APPLICATION OF $^{13}$C NMR SPECTROSCOPY IN THE ASSIGNMENT OF $^1$H NMR SIGNALS OF NONEQUIVALENT SCH$_3$ GROUPS

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The SCH$_3$ groups of 3- and/or 5 alkyl substituted 2,4,6-trithiaheptanes have almost identical chemical shifts in both $^1$H and $^{13}$C nmr spectra. A combination of gated decoupling and single-frequency off-resonance decoupling, followed by the construction of graphs of the type proposed by Pachler, allows the assignment of the $^1$H nmr signals.

Les graphes SCH$_3$ des composés 2,4,6-trithiaheptanes substitués en position 3 et 5 par des groupes alkyl ont des déplacements chimiques presque identiques dans leurs spectres rnm au $^{13}$C et $^1$H. Une combinaison de découplage à fenêtre et de découplage à fréquence unique hors-résonance, suivie par la construction de graphiques de type proposé par Pachler, permet l'attribution des signaux rnm $^1$H.

The $^1$H and $^{13}$C nuclear magnetic resonance spectra of the 2,4,6-trithiaheptanes la-e provide some examples of a familiar problem in the interpretation of nmr spectra. The problem, common to compounds with several chemically nonequivalent -OR, -SR, or -NR$_2$ groups, is the assignment of singlet resonances with very small chemical shift differences, and is illustrated here by the assignment of the nonequivalent S-CH$_3$ groups of Ib and Ic. In both these examples the C-1 and C-7 S-CH$_3$ signals are sharp singlets in both the usual fully decoupled $^{13}$C spectrum and in the $^1$H spectrum, with such a small range of chemical shifts observed for the series la-e that assignments based on the effect of substituents on chemical shifts must be questionable. There are many reports (Freeman and Hill 1971, Shaw 1973) on the correlation of $^{13}$C spectra with $^1$H spectra followed by assignment of the $^{13}$C spectrum from easy assignment of the $^1$H spectrum, and a few cases have been reported (Luzikov et al. 1975, McCabe and Nelson 1976) in which the $^1$H spectrum has been assigned from correlation with an easily interpreted $^{13}$C spectrum. We report an example in which neither $^1$H or $^{13}$C spectrum is readily assigned, yet both assignments are accessible from various combinations of decoupling experiments.

The starting point of our assignment is the observation that in the $^{13}$C spectrum of la, measured under conditions of gated decoupling, (Feeney et al. 1970) the S-CH$_3$ signal is a quartet (J = 139.0 Hz) of triplets (J = 4.7), with the triplet splitting the result of the three-bond proton-carbon coupling through sulphenyl sulfur. In Ib and Ic the gated decoupling gives a quartet (J = 138.9) of triplets (J = 4.5) for C-7, while C-1 appears as a quartet (J = 138.8) of doublets (J = 4.0 for Ib, J = 4.2 for Ic). Hence, the gated decoupling experiment acts as a probe of the asymmetry of the molecule and the $^{13}$C spectrum may be assigned.

Correlation of the $^1$H and $^{13}$C spectra was made for each compound from measurement of a series of 6-8 off-resonance decoupled spectra with a different value of the decoupling frequency for each spectrum of the series. These spectra yield values of J$_{RED}$, the residual directly bonded carbon-proton coupling constant, as a function of decoupling frequency. These J$_{RED}$ measurements are then used to construct plots of the type proposed by Pachler (Pachler 1972) in which values of the ratio J$_{RED}$/s(J$_o$ - J$_{RED}$)$^{1/2}$, where J$_o$ is the magnitude of the directly bonded C-H

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coupling constant measured in the gated decoupling experiment, are plotted vs decoupler frequency, with the zero intercept on the x-axis giving the resonance frequency of the directly bonded proton. This method has been showed valid (Pachler 1972) for values of $\frac{\delta H}{J_{\text{red}}} > \frac{1}{2} J_{\text{red}}$, a condition easily satisfied by the maximum decoupler power of the Varian CFT-20 spectrometer. The plots were excellent straight lines over a range of decoupling frequencies 1000 Hz on either side of the resonance frequency and the intercepts were determined by linear regression analysis. The assignments Ib and Ic agree with what might be expected, in that substitution at C-3 should affect the chemical shift of C-1 protons more than that of C-7 protons, however the real test of the method is the assignment of S-CH$_3$ proton signals in Id and le. Id and le were prepared as a diastereometric mixture and all spectra recorded on solutions of mixture. The graphical method predicts the signal of the S-CH$_3$ protons for the major product Id and the minor product le. These are easily distinguished by the relative peak areas and the experimental measurement places le 4.8 Hz above Id. The usual plots of $J_{\text{red}}$ vs decoupler frequency (Birdsall et al. 1981), even for much narrower ranges of decoupling frequency, were much less accurate and could give misleading results in cases such as this where chemical shift differences are small.

The assignment method outlined here should be applicable to other -SCH$_3$, -OCH$_3$, or -N(CH$_3$)$_2$ examples for which an internal asymmetry of the molecule may be exploited to assign the $^{13}$C spectrum. It is particularly applicable to cases for which chemical shift differences are so small that low-power selective decoupling is impractical, and for which 2-D experiments would require inordinate spectrometer time in order to achieve the resolution needed.

**Experimental**

$^{13}$C nmr spectra were recorded at 20 MHz and $^1$H nmr spectra recorded at 80 MHz using a Varian CFT-20 spectrometer. The same solution containing 100-250 mg/ml CDC$_1$ was used for both sets of spectra. The fully decoupled $^{13}$C spectra were recorded with a spectral width of 4000 Hz and the gated decoupling experiments were carried out with the smallest possible spectral width for which "foldover" of spectral lines could be avoided, typically 1000 Hz. The preparation and characterization of compounds la-e has been reported on elsewhere (Grossert et al. 1981).

**Table I**

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<tr>
<th>Compound</th>
<th>R</th>
<th>R</th>
<th>$\delta_{13C}$ (C-1)</th>
<th>$\delta_{13C}$ (C-7)</th>
<th>$\delta_{1H}$ (C-1)</th>
<th>$\delta_{1H}$ (C-7)</th>
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<tr>
<td>la</td>
<td>H</td>
<td>H</td>
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<td></td>
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<tr>
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<td>Me</td>
<td>H</td>
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<td>14.23</td>
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<td>2.16</td>
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<td>lc</td>
<td>Bu$^0$</td>
<td>H</td>
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<td>Id</td>
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<td>12.8</td>
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<td>2.16</td>
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<tr>
<td>le</td>
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<td>Me</td>
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References


