

**Long Range $^4J_{HH}$ Couplings in
1',3',3'-Trimethylspiro-(indoline-2',3-thietane)-
1,1-dioxide***

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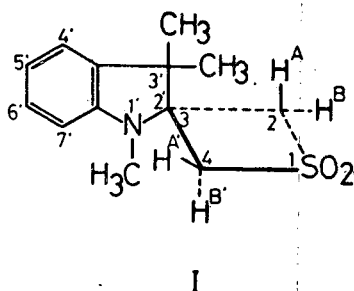
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Iterative analysis of the $AA'BB'$ and $ABCD$ parts of the 100 MHz proton magnetic resonance spectrum of 1',3',3'-trimethylspiro-(indoline-2',3-thietane)-1,1-dioxide(I) using a LAOCOON 3 computer programme has yielded the magnitudes and relative signs of long range proton couplings across four bonds.

WE wish to report here the iterative analysis of two sets of four-coupled protons forming AA' , BB' and $ABCD$ systems in the proton magnetic resonance spectrum of 1',3',3'-trimethylspiro-(indoline-2',3-thietane)-1,1-dioxide (I) obtained by the



reaction of 1,3,3-trimethyl-2-methylene-indoline (Fischer's base) with methanesulphonyl chloride in the presence of triethylamine¹. The present NMR analysis has yielded the magnitudes and relative signs of four-bond long range proton couplings.

The 100 MHz NMR spectrum of I in $CDCl_3$ is reproduced in Fig. 1. The following assignments can be made readily to the various signals: δ 1.36 ($\times CH_3, s$); 2.94 (N- CH_3, s); 4.28 (approximate centre of $AA'BB'$ multiplet due to protons at C-2 and C-4); $\sim 6.5-7.2$ ($ABCD$ multiplet due to 4', 5', 6' and

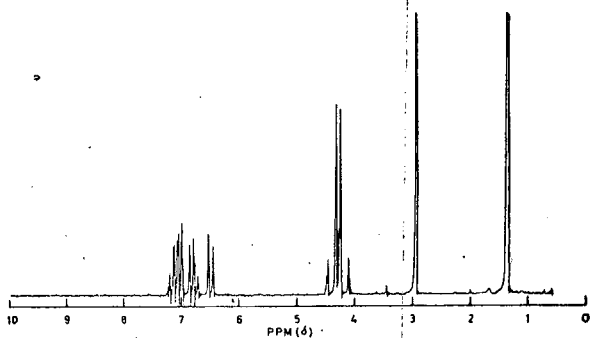


Fig. 1 — 100 MHz PMR spectrum of compound I in $CDCl_3$

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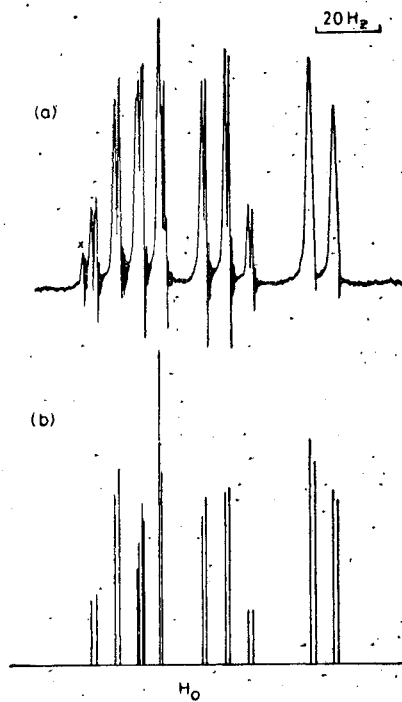


Fig. 2 — (a) Observed and (b) theoretical spectrum of the phenyl protons in I ($ABCD$ analysis)

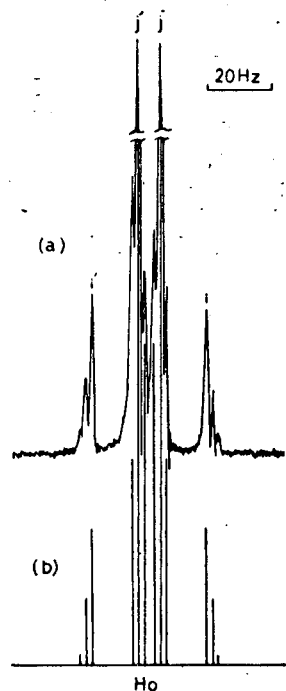


Fig. 3 — (a) Observed and (b) theoretical spectra of protons at C-2 and C-4 in I ($AA'BB'$ analysis)

7' protons). The low field multiplet lines arising from the aromatic protons 4', 5', 6' and 7' and constituting a $ABCD$ system are shown in detail in Fig. 2a. Iterative computer analysis using a LAOCOON 3 programme² in an IBM 7044 computer yielded the following parameters (δ in ppm and J in Hz):

$$\begin{aligned} J_{4'5'} &= 6.97 & J_{4'6'} &= 1.03 & J_{4'7'} &= 0.00 \\ J_{5'6'} &= 7.52 & J_{5'7'} &= 1.16 & J_{6'7'} &= 7.50 \\ \delta_{4'} &= 7.005 & \delta_{5'} &= 6.785 & \delta_{6'} &= 7.112 & \delta_{7'} &= 6.480 \end{aligned}$$

The computed spectrum is shown in Fig. 2b. The rms error is 0.38 Hz. The line on the lowest field marked 'x' in Fig. 2a is due to an impurity. It is of interest to note here that the ${}^4J_{HH}$ coupling between 4' and 6' protons as well as the coupling between 5' and 7' protons across four bonds is about 1 Hz. The sign of all the couplings in the aromatic ring is known to be positive^{3,4} and in our present analysis also all these couplings have the same sign.

The observed spectrum due to the $AA'BB'$ ring protons at C-2 and C-4 is given in Fig. 3a. The spectrum is symmetrical about its centre and is typical of a $AA'BB'$ spin system. The theoretical transition frequencies and intensities for a $AA'BB'$ spin system have been listed by Corio³. It is possible to identify in the observed $AA'BB'$ spectrum four lines that form an AB -type quartet. The identification of these transitions leads to the direct determination of $|\delta_{AB}|$ and $|J_{AB}+J_{AB'}|$. These four transitions are marked i, i', j and j' in Fig. 3a. We thus have $|\delta_{AB}| = [(v_i - v_{i'}) - (v_j - v_{j'})]^\dagger = 15.5$ Hz and $|J_{AB}+J_{AB'}| = \frac{1}{2}[(v_i - v_{i'}) - (v_j - v_{j'})] = 14.00$ Hz. The above values of $|\delta_{AB}|$ and $|J_{AB}+J_{AB'}|$ together with the symmetry relations, $J_{A'B'} = J_{AB}$, $J_{AA'} = J_{BB'}$, $J_{A'B} = J_{AB'}$, were used in the iterative analysis employing the LAOCOON 3 programme. The best values obtained from the analysis (which corresponds to a rms error of 0.45 Hz between observed and calculated transition frequencies) are

$$\begin{aligned} |\delta_{AB}| &= 14.13 \text{ Hz} \\ J_{A'B'} &= J_{AB} = \pm 15.17 \text{ Hz} \\ J_{AA'} &= J_{BB'} = \pm 0.86 \text{ Hz} \\ J_{A'B} &= J_{AB'} = \pm 1.26 \text{ Hz} \end{aligned}$$

and

The computed spectrum corresponding to these parameters is shown in Fig. 3b. Only the absolute value of the chemical shift and the relative signs of

the coupling constants can be determined from the analysis. However, it is known that the sign of the geminal coupling constant is negative in four-membered ring systems^{4,5}. Thus it is reasonable to assign a negative sign to J_{AB} . The long range couplings $J_{AA'} = J_{BB'}$ and $J_{A'B} = J_{AB'}$ are then seen to be positive. The appreciable magnitudes of the long range couplings in this part of the molecule can be attributed to the fact that there are two four-bond coupling paths which link the coupled protons, viz. the H-C₂-C₃-C₄-H and the H-C₂-S-C₄-H paths. It seems to be established^{6,7} now that the magnitude of ${}^4J_{HH}$ depends on the number of coupling paths available. It is also known that a positive maximum value for this coupling is realized for a H-C-C-C-H system when it can assume the W -configuration^{4,8}. Since a fully planar W -configuration is not attained in I, the maximum contribution to coupling by these paths is not realized. However, the π orbitals of the SO₂ group can also be expected to contribute to the coupling since it is known^{8,9} that π -bonds adjacent to an atom in the coupling path can affect the coupling significantly.

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