9)	0.052(5)	0.035(4)	0.036(4)	0.003(3)	0.008(4)	-0.000(3)
C(10)	0.045(4)	0.039(4)	0.035(4)	-0.003(3)	0.004(3)	-0.002(3)
C(61)	0.053(5)	0.042(4)	0.047(4)	-0.000(4)	0.016(4)	-0.007(4)
C(62)	0.063(5)	0.060(5)	0.053(5)	-0.005(4)	0.017(4)	-0.008(4)
C(63)	0.067(6)	0.069(6)	0.066(5)	-0.015(5)	0.033(4)	-0.015(5)

Table 107. Anisotropic temperature factors ($\text{\AA}^2$) for TMTB.MeCN (with e.s.d.'s in parentheses - continued).

Atom	U11	U22	U33	U23	U13	U12
C(64)	0.049(5)	0.065(6)	0.087(6)	0.002(4)	0.026(5)	-0.018(5)
C(65)	0.053(5)	0.060(5)	0.079(6)	0.006(4)	0.004(4)	-0.006(4)
C(66)	0.057(5)	0.050(5)	0.057(5)	0.001(4)	0.008(4)	0.005(4)
N(9)	0.091(6)	0.072(5)	0.076(5)	0.000(4)	0.026(4)	-0.005(4)
C(91)	0.087(7)	0.059(6)	0.055(5)	0.013(5)	0.028(5)	0.000(4)
C(92)	0.101(7)	0.073(6)	0.080(6)	-0.012(5)	0.014(5)	-0.001(5)

Table 108. Hydrogen atom positional parameters for [1,3-Ad]2TB.MeCN

Atom	x/a	y/b	z/c	U_{iso}
H(112)	0.1207	0.2865	-0.1731	0.069
H(113)	0.2996	0.2804	-0.1688	0.087
H(114)	0.4297	0.2337	-0.0323	0.111
H(115)	0.3715	0.1949	0.0976	0.082
H(116)	0.1958	0.2007	0.0938	0.061
H(122)	0.0846	0.3371	-0.0539	0.060
H(123)	-0.0094	0.4111	-0.1247	0.095
H(124)	-0.1980	0.4084	-0.2208	0.090
H(125)	-0.2916	0.3321	-0.2263	0.072
H(126)	-0.1968	0.2577	-0.1612	0.067
H(132)	-0.1040	0.2258	-0.2555	0.077
H(133)	-0.1670	0.1494	-0.3487	0.119
H(134)	-0.1350	0.0723	-0.2586	0.141
H(135)	-0.0233	0.0701	-0.0782	0.125
H(136)	0.0369	0.1455	0.0136	0.081
H(142)	0.1407	0.2846	0.1327	0.068
H(143)	0.1251	0.2882	0.3052	0.084
H(144)	-0.0144	0.2407	0.3389	0.095
H(145)	-0.1369	0.1932	0.1992	0.086
H(146)	-0.1225	0.1943	0.0313	0.058
H(212)	0.0837	0.0037	0.6395	0.073
H(213)	-0.1037	0.0132	0.5851	0.086
H(214)	-0.2030	-0.0320	0.6727	0.100
H(215)	-0.1132	-0.0895	0.8074	0.105
H(216)	0.0767	-0.0978	0.8639	0.084
H(222)	0.3575	-0.1233	0.7714	0.072
H(223)	0.4424	-0.1885	0.8884	0.090
H(224)	0.4150	-0.1968	1.0552	0.094

Table 108. Hydrogen atom positional parameters for [1,3-Ad]2TB.MeCN (continued).

Atom	x/a	y/b	z/c	U _{iso}
H(225)	0.3010	-0.1398	1.1017	0.093
H(226)	0.2182	-0.0746	0.9870	0.071
H(232)	0.4234	-0.0011	0.8648	0.076
H(233)	0.4900	0.0678	0.9801	0.096
H(234)	0.3773	0.1091	1.0595	0.105
H(235)	0.1968	0.0826	1.0182	0.089
H(236)	0.1258	0.0176	0.8921	0.065
H(242)	0.1760	-0.1153	0.6433	0.080
H(243)	0.2187	-0.1231	0.4859	0.100
H(244)	0.3244	-0.0607	0.4392	0.107
H(245)	0.3835	0.0100	0.5504	0.099
H(246)	0.3421	0.0171	0.7077	0.075
H(N11)	0.3753	0.1653	0.5118	0.076
H(N12)	0.4126	0.1928	0.6240	0.076
H(N13)	0.4236	0.1337	0.6184	0.076
H(N21)	0.1962	0.1843	0.8471	0.072
H(N22)	0.1029	0.1429	0.8194	0.072
H(N23)	0.2265	0.1260	0.8577	0.072
H(21,1)	0.3286	0.1267	0.7435	0.051
H(21,2)	0.3132	0.1898	0.7398	0.051
H(22,1)	0.2368	0.2317	0.5648	0.064
H(22,2)	0.2003	0.1958	0.4537	0.064
H(23,1)	0.2280	0.1064	0.4665	0.066
H(23,2)	0.2799	0.0788	0.5872	0.066
H(32)	0.0483	0.2204	0.4990	0.076
H(33)	0.0890	0.0678	0.5145	0.084
H(41,1)	0.0239	0.1864	0.6531	0.070
H(41,2)	0.1316	0.2251	0.6857	0.070
H(42,1)	-0.0257	0.1392	0.4959	0.097
H(42,2)	0.0459	0.1427	0.4122	0.097
H(43,1)	0.1769	0.0727	0.7034	0.073
H(43,2)	0.0505	0.0964	0.6672	0.073
H(2,1)	0.2085	0.4763	0.3190	0.148
H(2,2)	0.1157	0.4845	0.3795	0.148
H(2,3)	0.1028	0.5155	0.2654	0.148

Table 109. Anisotropic temperature factors ($\text{\AA}^2$) for [1,3-Ad]2TB.MeCN (with e.s.d.'s in parentheses).

Atom	U11	U22	U33	U23	U13	U12
B(1)	0.040(10)	0.050(10)	0.070(10)	-0.007(8)	0.035(8)	-0.020(10)
C(111)	0.033(8)	0.050(10)	0.060(10)	-0.008(7)	0.019(8)	-0.017(8)
C(112)	0.050(10)	0.052(9)	0.080(10)	-0.002(7)	0.032(8)	0.011(8)
C(113)	0.060(10)	0.070(10)	0.110(10)	-0.020(10)	0.060(10)	-0.010(10)
C(114)	0.030(10)	0.100(10)	0.150(20)	-0.020(10)	0.050(10)	-0.030(10)
C(115)	0.040(10)	0.080(10)	0.090(10)	-0.003(8)	0.022(8)	-0.020(10)
C(116)	0.040(9)	0.060(10)	0.060(10)	-0.007(7)	0.017(7)	-0.012(8)
C(121)	0.060(10)	0.050(10)	0.031(8)	-0.004(8)	0.023(7)	-0.005(7)
C(122)	0.049(9)	0.038(9)	0.070(10)	0.009(8)	0.025(7)	0.002(8)
C(123)	0.060(10)	0.060(1)	0.120(10)	-0.005(9)	0.030(10)	-0.000(10)
C(124)	0.070(10)	0.070(10)	0.090(10)	0.010(10)	0.040(10)	0.020(10)
C(125)	0.040(9)	0.080(10)	0.060(10)	0.020(10)	0.015(7)	0.020(10)
C(126)	0.040(10)	0.070(10)	0.050(10)	-0.004(8)	0.018(7)	-0.007(8)
C(131)	0.041(8)	0.060(10)	0.060(10)	0.004(8)	0.025(8)	-0.010(10)
C(132)	0.060(10)	0.070(10)	0.070(10)	-0.013(8)	0.027(9)	-0.010(10)
C(133)	0.090(10)	0.140(20)	0.080(10)	-0.040(20)	0.030(10)	-0.060(20)
C(134)	0.100(20)	0.090(20)	0.180(30)	-0.050(20)	0.070(20)	-0.080(20)
C(135)	0.070(10)	0.070(10)	0.200(20)	-0.020(10)	0.070(10)	-0.030(20)
C(136)	0.050(10)	0.060(10)	0.090(10)	-0.010(10)	0.034(8)	-0.030(10)
C(141)	0.043(8)	0.039(8)	0.042(9)	-0.003(7)	0.017(7)	-0.014(7)
C(142)	0.046(9)	0.080(10)	0.050(10)	0.003(8)	0.023(8)	0.004(9)
C(143)	0.060(10)	0.100(10)	0.050(10)	0.008(8)	0.016(7)	-0.010(10)
C(144)	0.090(10)	0.100(10)	0.060(10)	0.030(10)	0.040(10)	0.020(10)
C(145)	0.090(10)	0.070(10)	0.080(10)	0.010(10)	0.060(10)	0.020(10)
C(146)	0.060(10)	0.040(9)	0.050(10)	-0.005(7)	0.026(8)	0.000(7)
B(2)	0.050(10)	0.050(10)	0.070(10)	0.009(9)	0.026(9)	0.010(10)
C(211)	0.050(10)	0.040(10)	0.070(10)	-0.000(8)	0.008(8)	0.003(8)
C(212)	0.040(10)	0.050(10)	0.090(10)	0.004(7)	0.015(8)	0.007(9)
C(213)	0.050(10)	0.050(10)	0.090(10)	0.000(9)	0.010(10)	-0.006(9)
C(214)	0.040(10)	0.100(10)	0.100(10)	0.010(10)	0.010(10)	-0.010(10)
C(215)	0.050(10)	0.100(10)	0.110(10)	-0.020(10)	0.030(10)	0.010(10)
C(216)	0.060(10)	0.070(10)	0.080(10)	-0.003(8)	0.014(9)	0.022(8)
C(221)	0.049(9)	0.050(10)	0.060(10)	-0.017(7)	0.014(8)	-0.008(9)
C(222)	0.060(10)	0.050(10)	0.060(10)	0.001(8)	0.016(8)	-0.008(9)
C(223)	0.070(10)	0.060(10)	0.090(10)	0.030(8)	0.030(10)	0.020(10)
C(224)	0.090(10)	0.060(10)	0.070(10)	0.015(9)	0.010(10)	0.010(10)
C(225)	0.090(10)	0.070(10)	0.070(10)	0.010(10)	0.020(10)	0.010(10)
C(226)	0.060(10)	0.040(10)	0.070(10)	0.004(7)	0.019(9)	-0.005(9)

Table 109. Anisotropic temperature factors ($\text{\AA}^2$) for [1,3-Ad]2TB.MeCN (with e.s.d.'s in parentheses - continued).

Atom	U11	U22	U33	U23	U13	U12
C(231)	0.037(9)	0.037(9)	0.070(10)	0.007(7)	0.012(8)	-0.002(8)
C(232)	0.040(10)	0.070(10)	0.070(10)	-0.008(8)	0.011(8)	-0.018(9)
C(233)	0.070(10)	0.060(10)	0.090(10)	-0.020(10)	-0.010(10)	-0.010(10)
C(234)	0.090(10)	0.050(10)	0.080(10)	-0.000(10)	-0.010(10)	-0.030(10)
C(235)	0.080(10)	0.070(10)	0.060(10)	0.010(10)	0.000(10)	-0.010(9)
C(236)	0.046(9)	0.050(10)	0.060(10)	-0.001(8)	0.004(7)	-0.010(8)
C(241)	0.034(8)	0.050(10)	0.060(10)	0.006(7)	0.002(7)	0.000(10)
C(242)	0.060(10)	0.070(10)	0.060(10)	-0.008(8)	-0.005(8)	-0.010(10)
C(243)	0.070(10)	0.110(10)	0.040(10)	0.030(10)	-0.010(8)	-0.010(10)
C(244)	0.070(10)	0.130(20)	0.080(10)	0.030(10)	0.030(10)	0.040(10)
C(245)	0.090(10)	0.070(10)	0.080(10)	0.000(10)	0.020(10)	-0.010(10)
C(246)	0.070(10)	0.080(10)	0.040(10)	0.023(9)	0.016(8)	0.002(9)
N(1)	0.062(7)	0.063(7)	0.076(8)	0.003(6)	0.033(6)	0.023(6)
N(2)	0.073(7)	0.051(7)	0.072(8)	0.002(6)	0.043(6)	0.002(6)
C(11)	0.035(8)	0.050(10)	0.070(10)	-0.008(7)	0.030(7)	0.004(9)
C(21)	0.044(8)	0.032(8)	0.050(10)	0.002(6)	0.014(7)	0.009(7)
C(31)	0.070(10)	0.050(10)	0.050(10)	-0.001(8)	0.041(8)	0.001(8)
C(41)	0.050(8)	0.070(10)	0.060(10)	0.010(7)	0.029(7)	0.012(8)
C(22)	0.061(9)	0.050(10)	0.050(10)	0.019(8)	0.023(7)	0.026(7)
C(32)	0.050(10)	0.080(10)	0.050(10)	0.017(8)	0.009(7)	0.032(9)
C(42)	0.050(10)	0.130(20)	0.060(10)	-0.020(10)	0.015(8)	-0.020(10)
C(23)	0.080(10)	0.040(10)	0.050(10)	-0.010(8)	0.039(8)	-0.002(7)
C(33)	0.080(10)	0.060(10)	0.080(10)	-0.043(9)	0.040(10)	-0.030(10)
C(43)	0.070(10)	0.060(10)	0.060(10)	-0.013(8)	0.042(8)	0.002(8)
N(3)	0.080(10)	0.100(10)	0.120(10)	-0.024(8)	0.008(9)	-0.040(10)
C(1)	0.070(10)	0.080(10)	0.100(10)	-0.000(10)	0.020(10)	-0.010(10)
C(2)	0.130(10)	0.100(10)	0.120(10)	-0.040(10)	0.020(10)	-0.020(10)

Table 110. Hydrogen atom positional parameters for ImBTB.

Atom	x/a	y/b	z/c	U_{iso}
H(12)	0.385(0)	0.089(0)	0.293(0)	0.079(6)
H(13)	0.243(0)	-0.021(0)	0.293(0)	0.092(7)
H(14)	0.168(0)	-0.073(0)	0.377(0)	0.068(6)
H(15)	0.249(0)	-0.029(0)	0.462(0)	0.121(7)
H(16)	0.391(0)	0.081(0)	0.462(0)	0.123(7)
H(22)	0.340(0)	0.245(0)	0.436(0)	0.131(7)
H(23)	0.340(0)	0.364(0)	0.507(0)	0.116(7)
H(24)	1/2	0.419(4)	0.544(3)	0.111(8)
H(32)	0.340(0)	0.247(0)	0.320(0)	0.080(7)
H(33)	0.339(0)	0.363(0)	0.249(0)	0.103(7)
H(34)	1/2	0.418(3)	0.210(2)	0.061(7)
H(N11)	0.680(0)	0.176(0)	0.154(0)	0.198(8)
H(N12)	0.666(0)	0.297(0)	0.149(0)	0.183(8)
H(N13)	0.664(0)	0.227(0)	0.091(0)	0.172(8)
H(N21)	0.569(0)	0.090(4)	0.187(2)	0.111(8)
H(N22)	0.454(0)	0.080(4)	0.151(2)	0.059(8)
H(N23)	0.458(0)	0.145(4)	0.210(2)	0.098(8)
H(C11)	0.432(0)	0.376(3)	0.075(2)	0.163(8)
H(C12)	0.544(0)	0.321(3)	0.054(2)	0.123(8)
H(C13)	0.544(0)	0.387(3)	0.113(2)	0.061(8)

Table 111. Anisotropic temperature factors ($\text{\AA}^2$) for ImBTB (with e.s.d.'s in parentheses).

Atom	U11	U22	U33	U23	U13	U12
B	0.049(3)	0.044(3)	0.041(3)	-0.001(3)	0	0
C(11)	0.048(2)	0.044(2)	0.045(2)	-0.000(2)	0.006(2)	0.007(2)
C(12)	0.066(3)	0.061(2)	0.050(2)	-0.015(2)	0.013(2)	-0.010(2)
C(13)	0.064(3)	0.064(2)	0.077(3)	-0.025(2)	0.005(2)	-0.011(2)
C(14)	0.058(3)	0.054(2)	0.088(3)	-0.005(2)	0.019(3)	-0.010(2)
C(15)	0.077(3)	0.080(3)	0.071(3)	0.014(3)	0.009(3)	-0.023(3)
C(16)	0.066(3)	0.069(2)	0.061(3)	0.010(2)	-0.001(2)	-0.015(2)
C(21)	0.075(4)	0.039(3)	0.046(3)	0.006(3)	0	0
C(22)	0.103(3)	0.075(2)	0.054(2)	-0.008(2)	-0.016(3)	0.043(3)
C(23)	0.182(5)	0.086(3)	0.050(3)	-0.005(2)	-0.003(3)	0.073(4)
C(24)	0.195(7)	0.052(4)	0.055(4)	0.005(3)	0	0
C(31)	0.047(3)	0.043(3)	0.041(3)	-0.003(2)	0	0
C(32)	0.056(2)	0.077(2)	0.056(2)	0.016(2)	0.016(2)	0.019(2)
C(33)	0.079(3)	0.074(3)	0.065(3)	0.017(2)	0.009(2)	0.034(2)
C(34)	0.095(4)	0.052(3)	0.048(3)	0.011(3)	0	0
N	0.072(6)	0.090(4)	0.070(4)	-0.017(4)	-0.003(3)	0.006(4)
C(N1)=C(C2)'	0.032(2)	0.120(3)	0.148(4)	-0.024(3)	-0.004(3)	-0.001(2)
C(N2)=C(N2)'	0.099(4)	0.085(4)	0.080(4)	0.020(3)	0	0
C	0.053(5)	0.051(4)	0.046(4)	-0.012(4)	0.000(4)	0.005(3)
C(C1)=C(C1)'	0.118(5)	0.055(3)	0.089(4)	0.001(3)	0	0
C(C2)=C(N1)'	0.032(2)	0.120(3)	0.148(4)	-0.024(3)	0.004(3)	0.001(2)

Table 112. Hydrogen atom positional parameters for AzPpTB.

Atom	x/a	y/b	z/c	U _{iso}
H(12)	-0.0439	1.1075	0.6767	0.0512
H(13)	-0.1570	1.1803	0.5535	0.0591
H(14)	-0.0312	1.2726	0.4776	0.0649
H(15)	0.2069	1.2933	0.5309	0.0596
H(16)	0.3168	1.2226	0.6574	0.0531
H(22)	0.0149	1.0418	0.8737	0.0536
H(23)	-0.1013	1.0815	1.0189	0.0661
H(24)	-0.0453	1.1923	1.0907	0.0691
H(25)	0.1313	1.2615	1.0186	0.0670
H(26)	0.2469	1.2217	0.8738	0.0552
H(32)	0.2552	0.9891	0.8733	0.0542
H(33)	0.2376	0.8700	0.8313	0.0664
H(34)	0.1629	0.8350	0.6629	0.0747
H(35)	0.1120	0.9220	0.5394	0.0712
H(36)	0.1280	1.0406	0.5810	0.0532
H(42)	0.3888	1.1022	0.9304	0.0619
H(43)	0.6364	1.1034	0.9516	0.0825
H(44)	0.7777	1.1168	0.8104	0.0918
H(45)	0.6686	1.1290	0.6444	0.0851
H(46)	0.4217	1.1226	0.6223	0.0635
H(N111)	0.4497	0.9532	0.6417	0.0864
H(N112)	0.4948	0.8812	0.5750	0.0864
H(N121)	0.6218	0.9662	0.5013	0.0810
H(N122)	0.6568	1.0071	0.6143	0.0810
H(N131)	0.8582	0.9445	0.5915	0.0803
H(N132)	0.7680	0.8747	0.5433	0.0803
H(N211)	0.5062	0.9149	0.8524	0.0814
H(N212)	0.5603	0.9851	0.7856	0.0814
H(N221)	0.7358	0.9726	0.9086	0.0820
H(N222)	0.7303	0.8842	0.9015	0.0820
H(N231)	0.9150	0.9124	0.8019	0.0847
H(N232)	0.8295	0.9828	0.7511	0.0847
H(N311)	0.4557	0.8101	0.6962	0.0927
H(N312)	0.5502	0.8068	0.8086	0.0927
H(N321)	0.6636	0.7267	0.7133	0.1007
H(N322)	0.6411	0.7745	0.6049	0.1007
H(N331)	0.8664	0.8003	0.6566	0.0930
H(N332)	0.8265	0.8023	0.7815	0.0930

Table 113. Anisotropic temperature factors ($\text{\AA}^2$) for AzPpTB (with e.s.d.'s in parentheses).

Atom	U11	U22	U33	U12	U13	U23
B	0.034(2)	0.042(3)	0.033(2)	-0.005(2)	0.001(2)	-0.001(2)
C(11)	0.037(2)	0.040(2)	0.035(2)	-0.002(2)	0.003(2)	-0.004(2)
C(12)	0.042(2)	0.043(2)	0.043(2)	-0.001(2)	0.001(2)	0.003(2)
C(13)	0.044(2)	0.051(3)	0.053(3)	0.002(2)	-0.008(2)	-0.004(2)
C(14)	0.068(3)	0.047(3)	0.046(2)	0.012(2)	-0.008(2)	0.003(2)
C(15)	0.060(3)	0.042(2)	0.047(2)	-0.002(2)	0.002(2)	0.009(2)
C(16)	0.047(2)	0.041(2)	0.045(2)	-0.006(2)	0.001(2)	0.003(2)
C(21)	0.033(2)	0.045(2)	0.031(2)	0.004(2)	-0.002(2)	0.000(2)
C(22)	0.037(2)	0.060(3)	0.038(2)	0.001(2)	0.003(2)	-0.002(2)
C(23)	0.039(2)	0.083(3)	0.045(2)	0.003(2)	0.005(2)	0.001(3)
C(24)	0.048(3)	0.085(4)	0.040(2)	0.022(3)	-0.001(2)	-0.005(2)
C(25)	0.058(3)	0.059(3)	0.050(3)	0.015(2)	-0.010(2)	-0.017(2)
C(26)	0.044(2)	0.048(3)	0.046(2)	0.003(2)	-0.000(2)	-0.004(2)
C(31)	0.027(2)	0.041(2)	0.038(2)	-0.002(2)	0.006(2)	0.001(2)
C(32)	0.045(2)	0.045(3)	0.046(2)	0.002(2)	0.005(2)	0.005(2)
C(33)	0.049(3)	0.039(3)	0.078(3)	0.004(2)	0.013(2)	0.012(2)
C(34)	0.050(3)	0.040(3)	0.098(4)	-0.005(2)	0.013(2)	-0.012(3)
C(35)	0.055(3)	0.055(3)	0.067(3)	-0.001(2)	-0.001(2)	-0.021(3)
C(36)	0.045(2)	0.045(2)	0.043(2)	-0.002(2)	0.002(2)	-0.005(2)
C(41)	0.038(2)	0.034(2)	0.047(2)	-0.001(2)	0.002(2)	-0.004(2)
C(42)	0.045(3)	0.052(3)	0.056(3)	0.007(2)	-0.011(2)	-0.014(2)
C(43)	0.051(3)	0.061(3)	0.092(4)	0.009(2)	-0.023(3)	-0.030(3)
C(44)	0.041(3)	0.052(3)	0.137(5)	-0.004(2)	-0.005(3)	-0.017(3)
C(45)	0.050(3)	0.048(3)	0.118(4)	-0.003(2)	0.033(3)	0.006(3)
C(46)	0.043(2)	0.048(2)	0.069(3)	-0.001(2)	0.014(2)	0.003(2)
N	0.049(2)	0.053(2)	0.055(2)	0.001(2)	0.002(2)	0.003(2)
C(1,1)	0.053(3)	0.094(4)	0.068(3)	0.011(3)	-0.013(2)	0.019(3)
C(1,2)	0.073(3)	0.083(4)	0.047(3)	0.008(3)	0.000(2)	0.013(2)
C(1,3)	0.056(3)	0.094(4)	0.052(3)	-0.001(3)	0.005(2)	0.015(2)
C(2,1)	0.065(3)	0.081(3)	0.058(3)	0.011(3)	0.016(2)	-0.014(3)
C(2,2)	0.074(3)	0.092(4)	0.039(2)	0.028(3)	-0.006(2)	-0.009(2)
C(2,3)	0.057(3)	0.094(4)	0.060(3)	-0.004(3)	-0.008(2)	-0.013(3)
C(3,1)	0.078(3)	0.050(3)	0.106(4)	-0.010(3)	0.024(3)	0.004(3)
C(3,2)	0.098(4)	0.046(3)	0.109(4)	0.009(3)	0.007(3)	-0.001(3)
C(3,3)	0.077(4)	0.075(4)	0.082(4)	0.027(3)	0.004(3)	-0.003(3)
C	0.029(2)	0.048(2)	0.034(2)	0.006(2)	0.001(2)	0.000(2)

Table 114. Hydrogen atom positional parameters for 2PhITB (free refinement)

Atom	x/a	y/b	z/c	U_{iso}
H(12)	0.414	0.171	0.428	0.082
H(13)	0.358	0.055	0.308	0.101
H(14)	0.241	-0.008	0.392	0.095
H(15)	0.186	0.039	0.607	0.090
H(16)	0.246	0.152	0.726	0.071
H(22)	0.357	0.121	0.854	0.103
H(23)	0.332	0.120	1.093	0.128
H(24)	0.332	1/4	1.217	0.083
H(32)	0.480	0.122	0.652	0.193
H(33)	0.616	0.123	0.653	0.194
H(34)	0.689	1/4	0.631	0.078
H(2)	0.025	0.341	0.504	0.157
H(3)	-0.055	0.451	0.406	0.205
H(4)	-0.002	0.525	0.216	0.189
H(5)	0.099	0.471	0.080	0.185
H(6)	0.175	0.355	0.177	0.185

Table 115. Anisotropic temperature factors ($\text{\AA}^2$) for 2PhITB (with e.s.d.'s in parentheses) (free refinement).

Atom	U11	U22	U33	U23	U13	U12
B	0.051(3)	0.024(3)	0.054(3)	0.000(0)	-0.001(3)	0.000(0)
C(11)	0.057(3)	0.027(3)	0.049(3)	0.007(3)	-0.002(3)	0.001(3)
C(12)	0.098(3)	0.028(3)	0.061(3)	-0.007(3)	0.011(3)	-0.019(3)
C(13)	0.126(3)	0.047(3)	0.056(3)	-0.015(3)	0.004(3)	0.000(3)
C(14)	0.097(3)	0.046(3)	0.084(3)	-0.014(3)	-0.023(3)	-0.008(3)
C(15)	0.073(3)	0.050(3)	0.095(3)	-0.005(3)	-0.003(3)	-0.014(3)
C(16)	0.061(3)	0.042(3)	0.071(3)	-0.012(3)	-0.003(3)	-0.008(3)
C(21)	0.060(3)	0.033(3)	0.047(3)	0.000(0)	-0.000(3)	0.000(0)
C(22)	0.133(4)	0.042(3)	0.052(3)	0.003(3)	-0.009(3)	-0.021(3)
C(23)	0.153(4)	0.077(3)	0.070(3)	0.032(3)	-0.005(3)	-0.017(3)
C(24)	0.091(4)	0.118(4)	0.053(3)	0.000(0)	-0.011(4)	0.000(0)
C(31)	0.054(3)	0.048(3)	0.047(3)	0.000(0)	-0.001(3)	0.000(0)
C(32)	0.069(3)	0.039(3)	0.267(4)	0.000(0)	-0.017(4)	0.000(0)
C(33)	0.073(3)	0.070(3)	0.261(4)	-0.001(4)	-0.032(4)	0.020(3)
C(34)	0.069(4)	0.063(4)	0.117(4)	0.000(0)	0.008(4)	0.000(0)
I	0.089(1)	0.100(1)	0.091(1)	0.000(0)	-0.035(1)	0.000(0)
C(1)	0.081(3)	0.097(3)	0.092(3)	0.018(3)	-0.029(3)	-0.034(3)
C(2)	0.151(4)	0.102(3)	0.134(4)	0.034(3)	-0.035(3)	0.021(3)
C(3)	0.168(4)	0.155(4)	0.187(4)	-0.014(4)	-0.021(4)	0.025(4)
C(4)	0.181(4)	0.079(3)	0.188(4)	0.046(3)	-0.075(4)	-0.038(3)
C(5)	0.157(4)	0.145(4)	0.161(4)	0.092(3)	-0.012(4)	-0.058(3)
C(6)	0.102(3)	0.193(4)	0.154(4)	0.102(3)	-0.028(3)	-0.030(3)

Table 116. Hydrogen atom positional parameters for 2PhITB (disorder resolved).

Atom	x/a	y/b	z/c	U_{iso}
H(12)	0.415	0.171	0.430	0.068
H(13)	0.357	0.055	0.307	0.081
H(14)	0.241	-0.008	0.394	0.076
H(15)	0.186	0.039	0.605	0.072
H(16)	0.247	0.152	0.728	0.057
H(22)	0.354	0.121	0.852	0.080
H(23)	0.332	0.121	1.095	0.099
H(24)	0.332	1/4	1.218	0.086
H(32)	0.463	0.173	0.768	0.068
H(32*)	0.469	0.187	0.538	0.069
H(33)	0.627	0.188	0.765	0.068
H(33*)	0.574	0.141	0.526	0.087
H(34)	0.687	1/4	0.632	0.075
H(2)	0.011	0.325	0.503	0.095
H(3)	-0.065	0.444	0.430	0.115
H(4)	-0.021	0.528	0.241	0.077
H(5)	0.094	0.493	0.113	0.063
H(6)	0.175	0.382	0.205	0.068
H(2*)	0.039	0.364	0.500	0.098
H(3*)	-0.037	0.465	0.371	0.129
H(4*)	0.013	0.514	0.153	0.089
H(5*)	0.115	0.437	0.043	0.108
H(6*)	0.178	0.322	0.155	0.095

Table 117. Anisotropic temperature factors ($\text{\AA}^2$) for 2PhITB (with e.s.d.'s in parentheses) (disorder resolved).

Atom	U11	U22	U33	U23	U13	U12
B	0.053(3)	0.027(3)	0.052(3)	0.000(0)	-0.000(3)	0.000(0)
C(11)	0.059(3)	0.029(3)	0.050(3)	0.007(3)	-0.002(3)	-0.002(3)
C(12)	0.104(3)	0.028(3)	0.057(3)	-0.008(3)	0.007(3)	-0.015(3)
C(13)	0.125(3)	0.052(3)	0.056(3)	-0.013(3)	0.007(3)	0.002(3)
C(14)	0.097(3)	0.056(3)	0.082(3)	-0.012(3)	-0.021(3)	-0.004(3)
C(15)	0.076(3)	0.047(3)	0.096(3)	-0.003(3)	-0.004(3)	-0.012(3)
C(16)	0.064(3)	0.039(3)	0.073(3)	-0.013(3)	-0.001(3)	-0.003(3)
C(21)	0.066(3)	0.027(3)	0.054(3)	0.000(0)	0.003(3)	0.000(0)
C(22)	0.125(3)	0.043(3)	0.063(3)	0.003(3)	-0.013(3)	-0.019(3)
C(23)	0.145(3)	0.083(3)	0.071(3)	0.032(3)	-0.002(3)	-0.015(3)
C(24)	0.099(3)	0.110(3)	0.056(3)	0.000(0)	-0.011(3)	0.000(0)
C(31)	0.060(3)	0.043(3)	0.043(3)	0.000(0)	0.002(3)	0.000(0)
C(32)	0.069(3)	0.021(3)	0.100(3)	0.000(0)	-0.006(3)	0.000(0)
C(32*)	0.058(3)	0.086(3)	0.071(3)	0.011(3)	-0.008(3)	-0.012(3)
C(33)	0.063(3)	0.039(3)	0.101(3)	-0.027(3)	-0.030(3)	0.015(3)
C(33*)	0.084(3)	0.108(3)	0.080(3)	-0.060(3)	-0.002(3)	-0.010(3)
C(34)	0.070(3)	0.063(3)	0.100(3)	0.000(0)	-0.001(3)	0.000(0)
I	0.091(1)	0.105(1)	0.093(1)	-0.025(2)	-0.033(1)	-0.026(2)
C(1)	0.069(3)	0.036(3)	0.059(3)	-0.011(3)	-0.009(3)	-0.002(3)
C(1*)	0.081(3)	0.092(3)	0.052(3)	-0.021(3)	-0.017(3)	-0.026(3)
C(2)	0.110(3)	0.093(3)	0.099(3)	0.032(3)	-0.001(3)	0.008(3)
C(2*)	0.115(3)	0.096(3)	0.098(3)	0.023(3)	-0.003(3)	0.012(3)
C(3)	0.112(3)	0.129(3)	0.124(3)	0.011(3)	0.025(3)	0.017(3)
C(3*)	0.134(3)	0.145(3)	0.131(3)	0.009(3)	-0.007(3)	0.026(3)
C(4)	0.092(3)	0.060(3)	0.089(3)	0.027(3)	0.013(3)	-0.020(3)
C(4*)	0.091(3)	0.077(3)	0.113(3)	0.009(3)	-0.011(3)	0.006(3)
C(5)	0.068(3)	0.037(3)	0.084(3)	0.014(3)	0.013(3)	-0.009(3)
C(5*)	0.119(3)	0.114(3)	0.109(3)	0.022(3)	-0.009(3)	-0.008(3)
C(6)	0.078(3)	0.074(3)	0.064(3)	0.001(3)	0.002(3)	0.000(3)
C(6*)	0.096(3)	0.106(3)	0.098(3)	0.013(3)	0.002(3)	0.016(3)

Table 118. Best planes through phenyl rings of anions.

Ring	$\delta(C)$	$\delta(B)$	Angles between ring planes					
ImATB								
1	0.004	-0.112						
2	0.004	-0.137	2/1	122.9				
3 = 1'	0.004	-0.112	3/1	84.4	3/2	122.9		
4 = 2'	0.004	0.137	4/1	57.1	4/2	94.3	4/3	57.1
ImCTB								
1	0.003	0.114						
2	0.004	0.102	2/1	119.5				
3	0.002	0.117	3/1	115.8	3/2	86.8		
4	0.009	-0.062	4/1	94.8	4/2	49.8	4/3	57.3
ImDTB								
1	0.014	0.214						
2	0.013	0.098	2/1	86.9				
3	0.003	0.121	3/1	121.8	3/2	122.9		
4 = 3'	0.003	-0.121	4/1	58.2	4/2	57.2	4/3	94.9
ImETBw								
1	0.006	0.172						
2	0.006	-0.170	2/1	91.5				
3	0.008	0.127	3/1	121.5	3/2	58.1		
4	0.008	-0.138	4/1	63.7	4/2	125.1	4/3	92.7
QTB								
1	0.004	0.226						
2	0.003	0.088	2/1	56.1				
3	0.001	0.039	3/1	57.1	3/2	67.9		
4 = 1'	0.004	-0.226	4/1	85.5	4/2	124.9	4/3	54.5
DaHTB								
1	0.003	0.218						
2	0.010	0.028	2/1	55.4				
3	0.011	-0.062	3/1	56.7	3/2	70.7		
4 = 1'	0.003	-0.218	4/1	86.5	4/2	124.6	4/3	56.7

Table 118. Best planes through phenyl rings of anions (continued).

Ring	$\delta(C)$	$\delta(B)$	Angles between ring planes					
1MPzBTB.Me ₂ CO								
11	0.007	-0.001						
12	0.005	-0.069	12/11	67.4				
13	0.010	-0.088	13/11	75.1	13/12	53.1		
14	0.008	0.119	14/11	49.6	14/12	113.8	14/13	89.4
21	0.005	-0.101						
22	0.004	0.134	22/21	60.2				
23	0.007	-0.088	23/21	117.8	23/22	99.0		
BPTB								
1	0.006	0.111						
2	0.007	-0.219	2/1	91.4				
3	0.002	0.141	3/1	125.1	3/2	53.4		
4	0.004	-0.083	4/1	52.6	4/2	106.4	4/3	94.3
PTB								
1	0.009	0.090						
2	0.007	0.160	2/1	116.3				
3	0.005	-0.102	3/1	61.2	3/2	73.5		
4	0.004	0.036	4/1	117.2	4/2	80.9	4/3	69.2
2MTB.MeCN								
1	0.005	0.185						
2	0.008	-0.109	2/1	91.7				
3	0.005	-0.099	3/1	59.8	3/2	123.9		
4	0.007	-0.053	4/1	57.6	4/2	123.1	4/3	83.4
2PiTB								
1	0.002	-0.153						
2	0.003	0.055	2/1	59.5				
3	0.003	-0.105	3/1	84.8	3/2	51.1		
4	0.007	-0.102	4/1	120.1	4/2	95.2	4/3	122.4

Table 118. Best planes through phenyl rings of anions (continued).

Ring	$\delta(C)$	$\delta(B)$	Angles between ring planes					
AC7TB								
1	0.004	-0.214						
2	0.002	-0.167	2/1	117.9				
3	0.009	0.136	3/1	111.1	3/2	78.3		
4 = 1'	0.004	0.214	4/1	82.5	4/2	117.9	4/3	111.1
[1-Ad]TBw								
11	0	0.166						
12	0	0.122	12/11	86.1				
13	0	0.027	13/11	126.0	13/12	124.8		
14	0	0.088	14/11	121.7	14/12	122.6	14/13	80.9
21	0	0.189						
22	0	0.099	22/21	127.5				
23	0	0.085	23/21	123.6	23/22	82.4		
24	0	-0.172	24/21	90.3	24/22	62.4	24/23	60.0
[1,3-Ad]2TB.MeCN								
11	0.007	-0.118						
12	0.010	-0.021	12/11	128.7				
13	0.011	0.050	13/11	98.9	13/12	48.1		
14	0.007	-0.050	14/11	120.0	14/12	78.9	14/13	58.1
21	0.006	0.208						
22	0.008	0.030	22/21	50.5				
23	0.010	0.153	23/21	88.8	23/22	92.5		
24	0.003	-0.001	24/21	96.6	24/22	65.2	24/23	45.0
TMTB								
1	0.004	-0.089						
2	0.008	0.074	2/1	53.6				
3	0.003	0.153	3/1	64.2	3/2	86.9		
4	0.006	0.076	4/1	94.4	4/2	122.2	4/3	124.4
LiTBw								
1	0.011	-0.081						
2	0.001	0.176	2/1	92.8				
3	0.004	-0.154	3/1	120.9	3/2	66.9		
4	0.015	0.025	4/1	48.3	4/2	122.8	4/3	96.0

Table 118. Best planes through phenyl rings of anions (continued).

Ring	$\delta(\text{C})$	$\delta(\text{B})$	Angles between ring planes					
ImBTB								
1	0.009	-0.040						
2	0.004	-0.151	2/1	122.3				
3	0.002	-0.137	3/1	126.1	3/2	87.0		
4 = 1'	0.009	-0.040	4/1	78.3	4/2	122.3	4/3	126.1
AzPpTB								
1	0.011	-0.022						
2	0.002	-0.111	2/1	87.6				
3	0.002	0.105	3/1	59.7	3/2	60.7		
4	0.007	0.104	4/1	46.6	4/2	67.2	4/3	86.8
2PhITB (free refinement)								
1	0.006	0.083						
2	0.004	-0.008	2/1	50.3				
3	0.010	0.075	3/1	121.4	3/2	101.7		
4 = 1'	0.006	0.083	4/1	97.9	4/2	129.8	4/3	58.6

Appendix 3

Other Structures Solved

1) Hexakis(phenylthiobenzene)

$C_{42}H_{30}S_6$	MW = 727.1	$t = 18\text{ }^{\circ}\text{C}$
triclinic	P-1 (No. 2)	centrosymmetric
$a = 9.589(2)\text{ \AA}$	$b = 10.256(0)\text{ \AA}$	$c = 10.645(2)\text{ \AA}$
$\alpha = 68.42(1)^{\circ}$	$\beta = 76.92(2)^{\circ}$	$\gamma = 65.52(1)^{\circ}$
$F(000) = 378\text{ e}$	$\mu = 4.01\text{ cm}^{-1}$	$V = 882.6\text{ \AA}^3$
$Z = 1$	$d_c = 1.368\text{ g/cm}^3$	$\lambda = 0.70926\text{ \AA}$
$N_{me} = 5556$	$N_{un} = 5138$	$N_{ob} = 3373$
obs. if $I > 3\sigma(I)$	$N_v = 218$	$N_{ob}/N_v = 15.5$
$2\theta_{max} = 59.8^{\circ}$	$R = 0.044$	$R_w = 0.036$

2) Hexakis(phenylthiobenzene) carbontetrabromide clathrate

$C_{42}H_{30}S_6 \cdot 2CBr_4$	MW = 1390.3	$t = 18\text{ }^{\circ}\text{C}$
rhombohedral	R-3 (No. 148)	centrosymmetric
$a = 14.327(4)\text{ \AA}$	$b = 14.327(4)\text{ \AA}$	$c = 20.666(8)\text{ \AA}$
$\alpha = 90^{\circ}$	$\beta = 90^{\circ}$	$\gamma = 120^{\circ}$
$F(000) = 2010\text{ e}$	$\mu = 67.63\text{ cm}^{-1}$	$V = 3674(2)\text{ \AA}^3$
$Z = 3$	$d_c = 1.885\text{ g/cm}^3$	$\lambda = 0.71069\text{ \AA}$
$N_{me} = 1624$	$N_{un} = 1440$	$N_{ob} = 643$
obs. if $I > 3\sigma(I)$	$N_v = 92$	$N_{ob}/N_v = 7.0$
$2\theta_{max} = 50.0^{\circ}$	$R = 0.057$	$R_w = 0.048$

3) Hexakis(phenylthiobenzene) bromotrichloromethane clathrate

$C_{42}H_{30}S_6 \cdot 2CCl_3Br$	MW = 1123.6	$t = 18\text{ }^\circ\text{C}$
rhombohedral	$R\bar{3}$ (No. 148)	centrosymmetric
$a = 14.293(2)\text{ \AA}$	$b = 14.293(2)\text{ \AA}$	$c = 20.692(3)\text{ \AA}$
$\alpha = 90^\circ$	$\beta = 90^\circ$	$\gamma = 120^\circ$
$F(000) = 1686\text{ e}$	$\mu = 22.53\text{ cm}^{-1}$	$V = 3661(1)\text{ \AA}^3$
$Z = 3$	$d_c = 1.529\text{ g/cm}^3$	$\lambda = 0.71069\text{ \AA}$
$N_{me} = 2571$	$N_{un} = 2379$	$N_{ob} = 922$
obs. if $ I > 3\sigma(I)$	$N_v = 106$	$N_{ob}/N_v = 8.7$
$2\theta_{max} = 60.0^\circ$	$R = 0.055$	$R_w = 0.061$

4) Chloro-tetraisopropylidiamino-chloromethyl-phosphonium tetraphenylborate

$C_{37}H_{50}BN_2PCl_2$	MW = 635.5	$t = 18\text{ }^\circ\text{C}$
monoclinic	$P2_1/n$ (No. 14)	centrosymmetric
$a = 10.049(3)\text{ \AA}$	$b = 21.794(3)\text{ \AA}$	$c = 16.391(3)\text{ \AA}$
$\alpha = 90^\circ$	$\beta = 92.78(2)^\circ$	$\gamma = 90^\circ$
$F(000) = 1360\text{ e}$	$\mu = 2.50\text{ cm}^{-1}$	$V = 3585(1)\text{ \AA}^3$
$Z = 4$	$d_c = 1.177\text{ g/cm}^3$	$\lambda = 0.71069\text{ \AA}$
$N_{me} = 7346$	$N_{un} = 6796$	$N_{ob} = 1946$
obs. if $ I > 3\sigma(I)$	$N_v = 387$	$N_{ob}/N_v = 5.03$
$2\theta_{max} = 59.9^\circ$	$R = 0.0541$	$R_w = 0.0569$

5) Tetraisopropyldiamino-phosphenium tetrachlorogallate

$C_{12}H_{28}N_2PGaCl_4$	MW = 442.9	$t = 18\text{ }^\circ\text{C}$
tetragonal	$I4_1cd$ (No. 110)	noncentrosymmetric
$a = 20.014(4)\text{ \AA}$	$b = 20.014(4)\text{ \AA}$	$c = 21.466(6)\text{ \AA}$
$\alpha = 90^\circ$	$\beta = 90^\circ$	$\gamma = 90^\circ$
$F(000) = 3648\text{ e}$	$\mu = 18.45\text{ cm}^{-1}$	$V = 8598(6)\text{ \AA}^3$
$Z = 16$	$d_c = 1.368\text{ g/cm}^3$	$\lambda = 0.70926\text{ \AA}$
$N_{me} = 2598$	$N_{un} = 1893$	$N_{ob} = 617$
obs. if $I > 3\sigma(I)$	$N_v = 158$	$N_{ob}/N_v = 3.9$
$2\theta_{max} = 46.0^\circ$	$R = 0.0540$	$R_w = 0.0640$

6) 2,2-dibutyl-1,3,2-dioxastannane

$(C_{11}H_{24}O_2Sn)_n$	MW = 306.9(monomer)	$t = 18\text{ }^\circ\text{C}$
orthorhombic	$Pnma$ (No. 53)	centrosymmetric
$a = 7.663(3)\text{ \AA}$	$b = 18.437(2)\text{ \AA}$	$c = 9.277(4)\text{ \AA}$
$\alpha = 90^\circ$	$\beta = 90^\circ$	$\gamma = 90^\circ$
$F(000) = 624\text{ e}$	$\mu = 19.33\text{ cm}^{-1}$	$V = 1311(2)\text{ \AA}^3$
$Z = 4$	$d_c = 1.555\text{ g/cm}^3$	$\lambda = 0.70926\text{ \AA}$
$N_{me} = 1363$	$N_{un} = 1183$	$N_{ob} = 867$
obs. if $I > 3\sigma(I)$	$N_v = 104$	$N_{ob}/N_v = 8.3$
$2\theta_{max} = 50.0^\circ$	$R = 0.0568$	$R_w = 0.0551$

7) Methyl 4,6-O-benzylidene-2,3-O-dibutylstannylene- α -D-glucopyranoside

$C_{44}H_{68}O_{12}Sn_2$	MW = 1026.2	$t = -70\text{ }^\circ\text{C}$
orthorhombic	$P2_12_12_1$ (No. 19)	noncentrosymmetric
$a = 12.479(2)\text{ \AA}$	$b = 19.202(5)\text{ \AA}$	$c = 19.654(6)\text{ \AA}$
$\alpha = 90^\circ$	$\beta = 90^\circ$	$\gamma = 90^\circ$
$F(000) = 2112\text{ e}$	$\mu = 11.18\text{ cm}^{-1}$	$V = 4710(3)\text{ \AA}^3$
$Z = 4$	$d_c = 1.447\text{ g/cm}^3$	$\lambda = 0.70926\text{ \AA}$
$N_{me} = 4038$	$N_{un} = 3975$	$N_{ob} = 3623$
obs. if $I > 3\sigma(I)$	$N_v = 627$	$N_{ob}/N_v = 5.8$
$2\theta_{max} = 46.0^\circ$	$R = 0.0597$	$R_w = 0.0612$

8) Methyl 4,6-O-benzylidene-2,3-O-di-tert-butylstannylene- α -D-glucopyranoside

$C_{44}H_{68}O_{12}Sn_2$	MW = 1026.2	$t = 18\text{ }^\circ\text{C}$
orthorhombic	$P2_12_12_1$ (No. 19)	noncentrosymmetric
$a = 14.525(3)\text{ \AA}$	$b = 15.535(3)\text{ \AA}$	$c = 21.428(3)\text{ \AA}$
$\alpha = 90^\circ$	$\beta = 90^\circ$	$\gamma = 90^\circ$
$F(000) = 2112\text{ e}$	$\mu = 10.88\text{ cm}^{-1}$	$V = 4835(1)\text{ \AA}^3$
$Z = 4$	$d_c = 1.410\text{ g/cm}^3$	$\lambda = 0.70926\text{ \AA}$
$N_{me} = 3758$	$N_{un} = 3731$	$N_{ob} = 2793$
obs. if $I > 3\sigma(I)$	$N_v = 638$	$N_{ob}/N_v = 4.4$
$2\theta_{max} = 46.0^\circ$	$R = 0.0354$	$R_w = 0.0382$

9) Benzyl 4,6-O-benzylidene-2,3-O-dibutylstannylene- α -D-glucopyranoside

$C_{56}H_{76}O_{12}Sn_2$	MW = 1178.4	$t = 18\text{ }^\circ\text{C}$
triclinic	P1 (No. 1)	noncentrosymmetric
$a = 9.887(3)\text{ \AA}$	$b = 10.595(3)\text{ \AA}$	$c = 14.421(3)\text{ \AA}$
$\alpha = 77.09(2)^\circ$	$\beta = 77.74(2)^\circ$	$\gamma = 75.09(2)^\circ$
$F(000) = 608\text{ e}$	$\mu = 9.47\text{ cm}^{-1}$	$V = 1403(1)\text{ \AA}^3$
$Z = 1$	$d_c = 1.394\text{ g/cm}^3$	$\lambda = 0.70926\text{ \AA}$
$N_{me} = 4059$	$N_{un} = 4059$	$N_{ob} = 3046$
obs. if $I > 3\sigma(I)$	$N_v = 771$	$N_{ob}/N_v = 4.0$
$2\theta_{max} = 46.0^\circ$	$R = 0.0586$	$R_w = 0.0626$

10) Tetrasulfur tetranitride arsenic pentafluoride adduct

$S_4N_4 \cdot AsF_5$	MW = 354.2	$t = 18\text{ }^\circ\text{C}$
monoclinic	P2 ₁ (No. 4)	noncentrosymmetric
$a = 5.609(6)\text{ \AA}$	$b = 11.115(7)\text{ \AA}$	$c = 7.709(4)\text{ \AA}$
$\alpha = 90^\circ$	$\beta = 109.03(4)^\circ$	$\gamma = 90^\circ$
$F(000) = 340\text{ e}$	$\mu = 46.56\text{ cm}^{-1}$	$V = 454\text{ \AA}^3$
$Z = 4$	$d_c = 2.588\text{ g/cm}^3$	$\lambda = 0.70926\text{ \AA}$
$N_{me} = 1516$	$N_{un} = 1393$	$N_{ob} = 788$
obs. if $I > 3\sigma(I)$	$N_v = 126$	$N_{ob}/N_v = 6.3$
$2\theta_{max} = 60.0^\circ$	$R = 0.041$	$R_w = 0.040$

11) Trichloroselenium(IV) hexafluoroarsenate(V)

$\text{SeCl}_3\text{AsF}_6$	MW = 374.2	$t = 18^\circ\text{C}$
monoclinic	$P2_1/c$ (No. 14)	centrosymmetric
$a = 7.678(1) \text{ \AA}$	$b = 9.380(3) \text{ \AA}$	$c = 11.920(3) \text{ \AA}$
$\alpha = 90^\circ$	$\beta = 98.19(2)^\circ$	$\gamma = 90^\circ$
$F(000) = 688 \text{ e}$	$\mu = 92.16 \text{ cm}^{-1}$	$V = 849(1) \text{ \AA}^3$
$Z = 4$	$d_c = 2.925 \text{ g/cm}^3$	$\lambda = 0.70926 \text{ \AA}$
$N_{\text{me}} = 1664$	$N_{\text{un}} = 1484$	$N_{\text{ob}} = 1151$
obs. if $I > 3\sigma(I)$	$N_v = 100$	$N_{\text{ob}}/N_v = 11.5$
$2\theta_{\text{max}} = 50.0^\circ$	$R = 0.0525$	$R_w = 0.0554$

12) 4-(N-ethylanilo)-2-ethoxycyclohexyltelluriumdibromide

$\text{C}_{16}\text{H}_{25}\text{NOBr}_2\text{Te}$	MW = 534.8	$t = 18^\circ\text{C}$
monoclinic	$P2_1/c$ (No. 14)	centrosymmetric
$a = 9.304(5) \text{ \AA}$	$b = 8.179(2) \text{ \AA}$	$c = 24.932(5) \text{ \AA}$
$\alpha = 90^\circ$	$\beta = 92.34(4)^\circ$	$\gamma = 90^\circ$
$F(000) = 1032 \text{ e}$	$\mu = 57.48 \text{ cm}^{-1}$	$V = 1895(1) \text{ \AA}^3$
$Z = 4$	$d_c = 1.874 \text{ g/cm}^3$	$\lambda = 0.70926 \text{ \AA}$
$N_{\text{me}} = 2905$	$N_{\text{un}} = 2614$	$N_{\text{ob}} = 1299$
obs. if $I > 3\sigma(I)$	$N_v = 232$	$N_{\text{ob}}/N_v = 5.6$
$2\theta_{\text{max}} = 46.0^\circ$	$R = 0.0538$	$R_w = 0.0633$

13) 3,5-dimethoxy-4-phenylcyclohexanecarbonitrile

$C_{15}H_{19}NO_2$	MW = 245.3	$t = 18\text{ }^{\circ}\text{C}$
monoclinic	$P2_1/a$ (No. 14)	centrosymmetric
$a = 8.292(3)\text{ \AA}$	$b = 15.412(3)\text{ \AA}$	$c = 10.681(3)\text{ \AA}$
$\alpha = 90^{\circ}$	$\beta = 93.41(3)^{\circ}$	$\gamma = 90^{\circ}$
$F(000) = 528\text{ e}$	$\mu = 0.73\text{ cm}^{-1}$	$V = 1362\text{ \AA}^3$
$Z = 4$	$d_c = 1.195\text{ g/cm}^3$	$\lambda = 0.70926\text{ \AA}$
$N_{me} = 2094$	$N_{un} = 1887$	$N_{ob} = 926$
obs. if $ I > 3\sigma(I)$	$N_v = 190$	$N_{ob}/N_v = 4.9$
$2\theta_{max} = 46.0^{\circ}$	$R = 0.0624$	$R_w = 0.0688$

**14) 1,1,3,3-tetramethyl-2-phenyl-2-(2',6'-diphenyl-4'-pyrylio)-guanidinium
diperchlorate**

$C_{28}H_{29}N_3O \cdot 2ClO_4$	MW = 622.5	$t = 18\text{ }^{\circ}\text{C}$
monoclinic	$P2_1/n$ (No. 14)	centrosymmetric
$a = 14.535(3)\text{ \AA}$	$b = 13.685(3)\text{ \AA}$	$c = 23.579(7)\text{ \AA}$
$\alpha = 90^{\circ}$	$\beta = 140.38(2)^{\circ}$	$\gamma = 90^{\circ}$
$F(000) = 1296\text{ e}$	$\mu = 2.70\text{ cm}^{-1}$	$V = 2991\text{ \AA}^3$
$Z = 4$	$d_c = 1.382\text{ g/cm}^3$	$\lambda = 0.70926\text{ \AA}$
$N_{me} = 3016$	$N_{un} = 2774$	$N_{ob} = 1595$
obs. if $ I > 3\sigma(I)$	$N_v = 526$	$N_{ob}/N_v = 3.0$
$2\theta_{max} = 40.0^{\circ}$	$R = 0.0636$	$R_w = 0.0671$

15) (2,4,6-tri-*t*-butylphenyl)di-fluoro-tri-phenyl-iminophosphorane

$2(C_{37}H_{44}NF_2P)$	MW = 1143.46	$t = 18\text{ }^\circ\text{C}$
triclinic	P-1 (No. 2)	centrosymmetric
$a = 13.728(3)\text{ \AA}$	$b = 23.808(5)\text{ \AA}$	$c = 10.125(2)\text{ \AA}$
$\alpha = 95.69(1)^\circ$	$\beta = 101.37(1)^\circ$	$\gamma = 91.62(2)^\circ$
$F(000) = 1224\text{ e}$	$\mu = 1.17\text{ cm}^{-1}$	$V = 3224(1)\text{ \AA}^3$
$Z = 2$	$d_c = 1.178\text{ g/cm}^3$	$\lambda = 0.71069\text{ \AA}$
$N_{me} = 19553$	$N_{un} = 18827$	$N_{ob} = 5430$
obs. if $I > 3\sigma(I)$	$N_v = 919$	$N_{ob}/N_v = 5.9$
$2\theta_{max} = 60.0^\circ$	$R = 0.0498$	$R_w = 0.0498$

16) ((eta⁶-Toluene)-(2,4,6-tri-*t*-butylphenyl)iminophosphenium)
tetrachlorogallate

$C_{25}H_{37}NPCI_4Ga$	MW = 594.08	$t = 18\text{ }^\circ\text{C}$
orthorhombic	Pbca (No. 61)	centrosymmetric
$a = 25.006(9)\text{ \AA}$	$b = 20.358(8)\text{ \AA}$	$c = 12.126(5)\text{ \AA}$
$\alpha = 90^\circ$	$\beta = 90^\circ$	$\gamma = 90^\circ$
$F(000) = 2464\text{ e}$	$\mu = 13.01\text{ cm}^{-1}$	$V = 6173(8)\text{ \AA}^3$
$Z = 8$	$d_c = 1.278\text{ g/cm}^3$	$\lambda = 0.71069\text{ \AA}$
$N_{me} = 3719$	$N_{un} = 3719$	$N_{ob} = 1136$
obs. if $I > 3\sigma(I)$	$N_v = 289$	$N_{ob}/N_v = 3.9$
$2\theta_{max} = 46.0^\circ$	$R = 0.0760$	$R_w = 0.0760$

17) 10-chloro-5-10-dihydrophenarsazine

$2C_{24}H_{18}NAsCl \cdot C_6H_6$	MW = 633.3	$t = 18^\circ C$
orthorhombic	Pbca (No. 61)	centrosymmetric
$a = 26.969(11) \text{ \AA}$	$b = 16.252(9) \text{ \AA}$	$c = 13.035(11) \text{ \AA}$
$\alpha = 90^\circ$	$\beta = 90^\circ$	$\gamma = 90^\circ$
$F(000) = 2544 \text{ e}$	$\mu = 25.42 \text{ cm}^{-1}$	$V = 5712(10) \text{ \AA}^3$
$Z = 8$	$d_c = 1.472 \text{ g/cm}^3$	$\lambda = 0.71069 \text{ \AA}$
$N_{me} = 5335$	$N_{un} = 5335$	$N_{ob} = 1042$
obs. if $I > 3\sigma(I)$	$N_v = 264$	$N_{ob}/N_v = 3.95$
$2\theta_{max} = 50.0^\circ$	$R = 0.0483$	$R_w = 0.0483$

18) 2-Amino ethylene sulphonate

$C_2H_7NO_3S$	MW = 125.1	$t = 18^\circ C$
monoclinic	$P2_1/c$ (No. 14)	centrosymmetric
$a = 5.289(2) \text{ \AA}$	$b = 11.663(7) \text{ \AA}$	$c = 7.935(2) \text{ \AA}$
$\alpha = 90^\circ$	$\beta = 94.02(3)^\circ$	$\gamma = 90^\circ$
$F(000) = 264 \text{ e}$	$\mu = 5.31 \text{ cm}^{-1}$	$V = 488.3(4) \text{ \AA}^3$
$Z = 4$	$d_c = 1.702 \text{ g/cm}^3$	$\lambda = 0.71069 \text{ \AA}$
$N_{me} = 1173$	$N_{un} = 1032$	$N_{ob} = 559$
obs. if $I > 3\sigma(I)$	$N_v = 64$	$N_{ob}/N_v = 8.7$
$2\theta_{max} = 57.5^\circ$	$R = 0.0332$	$R_w = 0.0343$

19) 2-benzyl-4,4-dichloro-2-trimethylsilylamino-3-trimethylsilyl-1,3,2,4-thiaazaphosphalimetidine

$C_6H_{18}N_2AlSi_2PSCl_2$	MW = 335.3	$t = 18\text{ }^\circ\text{C}$
monoclinic	$P2_1/n$ (No. 14)	centrosymmetric
$a = 6.599(3)\text{ \AA}$	$b = 12.602(2)\text{ \AA}$	$c = 20.070(2)\text{ \AA}$
$\alpha = 90^\circ$	$\beta = 96.02(2)^\circ$	$\gamma = 90^\circ$
$F(000) = 696\text{ e}$	$\mu = 7.80\text{ cm}^{-1}$	$V = 1659.8(8)\text{ \AA}^3$
$Z = 4$	$d_c = 1.342\text{ g/cm}^3$	$\lambda = 0.71069\text{ \AA}$
$N_{me} = 3344$	$N_{un} = 3064$	$N_{ob} = 1774$
obs. if $I > 3\sigma(I)$	$N_v = 137$	$N_{ob}/N_v = 12.95$
$2\theta_{max} = 50.0^\circ$	$R = 0.0330$	$R_w = 0.0350$

20) 1,3-dichloro-mu-chloro-tri-sulphinium hexafluoroarsenate

$S_3Cl_3AsF_6$	MW = 391.5	$t = 18\text{ }^\circ\text{C}$
monoclinic	$C2/c$ (No. 15)	centrosymmetric
$a = 14.584(5)\text{ \AA}$	$b = 7.648(1)\text{ \AA}$	$c = 11.674(3)\text{ \AA}$
$\alpha = 90^\circ$	$\beta = 126.63(1)^\circ$	$\gamma = 90^\circ$
$F(000) = 744\text{ e}$	$\mu = 46.32\text{ cm}^{-1}$	$V = 1044.9(9)\text{ \AA}^3$
$Z = 4$	$d_c = 2.488\text{ g/cm}^3$	$\lambda = 0.71069\text{ \AA}$
$N_{me} = 980$	$N_{un} = 936$	$N_{ob} = 544$
obs. if $I > 3\sigma(I)$	$N_v = 100$	$N_{ob}/N_v = 5.4$
$2\theta_{max} = 50.0^\circ$	$R = 0.0646$	$R_w = 0.0646$

21) bis((Chloro)-(eta⁵-cyclopentadienyl))-molybdenum tetraphenylborate

$C_{10}H_{10}F_4Cl_2Mo$	MW = 385.04	$t = 18\text{ }^{\circ}C$
orthorhombic	Pmn2 ₁ (No. 31)	noncentrosymmetric
$a = 9.330(2)\text{ \AA}$	$b = 6.882(1)\text{ \AA}$	$c = 9.599(1)\text{ \AA}$
$\alpha = 90^{\circ}$	$\beta = 90^{\circ}$	$\gamma = 90^{\circ}$
$F(000) = 376\text{ e}$	$\mu = 15.03\text{ cm}^{-1}$	$V = 616.3(3)\text{ \AA}^3$
$Z = 2$	$d_c = 2.075\text{ g/cm}^3$	$\lambda = 0.71069\text{ \AA}$
$N_{me} = 1078$	$N_{un} = 1078$	$N_{ob} = 874$
obs. if $I > 3\sigma(I)$	$N_v = 96$	$N_{ob}/N_v = 9.2$
$2\theta_{max} = 59.9^{\circ}$	$R = 0.0288$	$R_w = 0.0330$

22) ((eta⁶-Benzene)-(2,4,6-tri-*t*-butylphenyl)iminophosphenium)((mu²-chloro)-bis(trichloro))-gallium

$C_{24}H_{35}NPCI_7Ga_2$	MW = 756.1	$t = 18\text{ }^{\circ}C$
triclinic	P-1 (No. 2)	centrosymmetric
$a = 11.579(2)\text{ \AA}$	$b = 16.350(3)\text{ \AA}$	$c = 11.085(3)\text{ \AA}$
$\alpha = 90.74(2)^{\circ}$	$\beta = 118.00(2)^{\circ}$	$\gamma = 73.53(2)^{\circ}$
$F(000) = 764\text{ e}$	$\mu = 21.23\text{ cm}^{-1}$	$V = 1758.9(8)\text{ \AA}^3$
$Z = 2$	$d_c = 1.428\text{ g/cm}^3$	$\lambda = 0.71069\text{ \AA}$
$N_{me} = 5175$	$N_{un} = 4888$	$N_{ob} = 3338$
obs. if $I > 3\sigma(I)$	$N_v = 377$	$N_{ob}/N_v = 8.9$
$2\theta_{max} = 46.0^{\circ}$	$R = 0.0386$	$R_w = 0.0386$

23) 1,3-Dimethyl-1,3-diaza-2-phospholidinium tetrachloro-gallium

$C_4H_{10}N_2PCl_4Ga$	MW = 328.6	$t = 18\text{ }^\circ\text{C}$
monoclinic	$P2_1$ (No. 4)	noncentrosymmetric
$a = 6.489(3)\text{ \AA}$	$b = 13.893(5)\text{ \AA}$	$c = 7.066(5)\text{ \AA}$
$\alpha = 90^\circ$	$\beta = 92.58(5)^\circ$	$\gamma = 90^\circ$
$F(000) = 324\text{ e}$	$\mu = 30.86\text{ cm}^{-1}$	$V = 636.3(6)\text{ \AA}^3$
$Z = 2$	$d_c = 1.715\text{ g/cm}^3$	$\lambda = 0.71069\text{ \AA}$
$N_{me} = 1023$	$N_{un} = 934$	$N_{ob} = 499$
obs. if $ I > 3\sigma(I)$	$N_v = 107$	$N_{ob}/N_v = 4.7$
$2\theta_{max} = 46.0^\circ$	$R = 0.0516$	$R_w = 0.0516$

24) 1-methyl-2-chloro-3-methyl-3-tribromoborano-1,2,3-ethyldiaminoborane

$C_4H_{10}N_2B_2Cl_{0.5}Br_{3.5}$	MW = 405.2	$t = 18\text{ }^\circ\text{C}$
orthorhombic	$P2_12_12_1$ (No. 19)	noncentrosymmetric
$a = 11.971(2)\text{ \AA}$	$b = 13.235(1)\text{ \AA}$	$c = 7.202(3)\text{ \AA}$
$\alpha = 90^\circ$	$\beta = 90^\circ$	$\gamma = 90^\circ$
$F(000) = 756\text{ e}$	$\mu = 123.11\text{ cm}^{-1}$	$V = 1141.0(4)\text{ \AA}^3$
$Z = 4$	$d_c = 2.358\text{ g/cm}^3$	$\lambda = 0.71069\text{ \AA}$
$N_{me} = 963$	$N_{un} = 963$	$N_{ob} = 613$
obs. if $ I > 3\sigma(I)$	$N_v = 117$	$N_{ob}/N_v = 5.2$
$2\theta_{max} = 46.0^\circ$	$R = 0.0604$	$R_w = 0.0604$

25) 1,1-stannacycloheptane bischloroacetate

$C_{10}H_{16}O_4Cl_2Sn$	MW = 389.83	$t = 18\text{ }^{\circ}C$
orthorhombic	$P2_12_12_1$ (No. 19)	noncentrosymmetric
$a = 10.405(2)\text{ \AA}$	$b = 17.990(2)\text{ \AA}$	$c = 7.752(2)\text{ \AA}$
$\alpha = 90^{\circ}$	$\beta = 90^{\circ}$	$\gamma = 90^{\circ}$
$F(000) = 768\text{ e}$	$\mu = 21.37\text{ cm}^{-1}$	$V = 1451.2(5)\text{ \AA}^3$
$Z = 4$	$d_c = 1.784\text{ g/cm}^3$	$\lambda = 0.71069\text{ \AA}$
$N_{me} = 1517$	$N_{un} = 1516$	$N_{ob} = 1135$
obs. if $I > 3\sigma(I)$	$N_v = 169$	$N_{ob}/N_v = 6.7$
$2\theta_{max} = 50.0^{\circ}$	$R = 0.0284$	$R_w = 0.0284$

26) Lithium tetrakis(1-imidazolyl)borate solvate,

$C_{26}H_{34}B_2Li_2N_{16}O_3$	MW = 654.2	$t = 18\text{ }^{\circ}C$
triclinic	P-1 (No. 2)	centrosymmetric
$a = 12.380(2)\text{ \AA}$	$b = 14.434(2)\text{ \AA}$	$c = 9.683(3)\text{ \AA}$
$\alpha = 90.36(2)^{\circ}$	$\beta = 105.44(2)^{\circ}$	$\gamma = 90.75(2)^{\circ}$
$F(000) = 684\text{ e}$	$\mu = 0.840\text{ cm}^{-1}$	$V = 1668(1)\text{ \AA}^3$
$Z = 2$	$d_c = 1.303\text{ g/cm}^3$	$\lambda = 0.71069\text{ \AA}$
$N_{me} = 4901$	$N_{un} = 4648$	$N_{ob} = 2620$
obs. if $I > 3\sigma(I)$	$N_v = 442$	$N_{ob}/N_v = 5.9$
$2\theta_{max} = 46.0^{\circ}$	$R = 0.0386$	$R_w = 0.0396$

31) 1,10-phenanthroline tribromide

$C_{12}H_9N_2Br_3$	MW = 420.9	$t = 18\text{ }^\circ\text{C}$
triclinic	P-1 (No. 2)	centrosymmetric
$a = 8.370(2)\text{ \AA}$	$b = 10.410(4)\text{ \AA}$	$c = 8.171(1)\text{ \AA}$
$\alpha = 107.52(2)^\circ$	$\beta = 97.35(1)^\circ$	$\gamma = 94.82(2)^\circ$
$F(000) = 400\text{ e}$	$\mu = 90.67\text{ cm}^{-1}$	$V = 667(1)\text{ \AA}^3$
$Z = 2$	$d_c = 2.093\text{ g/cm}^3$	$\lambda = 0.71069\text{ \AA}$
$N_{me} = 1993$	$N_{un} = 1845$	$N_{ob} = 1061$
obs. if $I > 3\sigma(I)$	$N_v = 155$	$N_{ob}/N_v = 6.9$
$2\theta_{max} = 46.0^\circ$	$R = 0.0270$	$R_w = 0.0290$

32) tetrakis(1-imidazolyl)borate(2+) dichloride. monohydrate

$BC_{12}H_{17}N_8OCl_2$	MW = 371.0	$t = 18\text{ }^\circ\text{C}$
monoclinic	C2/c (No. 15)	centrosymmetric
$a = 16.366(2)\text{ \AA}$	$b = 6.903(2)\text{ \AA}$	$c = 16.088(1)\text{ \AA}$
$\alpha = 90^\circ$	$\beta = 113.13(1)^\circ$	$\gamma = 90^\circ$
$F(000) = 768\text{ e}$	$\mu = 4.068\text{ cm}^{-1}$	$V = 1672(1)\text{ \AA}^3$
$Z = 4$	$d_c = 1.474\text{ g/cm}^3$	$\lambda = 0.71069\text{ \AA}$
$N_{me} = 1327$	$N_{un} = 1275$	$N_{ob} = 832$
obs. if $I > 3\sigma(I)$	$N_v = 114$	$N_{ob}/N_v = 7.3$
$2\theta_{max} = 46.0^\circ$	$R = 0.0490$	$R_w = 0.0510$

29) Tetraethylammonium tetraphenylborate

$C_{32}H_{40}NB$	MW = 449.5	$t = 18\text{ }^{\circ}\text{C}$
trigonal	$P3_121$ (No. 152)	noncentrosymmetric
$a = 9.930(4)\text{ \AA}$	$b = 9.930(4)\text{ \AA}$	$c = 24.308(7)\text{ \AA}$
$\alpha = 90^{\circ}$	$\beta = 90^{\circ}$	$\gamma = 120^{\circ}$
$F(000) = 976\text{ e}$	$\mu = 0.75\text{ cm}^{-1}$	$V = 2076(2)\text{ \AA}^3$
$Z = 4$	$d_c = 1.439\text{ g/cm}^3$	$\lambda = 0.70926\text{ \AA}$
$N_{me} = 5449$	$N_{un} = 1984$	$N_{ob} = 2038$
obs. if $I > 3\sigma(I)$	$N_v = 216$	$N_{ob}/N_v = 9.4$
$2\theta_{max} = 40.0^{\circ}$	$R = 0.0699$	$R_w = 0.0726$

30) 2-phenylpyridinium tetraphenylborate

$BC_{35}H_{30}N$	MW = 475.4	$t = 18\text{ }^{\circ}\text{C}$
monoclinic	$P2_1/c$ (No. 14)	noncentrosymmetric
$a = 12.208(2)\text{ \AA}$	$b = 13.182(5)\text{ \AA}$	$c = 17.015(1)\text{ \AA}$
$\alpha = 90^{\circ}$	$\beta = 107.28(1)^{\circ}$	$\gamma = 90^{\circ}$
$F(000) = 1008\text{ e}$	$\mu = 0.64\text{ cm}^{-1}$	$V = 2615(1)\text{ \AA}^3$
$Z = 4$	$d_c = 1.208\text{ g/cm}^3$	$\lambda = 0.71069\text{ \AA}$
$N_{me} = 4032$	$N_{un} = 3831$	$N_{ob} = 2025$
obs. if $I > 3\sigma(I)$	$N_v = 334$	$N_{ob}/N_v = 6.1$
$2\theta_{max} = 46.0^{\circ}$	$R = 0.0410$	$R_w = 0.0400$

31) Tetramethylammonium Eneaiodide

$C_4H_{12}NI_9$	MW = 419.5	$t = 18\text{ }^\circ\text{C}$
monoclinic	$P2_1/n$ (No. 14)	centrosymmetric
$a = 11.618(3)\text{ \AA}$	$b = 15.161(4)\text{ \AA}$	$c = 13.192(3)\text{ \AA}$
$\alpha = 90^\circ$	$\beta = 95.60(2)^\circ$	$\gamma = 90^\circ$
$F(000) = 1040\text{ e}$	$\mu = 59.64\text{ cm}^{-1}$	$V = 2312(1)\text{ \AA}^3$
$Z = 8$	$d_c = 1.747\text{ g/cm}^3$	$\lambda = 0.71069\text{ \AA}$
$N_{me} = 4710$	$N_{un} = 4246$	$N_{ob} = 1614$
obs if $ I > 3\sigma(I)$	$N_v = 210$	$N_{ob}/N_v = 7.7$
$2\theta_{max} = 60.0^\circ$	$R = 0.0602$	$R_w = 0.0638$

32) 7,8-benzoquinolinium tetraphenylborate

$BC_{39}H_{33}N_2$	MW = 540.5	$t = 18\text{ }^\circ\text{C}$
triclinic	$P\bar{1}$ (No. 2)	centrosymmetric
$a = 11.502(5)\text{ \AA}$	$b = 14.949(4)\text{ \AA}$	$c = 9.810(2)\text{ \AA}$
$\alpha = 104.11(2)^\circ$	$\beta = 101.92(3)^\circ$	$\gamma = 70.26(3)^\circ$
$F(000) = 572\text{ e}$	$\mu = 0.630\text{ cm}^{-1}$	$V = 1525(1)\text{ \AA}^3$
$Z = 2$	$d_c = 1.177\text{ g/cm}^3$	$\lambda = 0.71069\text{ \AA}$
$N_{me} = 3769$	$N_{un} = 2699$	$N_{ob} = 1456$
obs. if $ I > 3\sigma(I)$	$N_v = 380$	$N_{ob}/N_v = 3.8$
$2\theta_{max} = 40.0^\circ$	$R = 0.0460$	$R_w = 0.0460$

33) Quinoclidinium Eneaiodide

$C_{14}H_{28}N_2I_9$	MW = 1254.3	$t = 18\text{ }^{\circ}\text{C}$
triclinic	$P\bar{1}$ (No. 2)	centrosymmetric
$a = 9.727(1)\text{ \AA}$	$b = 13.919(1)\text{ \AA}$	$c = 9.209(2)\text{ \AA}$
$\alpha = 100.21(1)^{\circ}$	$\beta = 105.84(1)^{\circ}$	$\gamma = 92.55(1)^{\circ}$
$F(000) = 1080\text{ e}$	$\mu = 11.862\text{ cm}^{-1}$	$V = 1174(1)\text{ \AA}^3$
$Z = 2$	$d_c = 3.546\text{ g/cm}^3$	$\lambda = 0.71069\text{ \AA}$
$N_{me} = 3493$	$N_{un} = 3265$	$N_{ob} = 2001$
obs. if $I > 2\sigma(I)$	$N_v = 208$	$N_{ob}/N_v = 9.6$
$2\theta_{max} = 46.0^{\circ}$	$R = 0.0328$	$R_w = 0.0772$

34) N,N,N',N'-Tetramethyl ethylenediammonium tetraphenylborate

$BC_{30}H_{37}N_2$	MW = 436.5	$t = 18\text{ }^{\circ}\text{C}$
monoclinic	$P2_1/n$ (No. 14)	centrosymmetric
$a = 15.789(6)\text{ \AA}$	$b = 18.377(6)\text{ \AA}$	$c = 9.636(6)\text{ \AA}$
$\alpha = 90^{\circ}$	$\beta = 105.91(6)^{\circ}$	$\gamma = 90^{\circ}$
$F(000) = 944\text{ e}$	$\mu = 4.340\text{ cm}^{-1}$	$V = 2689(4)\text{ \AA}^3$
$Z = 4$	$d_c = 1.078\text{ g/cm}^3$	$\lambda = 1.54178\text{ \AA}$
$N_{me} = 4929$	$N_{un} = 2456$	$N_{ob} = 1083$
obs. if $I > 3\sigma(I)$	$N_v = 299$	$N_{ob}/N_v = 3.6$
$2\theta_{max} = 108.2^{\circ}$	$R = 0.0690$	$R_w = 0.0740$

35) N,N,N',N'-Tetramethyl-1,3-propanediammonium tetraphenylborate chloride

$C_{31}H_{40}N_2BCl$	MW = 486.9	$t = 18\text{ }^{\circ}\text{C}$
orthorhombic	$P2_12_12_1$ (No. 19)	noncentrosymmetric
$a = 22.767(7)\text{ \AA}$	$b = 9.265(23)\text{ \AA}$	$c = 13.594(7)\text{ \AA}$
$\alpha = 90^{\circ}$	$\beta = 90^{\circ}$	$\gamma = 90^{\circ}$
$F(000) = 1048\text{ e}$	$\mu = 1.510\text{ cm}^{-1}$	$V = 2867(7)\text{ \AA}^3$
$Z = 2$	$d_c = 1.127\text{ g/cm}^3$	$\lambda = 0.71069\text{ \AA}$
$N_{me} = 2895$	$N_{un} = 2895$	$N_{ob} = 1730$
obs. if $I > 3\sigma(I)$	$N_v = 316$	$N_{ob}/N_v = 5.5$
$2\theta_{max} = 50.0^{\circ}$	$R = 0.0500$	$R_w = 0.0512$

36) N,N,N',N'-Tetramethyl-1,4-butanediammonium tetraphenylborate

$B_2C_{60}H_{68}N_4$	MW = 866.8	$t = -60\text{ }^{\circ}\text{C}$
monoclinic	$P2_1/n$ (No. 14)	centrosymmetric
$a = 9.192(3)\text{ \AA}$	$b = 20.415(4)\text{ \AA}$	$c = 13.586(3)\text{ \AA}$
$\alpha = 90^{\circ}$	$\beta = 97.46(2)^{\circ}$	$\gamma = 90^{\circ}$
$F(000) = 932\text{ e}$	$\mu = 4.600\text{ cm}^{-1}$	$V = 2527(1)\text{ \AA}^3$
$Z = 2$	$d_c = 1.139\text{ g/cm}^3$	$\lambda = 1.54178\text{ \AA}$
$N_{me} = 4178$	$N_{un} = 3908$	$N_{ob} = 1809$
obs. if $I > 3\sigma(I)$	$N_v = 298$	$N_{ob}/N_v = 6.1$
$2\theta_{max} = 120.3^{\circ}$	$R = 0.0668$	$R_w = 0.0671$

37) Tetramethylphosphonium triiodide

$C_4H_{12}PI_3$	MW = 471.8	$t = 18\text{ }^\circ\text{C}$
tetragonal	$P4_2/m$ (No. 84)	centrosymmetric
$a = 15.098(4)\text{ \AA}$	$b = 15.098(4)\text{ \AA}$	$c = 13.770(4)\text{ \AA}$
$\alpha = 90^\circ$	$\beta = 90^\circ$	$\gamma = 90^\circ$
$F(000) = 2100\text{ e}$	$\mu = 75.39\text{ cm}^{-1}$	$V = 3139(1)\text{ \AA}^3$
$Z = 10$	$d_c = 2.496\text{ g/cm}^3$	$\lambda = 0.71069\text{ \AA}$
$N_{me} = 2509$	$N_{un} = 2310$	$N_{ob} = 1198$
obs. if $I > 3\sigma(I)$	$N_v = 101$	$N_{ob}/N_v = 11.9$
$2\theta_{max} = 46.0^\circ$	$R = 0.0272$	$R_w = 0.0251$

38) 2,2',2''-tripyridinium tetraphenylborate monohydrate

$B_2C_{63}H_{55}N_3O$	MW = 891.8	$t = 18\text{ }^\circ\text{C}$
monoclinic	$C2/c$ (No. 15)	centrosymmetric
$a = 27.148(8)\text{ \AA}$	$b = 11.965(9)\text{ \AA}$	$c = 15.751(3)\text{ \AA}$
$\alpha = 90^\circ$	$\beta = 109.58(4)^\circ$	$\gamma = 90^\circ$
$F(000) = 1888\text{ e}$	$\mu = 0.670\text{ cm}^{-1}$	$V = 4820(6)\text{ \AA}^3$
$Z = 4$	$d_c = 1.229\text{ g/cm}^3$	$\lambda = 0.71069\text{ \AA}$
$N_{me} = 3639$	$N_{un} = 3551$	$N_{ob} = 1326$
obs. if $I > 3\sigma(I)$	$N_v = 313$	$N_{ob}/N_v = 4.3$
$2\theta_{max} = 46.0^\circ$	$R = 0.0360$	$R_w = 0.0359$

39) Tetraethylphosphonium heptafluoroborate

$C_8H_{20}PF_7$	MW = 1033.5	$t = 18\text{ }^\circ\text{C}$
orthorhombic	C2ca (No. 41)	noncentrosymmetric
$a = 12.844(3)\text{ \AA}$	$b = 15.838(10)\text{ \AA}$	$c = 11.651(5)\text{ \AA}$
$\alpha = 90^\circ$	$\beta = 90^\circ$	$\gamma = 90^\circ$
$F(000) = 2856\text{ e}$	$\mu = 92.20\text{ cm}^{-1}$	$V = 2370(2)\text{ \AA}^3$
$Z = 4$	$d_c = 2.902\text{ g/cm}^3$	$\lambda = 0.71069\text{ \AA}$
$N_{me} = 650$	$N_{un} = 650$	$N_{ob} = 586$
obs. if $I > 2\sigma(I)$	$N_v = 78$	$N_{ob}/N_v = 7.5$
$2\theta_{max} = 46.0^\circ$	$R = 0.0280$	$R_w = 0.0720$

40) tetrahexylammonium pentafluoroborate

$C_{24}H_{52}F_5N$	MW = 989.2	$t = -20\text{ }^\circ\text{C}$
triclinic	PT(No. 2)	centrosymmetric
$a = 10.288(3)\text{ \AA}$	$b = 21.047(4)\text{ \AA}$	$c = 9.434(2)\text{ \AA}$
$\alpha = 95.85(2)^\circ$	$\beta = 117.09(2)^\circ$	$\gamma = 96.41(2)^\circ$
$F(000) = 936\text{ e}$	$\mu = 43.8\text{ cm}^{-1}$	$V = 1780(1)\text{ \AA}^3$
$Z = 2$	$d_c = 1.846\text{ g/cm}^3$	$\lambda = 0.71069\text{ \AA}$
$N_{me} = 5282$	$N_{un} = 4957$	$N_{ob} = 4955$
obs. if $I > 3\sigma(I)$	$N_v = 320$	$N_{ob}/N_v = 15.5$
$2\theta_{max} = 46.0^\circ$	$R = 0.0619$	$R_w = 0.1584$

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