

NMR Experiments on Cyclic Sulfites

Analysis of the High Resolution Magnetic Resonance Spectrum of Trimethylene Sulfite

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The high resolution proton magnetic resonance spectrum of trimethylene sulfite has been completely analysed by an iterative method. Non-planar zig-zag four-bond coupling is shown to be non-zero, $J_{\text{acsa}} = -0.52$ Hz. The coupling constants involved indicate that the sulfite exists in an ideal staggered chair configuration.

Conformational studies on cyclic sulfites have been reported by several workers.¹⁻⁴ An NMR study,⁴ and dipole moment measurements and infrared analysis¹⁻³ have been reported. X-Ray analysis^{7,18} of trimethylene sulfite at -100°C has shown that this compound exists in a chair conformation with the S=O bond in an axial position. The ring is forced into a nearly ideal staggered conformation by the S=O group. Dipole moments and IR spectra^{2,3,6} of a variety of cyclic sulfites indicate that the S=O group preferentially occupies the axial position. This paper deals with the complete NMR analysis of trimethylene sulfite. The molecule is well suited for NMR analysis as the ring does not undergo inversion on the NMR time scale.

EXPERIMENTAL

The trimethylene sulfite was prepared from 1,3-propanediol and thionyl chloride according to the method of Pritchard and Vollmer.⁶ B.p. $58^\circ/9$ mmHg. GC-analysis showed purity better than 98%. The compound was introduced into a 5 mm O.D. sample tube, and a small quantity of TMS was added to serve as NMR locking and reference substance. The sample was degassed by freezing and thawing, using a vacuum line, and the tube was sealed under vacuum. The spectra were determined on a JEOL JNM-C-60H spectrometer, operating at 60 MHz. All calculated spectra were recorded, at ambient temperature (27.0°C), in one sample (internal) lock mode with frequency sweep at 54 Hz sweep width and calibrated every 5 Hz using a JEOL-SD-30 frequency counter. The counter is accurate to 0.1 Hz. The line position is taken as the average of six spectra and is assumed to be accurate to 0.05 Hz. The computation was carried out, using an IBM 360/50 computer, and the graphical output was obtained using a Calcomp Plotter.

SPECTRAL ANALYSIS

The spectrum of trimethylene sulfite (Fig. 1 and Table 1) consists of three main regions at 4.85 ppm (band A), 3.90 ppm (band B), and approximately

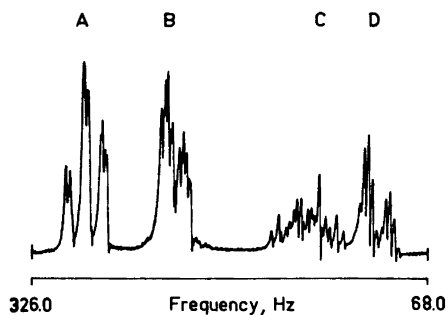


Fig. 1. 60 MHz PMR spectrum of trimethylenesulfite.

Table 1. Chemical shift data.^a

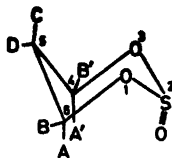
	axial	4.85
H ₄ and H ₅	equatorial	3.90
	axial	2.45
H ₆	equatorial	1.70

^a Chemical shift in ppm from tetramethylsilane.

Table 2. Spin-spin coupling constants (in Hz).

² J ₄₍₆₎	-11.38	J _{4e4a} or J _{6e6a}
² J ₅	-14.46	J _{5e5a}
³ J _{aa}	12.08	J _{4a5a} or J _{5a6a}
³ J _{ea}	4.63	J _{4e5a} or J _{5a6e}
³ J _{ee}	2.73	J _{4e5e} or J _{5e6e}
³ J _{ae}	2.61	J _{4a5e} or J _{5e6a}
⁴ J _{ee}	1.58	J _{4e5e}
⁴ J _{ea}	-0.52	J _{4e6a} or J _{4a6e}
⁴ J _{aa}	-0.04	J _{4a6a}

2.0 ppm (bands C and D). The separation between the three regions is at least five times the coupling constants involved. In order to explain qualitatively the splitting of the signal groups, it is assumed that the spin system can be treated as an [AB]₂XY system.



Use of the X approximation breaks the $[AB]_2$ part of the spin system down into $[ab]_2$ sub-spectra, with effective chemical shifts as follows

$$\begin{aligned} \nu_a &= \nu_A \pm \frac{1}{2}(J_{AX} \pm J_{AY}) \\ \nu_b &= \nu_B \pm \frac{1}{2}(J_{BX} \pm J_{BY}) \end{aligned}$$

The low field bands A and B (Fig. 1) are assigned to the protons at C_4 and C_6 , and bands C and D at high field to the C_5 protons. The triplet of doublet structure in band A indicates that there is one coupling of the same magnitude as the "N-doublet" together with a smaller coupling. The doublet splitting is $|N| = |^2J_{AB} + ^4J_{AB'}|$, and the greater coupling constant is assigned to a vicinal *trans* coupling. Band A is therefore assigned to the axial protons at C_4 and C_6 with $|J_{6gem}| = |J_{4gem}| \simeq |J_{4a5a}| \simeq 12$ Hz. Band B is very complex, but the N-doublet spacing is repeated four times due to the four $[ab]_2$ sub-spectra. The appearance of band B indicates two small couplings (2.2 and 4.5 Hz), assigned to J_{BX} and J_{BY} , and a greater coupling (12 Hz), assigned to J_{gem} . It is reasonable to assign the latter band to the equatorial protons at

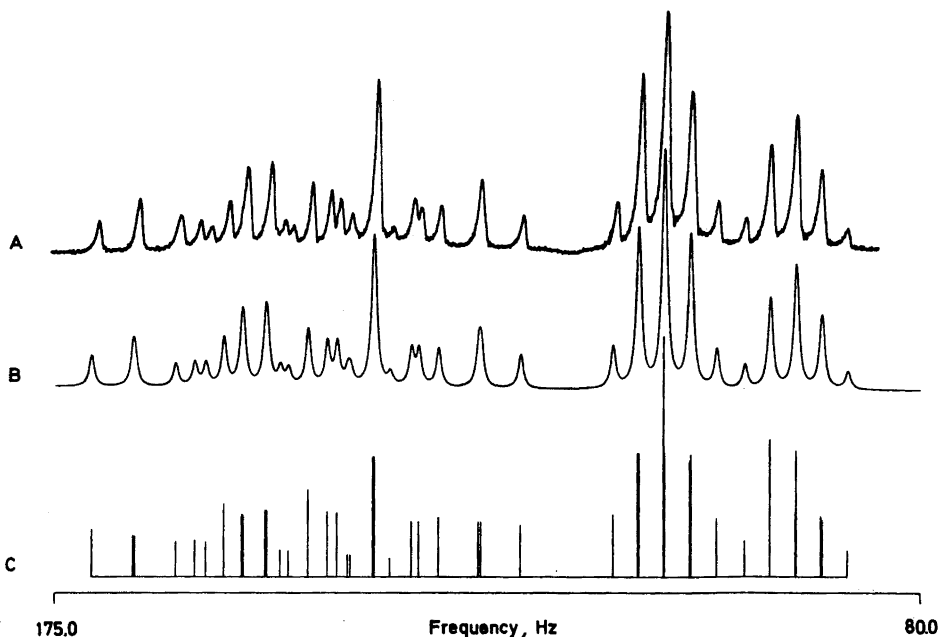


Fig. 2. Spectrum of protons H_{sc} and H_{sa} of trimethylenesulfite at 60 MHz; A, observed; B, computed with the parameters of tables (with a common half-width); C, stick plot of the computed spectrum.

C₄ and C₆. Band D (Fig. 1) appears to be a doublet ($|J| \simeq 14$ Hz) of quintets ($|J| \simeq 2.5$ Hz). The greater coupling is assigned to J_{gem} at C₅, and the quintets are assumed to arise from equal coupling to the four protons at C₄ and C₆. The lack of a second strong coupling ($|J| \simeq 12$ Hz) indicates that the signals are due to the equatorial proton at C₅. Band C is assigned to the axial proton C₅ (Fig. 1).

The spectrum was analysed on the basis of an [AB]₂CD spin system, using the iterative computer program LAOCN3⁹ with some modifications. An attempt to analyse the spectrum as an [AB]₂XY spin system did not account for all fine structure in the A, B, and C bands, and hence it is not possible to carry out a complete analysis of the spectrum by the X-approximation. The complete analysis of the spectrum as an [AB]₂CD system resulted in a good fit between calculated and experimental spectra (Fig. 2). The total spectrum is complex, and no attempt has been made to determine the signs by tickling experiments. The final RMS error on calculated transitions was -0.098 when all 21 parameters were allowed to vary. The computed probable errors of the coupling constants are 0.01 to 0.02 Hz, when 157 transitions were fitted.

RESULTS AND DISCUSSION

The advantages of trimethylene sulfite for conformational studies are that this compound does not undergo ring inversions⁵ on the NMR time scale. The NMR spectrum clearly demonstrates that the sulfite exists predominantly in one conformation, with S=O axial. Hamblin *et al.*¹⁰ conclude from acoustic measurements, that 4-methyl-trimethylene sulfite has a time average NMR spectrum. This contradicts NMR observations made in this laboratory.¹¹ The theoretical spectrum of trimethylene sulfite, based on a rigid spin system, fits the experimental spectrum very well (Fig. 2).

It may be noted that the relative shifts of axial and equatorial protons are reversed as compared with cyclohexanes.¹² The axial proton in the sulfite is always observed at lower field than the corresponding geminal equatorial proton. The cyclic sulfite resembles the dioxanes in respect to relative shift positions of geminal protons at C₅; the dioxanes also show this reversed relative position. Anteunis *et al.*¹³ pointed out that the reason for this, as regards dioxane, might be an interaction between H_{5e} and the *p*-orbitals of the ring oxygens. A similar effect can account for the high field shift of the H_{5e} in the sulfite as well. The shift difference between H_{5a} and H_{5e} is 0.75 ppm as compared to 0.8 ppm in dioxanes.¹³

The protons in 4 (or 6) position are differently shielded by the S=O group. Cazaux and Maroni⁴ have shown that an axial S=O group causes a greater down field shift (*ca.* 0.7 ppm) of the axial protons at C₄ and C₅ than does an equatorial S=O group. They quote $\delta = 4.77$ ppm for the axial H₄ and H₆ with the S=O group axial, and $\delta = 3.7$ ppm when the S=O group is equatorial. The chemical shift (4.85 ppm) of H_{4a} and H_{6a} and the position relative to the geminal equatorial protons in trimethylene sulfite indicate an axial S=O group. The observed S=O stretching frequency, 1190 cm⁻¹, also indicates an axial group.³ X-Ray data^{7,18} indicate an axial S=O group at -100°C . The greater stability of the axial S=O group might be due to an anomeric effect.¹⁴ X-Ray analysis of the sulfite^{7,18} has shown that the ring is held in an almost

staggered conformation by the sulfite group, the dihedral angles in the ring being close to 60° . It is likely that the ring exists in this staggered conformation even in the liquid at room temperature, as the H_{6c} is coupled equally to $H_{4e(6e)}$ and $H_{4a(6a)}$ (Table 2). In the dioxanes, where the ring is assumed to be somewhat "flattened", J_{5e4a} is substantially greater than J_{5e4c} (2.8 Hz and 1.7 Hz, respectively).¹⁵ J_{5a4e} is observed greater than J_{5e4a} , both in cyclohexane and dioxane derivatives.¹³ The magnitude of J_{5a4e} in the sulfite is greater than the other gauche coupling constants involved, but is lower compared with values obtained for 2-substituted dioxanes, and this also can be a result of the dihedral angles being close to 60° .

The smaller, more negative, value of 2J_4 as compared with dioxanes is due partly to a larger geminal angle, and partly to a lower ability of inductive removal of electrons by the sulfite group, as compared to the oxygen atoms of dioxanes. The lower value relative to dioxanes of 3J_5 is assumed to be caused by an increase in the H-C-H angle rather than by changes in electronegativity. The orientation of the electrons at the β -substituent¹⁶ is known to cause changes in the geminal coupling, but this effect is assumed to be similar in dioxanes and the sulfite. The lower values are paralleled by the variation in ${}^3J_{aa}$ (12.1 Hz in sulfite, and 9 to 11 Hz in dioxanes), and this observation indicates a more puckered sulfite ring. Studies on long range coupling in cyclic systems between protons in an extended zig-zag arrangement have been reported.^{15,17} The four-bond coupling of 1.58 Hz between the equatorial protons in 4 and 6 position is an expected value for this type.^{13,15} The coupling, -0.52 Hz, between H_{4e} and H_{6e} is more unusual when the magnitude is considered, but there has been observed four-bond coupling between protons where a perfect planar *W* arrangement is not possible.¹⁵

REFERENCES

1. van Woerden, H. F. and White, R. F. M. *Chem. Ind. (London)* 1963 1956.
2. van Woerden, H. F. and Havinga, E. *Rec. Trav. Chim.* 86 (1967) 341.
3. van Woerden, H. F. and Havinga, E. *Rec. Trav. Chim.* 86 (1967) 353.
4. Cazaux, M. M. L. and Maroni, P. *Tetrahedron Letters* 1969 3667.
5. Edmunsson, R. S. *Tetrahedron Letters* 1965 1649.
6. van Woerden, H. F., Cerfontain, H., Green, C. H. and Reijerkerk, R. J. *Tetrahedron Letters* 1968 6107.
7. Altona, C., Geise, H. J. and Romers, C. *Rec. Trav. Chim.* 85 (1966) 1197.
8. Pritchard, J. G. and Vollmer, R. L. *J. Org. Chem.* 28 (1963) 1545.
9. Castellano, S. and Bothner-By, A. A. *J. Phys. Chem.* 41 (1964) 3863.
10. Hamblin, P. C., White, R. F. M., Eccleston, G. and Wyn-Jones, E. *Can. J. Chem.* 47 (1969) 2731.
11. Albrigtsen, P. *Unpublished results*.
12. Emsley, J. W., Feeney, J. and Sutcliffe, L. H. *High Resolution NMR Spectroscopy*, Pergamon, London 1965, Vol. 2, pp. 696-703.
13. Anteunis, M., Tavernier, D. and Borremans, F. *Bull. Soc. Chim. Belges* 75 (1966) 396.
14. Eliel, E. L. and Giza, C. A. *J. Org. Chem.* 33 (1968) 3754.
15. Ramey, K. C. and Messick, J. *Tetrahedron Letters* 1965 4423.
16. Pople, J. A. and Bothner-By, A. A. *J. Chem. Phys.* 42 (1968) 1339.
17. Anderson, J. E. *J. Chem. Soc. B* 1967 712.
18. van Oyen, J. W. L., Hasekamp, R. C. D. E., Vershoor, G. C. and Romers, C. *Acta Cryst. B* 24 (1968) 1471.

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