

NMR Experiments of Cyclic Sulfites

IV.* Analysis of the High Resolution NMR Spectra of 4-Methyl-, 4-Phenyl-, and 4,6,6-Trimethyl-trimethylene Sulfite

PER ALBRIKTSEN

Chemical Institute, University of Bergen, N-5000 Bergen, Norway

The high resolution proton magnetic resonance spectra of 4-methyl-, 4-phenyl-, and 4,6,6-trimethyl-trimethylene sulfite have been studied in detail. The spectra are discussed in view of recent data on dipole moments and ultrasonic absorption measurements. The 4-methyl sulfite is shown to exist almost entirely in a chair conformation with equatorial methyl group. The 4,6,6-trimethyl- and 4-phenyl-trimethylene sulfite are found to exist in either a chair-nonchair equilibrium or a twist conformation.

Many data have been reported on the conformation of substituted trimethylene sulfites.^{2,3} The picture appears to be clear for the parent ring compound⁴ and 5-substituted sulfites.² The lack of coalescence in the NMR spectra from -100° to room temperature indicates a barrier to ring inversion substantially different from that found for cyclohexanes. Recent dipole moment and NMR measurements³ indicate a barrier to ring inversion for sulfites substantially higher than the cyclohexane barrier of 10.3 kcal/mol. The unsubstituted¹ and some 5-substituted trimethylene sulfites² are found by NMR experiments to exist predominantly in a chair conformation with an axially situated S=O group. The preference for the S=O axially as compared to the S=O equatorially oriented is estimated to 3.5 kcal/mol.⁵ NMR experiments² on *axial*-5-methyl trimethylene sulfite indicate almost entirely one conformation with the S=O bond axial. This requires a conformational energy of at least 3 kcal/mol of the axial S=O bond, assuming a similar conformation energy of 0.9 kcal/mol of the 5-methyl group as found for dioxanes.⁶ 4,6-Disubstituted trimethylene sulfites appear to exist either in chair-chair or chair-non-chair equilibrium.⁷ This paper reports the NMR analysis of sulfites substituted either in 4- or 4- and 6-positions.

* Part III: Ref. 1.

EXPERIMENTAL

The sulfites were prepared from appropriate diols and thionyl chloride according to the method previously described.²

4-Methyl trimethylene sulfite: B.p. 58.5°/8 mmHg. 4,6,6-Trimethyl-trimethylene sulfite: B.p. 73.0°/8 mmHg. The isomer of the highest yield was purified by GC.

4-Phenyl-trimethylene sulfite: B.p. 118°/11 mmHg. The compound was purified by GC.

The compounds were purified using 1.7 m × 0.6 cm columns filled with 20 % carbowax 20M and 10 % PDEAS on 60–80 mesh chromosorb acid washed on an Aerograph Auto-prep gas chromatograph. Isomeric purity was in all cases greater than 99 % by GC. The NMR spectra, as well, were taken as evidence of purity.

The material (neat liquid) and a small quantity of TMS to serve as lock substance were introduced into 5 mm O.D. sample tubes. The samples were degassed by pump-freeze-thaw technique using a vacuum line and the tubes were sealed under vacuum. The spectra were recorded on a JEOL JNM-C-60H and on a Varian Associates HA-100 spectrometer operating at 60 and 100 MHz, respectively. All 60 MHz spectra were recorded in internal lock mode with frequency sweep at *ca.* 50 Hz sweep width and calibrated every 5 Hz. Several spectra of each compound were recorded at 60 MHz. The 100 MHz spectra were recorded at 100 Hz sweep width in the field/frequency lock mode with frequency sweep and calibrated every 10 Hz. The spectra recorded were calibrated using a frequency counter accurate to 0.1 Hz. The line positions were taken as an average of four to six spectra for each compound at 60 MHz. Only one spectrum was recorded at 100 MHz of each compound studied. The computations were carried out using an IBM 360/50 computer. Graphical output was obtained using a Calcomp Plotter.

SPECTRAL ANALYSIS

The NMR spectrum of 4-methyl-trimethylene sulfite (Fig. 1) consists of three main regions at $\delta = 0.9 - 2.4$, $\delta = 3.5 - 4.1$, and $\delta = 4.4 - 5.4$. The low field region is assigned to the axial protons α to ring oxygen. The chemical shifts are different for the two axial protons, with the proton at carbon 4 to low field. The triplet structure in this band shows clearly that one proton is coupled equally, $J = 11$ Hz, to two protons. The signals at about 3.7 ppm consist of a doublet of quartets with equally intense lines. The absorption is assigned to the equatorial proton at carbon 6. The high field part of the

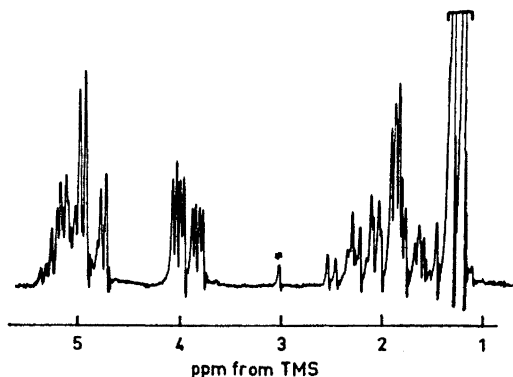


Fig. 1. 60 MHz NMR spectrum of 4-methyl-trimethylene sulfite.

spectrum has essentially the same appearance as obtained for the parent compound,⁴ two partly overlapping regions together with an additionally strong doublet due to the methyl group at carbon 4. The signals due to the axial proton at C₅ are to low field as compared to the equatorial proton with smaller chemical shift difference as regards the parent compound. The spectrum can be classified as an ABCDEX₃ spin system with strong coupling only between the nuclei at carbon 5. The fully analysed 60 and 100 MHz spectra resulted in a good correlation between calculated and experimental spectra. The final RMS value obtained was 0.08 when all parameters were allowed to vary. Probable errors were less than 0.02 Hz when *ca.* 700 transitions were fitted.

The spectrum of 4,6,6-trimethyl-trimethylene sulfite consists of two regions, a low field region (Fig. 2) due to the α proton to the ring oxygen and a high field region of overlapping signals due to the geminal protons at carbon 5 and the signals due to the methyl groups. The low field part was easily analysed as an M part of an ABMX₃ spin system with significant coupling between the M and the other nuclei involved. The computer analysis gave RMS=0.08 and probable errors less than 0.02 when about 50 transitions were fitted.

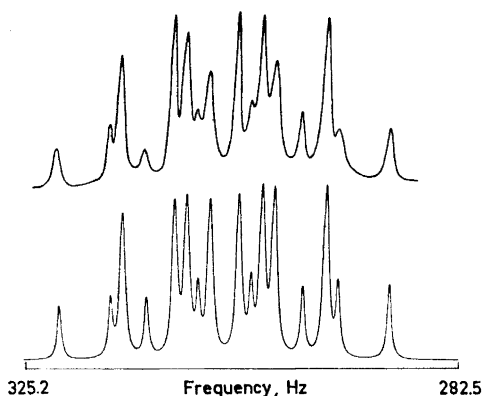


Fig. 2. Spectrum of proton H_{4a} of 4,6,6-trimethyl-trimethylene sulfite at 60 MHz. Upper, observed. Lower, computed with parameters of table with a common half-width.

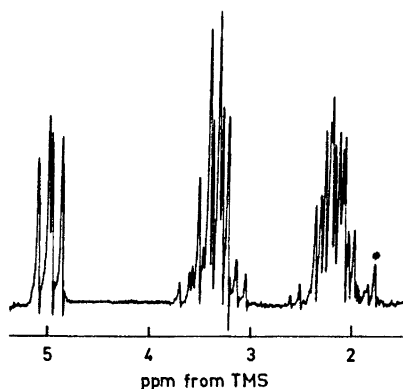
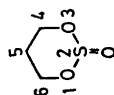


Fig. 3. 60 MHz NMR spectrum of 4-phenyl-trimethylene sulfite. The phenyl group is not recorded.

The NMR spectrum of 4-phenyl-trimethylene sulfite (Fig. 3) gave a spectrum not expected for a chair conformation with an equatorial substituent at C₄ as compared to the spectra obtained for the 4-methyl-trimethylene sulfite and 4-phenyl-1,3-dioxane.⁸ Apart from the phenyl signal, the spectrum consists of three signal groups at $\delta=1.5-2.7$, $\delta=3.0-3.8$ and $\delta=4.9-5.3$. The low field band appeared to be a doublet of doublets, integrating to one proton, and is assigned to the proton at C₄. The high field band is assigned to the protons at C₅ and the band at *ca.* 3.5 ppm is assigned to the protons at C₆. The chemical shifts between the protons at C₅ are small compared to the corresponding dioxane⁸ and the protons at C₆, as well, show a similar trend.

Table 1. Chemical shifts and coupling constants.^a



	2J_5	2J_6	$J_{4a,4Mc}$	J_{4aa}	J_{4asc}	J_{5aa}	J_{5asc}	J_{5ca}	J_{5cac}	J_{5ccc}	ν_{sc} ν_{ca}	ν_{cc} ν_{cc}	ν_{sc} ν_{ca}	MHz
	-14.27	-11.54	6.30	11.64	2.40	12.92	4.76	2.39	1.87					100
	-14.28	-11.40	6.30	11.56	2.32	12.91	4.71	2.40	1.89					60
	-14.75	-11.06		8.33	5.56	9.10	5.52	4.61	6.04					60
			6.25	8.93	4.67								305.2	60

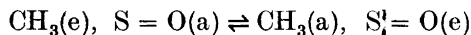
^a Chemical shift in Hz from TMS and coupling constants in Hz.

These hard coupled pairs of nuclei made the analysis of this compound tedious as rough estimates of trial parameters were not easily obtained. After some trial and error a good correlation was obtained between calculated and experimental spectra. The RMS value was 0.1 and probable errors in parameters were about 0.02 when *ca.* 70 transitions were fitted.

The iterative computations were performed using the computer program LAOCN3⁹ with some modifications² to accommodate eight coupled nuclei. The spectral parameters obtained are listed in Table 1.

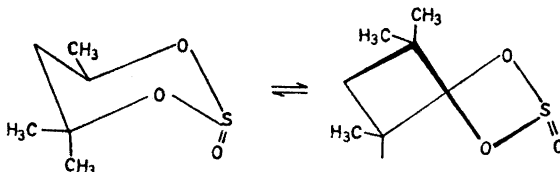
RESULTS AND DISCUSSION

Dipole moment measurements³ on trimethylene sulfite and 4-*e*-methyl sulfite, 3.34 D and 3.35 D, respectively, suggest that 4-*e*-methyl sulfite exists with an axial S=O bond. This is also found by considering chemical shift of protons and the coupling constants involved (Table 1). The two *trans* coupling constants are significantly different, $J_{4a5a} = 11.6$ Hz and $J_{5a6a} = 12.9$ Hz, and this is probably due to substituent effect caused by the methyl group. The *R* value, *ca.* 2.06, obtained for the $-\text{CH}_2-\text{CH}_2-$ moiety in the 4-methyl sulfite is comparable to the value, 2.05, of trimethylene sulfite and it is reasonable to assume equal dihedral angles in the two molecules. The large value of J_{5a6a} compared to the corresponding values of trimethylene sulfite, $J_{5a6a} = 12.1$ Hz, suggests that 4-methyl-trimethylene sulfite exists almost entirely in one conformer. Ultrasonic relaxation,¹⁰ is, however, observed in this compound and the result has been interpreted as an equilibrium between two chair conformations.



NMR spectra (Table 1) show clearly that the equilibrium is almost entirely to one side with $\text{CH}_3(e)$ and $\text{S} = \text{O}(a)$ and the large value of J_{5a6a} suggests at most one or two percent of other conformers. The conformational preference for an axial S=O bond as against equatorial S=O bond, *ca.* 3.5 kcal, and the preference of about 1.3 kcal (dioxane value¹³) for an equatorial 4-methyl group, support the interpretation of NMR data to account for 98 % of the more stable conformer. The equilibrium suggested by Hamblin *et al.*¹⁰ is more likely to be a chair-non-chair equilibrium, rather than a chair-chair equilibrium.

In a chair conformation the *trans* coupling constant ${}^3J_{aa}$ is about four times as large as ${}^3J_{ae}$, whereas equal coupling constants, ${}^3J_{aa} = {}^3J_{ae}$, are expected for a twist conformation. The coupling constants found in 4,6,6-trimethyl-trimethylene sulfite, ${}^3J_{4a5a} = 8.93$ Hz and ${}^3J_{4a5e} = 4.67$ Hz, indicate the existence of a distorted chair form or a chair-non-chair equilibrium.

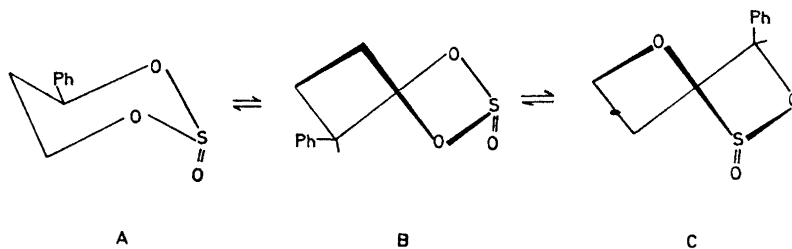


A similar equilibrium is suggested for the corresponding 1,3-dioxane.¹¹ No *trans* isomer of the 1,3-dioxane was detected. The *trans* isomer is assumed to be at least 5 kcal/mol less stable as compared to the *cis* compound. Hamblin *et al.*¹² studied the 4,6,6-trimethyl-trimethylene sulfite by the ultrasonic absorption technique and no relaxation was observed. This observation suggests one of the following assumptions:

- (a) The enthalpy difference between the isomers is zero.
- (b) Only one conformer exists.
- (c) The relaxation frequency lies outside the range examined.

Wood *et al.*³ report a dipole moment near 3.9 D for this compound. This implies either a non-chair or distorted chair with axial S=O bond or a chair-non-chair equilibrium. The magnitude of the coupling constants involved, as compared to the corresponding values of 4-methyl-trimethylene sulfite, suggests an equilibrium between a chair and a non-chair conformation. The trimethyl sulfite may be assigned as existing of about 50 % chair and 50 % non-chair based on coupling constants obtained. This assumption is also supported by the ultrasonic measurements performed by Hamblin *et al.*¹²

Finally, the NMR measurements on 4-phenyl trimethylene sulfite gave results (Table 1) unexpected for a chair conformation or a chair-chair equilibrium. The difference between the coupling constants obtained for 4-phenyl-trimethylene sulfite and 4-phenyl-1,3-dioxane⁷ or 4-methyl-trimethylene sulfite, suggests a non-chair conformation for the sulfite. The non-chair conformation is assumed from the observed coupling constants and the large $-\Delta G^\circ$ values¹³ expected for 4-axial substituents on six-membered ring compounds. The results obtained for the corresponding dioxane from ultrasonic absorption measurements¹⁴ do not support a chair-chair, but rather a chair-non-chair equilibrium. The NMR data of the dioxane,⁷ in contrast to the sulfite, indicates a chair-chair equilibrium with almost entirely presence of a chair conformer with equatorial phenyl group.



The twist conformation B is assumed to have dihedral angles of about 30° and 150° . The Karplus relation between dihedral angles and the magnitude of the vicinal coupling constants suggest the following values for 3J : 5–7 Hz (30°) and 7–9 Hz (150°). The values suggested for conformation C are *ca.* 10 Hz (190°), 1–2 Hz (70° – 80°), and 5–6 Hz (40°). The dihedral angles are estimated from Dreiding models. The coupling constants obtained (Table 1) suggest that 4-phenyl-trimethylene sulfite exists either in an $A \rightleftharpoons B$ equilibrium or almost entirely in conformation B.

REFERENCES

1. Albriktzen, P. *Acta Chem. Scand.* **26** (1972) 3671.
2. Albriktzen, P. *Acta Chem. Scand.* **26** (1972) 1783, and references therein.
3. Wood, G., McIntosh, J. M. and Miskow, M. H. *Can. J. Chem.* **49** (1971) 1202, and references therein.
4. Albriktzen, P. *Acta Chem. Scand.* **25** (1971) 478.
5. Woerden, H. F. van and Havinga, E. *Rec. Trav. Chim.* **86** (1967) 341; **86** (1967) 353.
6. Eliel, E. L. and Knoeber, M. E. *J. Am. Chem. Soc.* **90** (1968) 3444.
7. Cazaux, M. M. L. and Maroni, P. *Tetrahedron Letters* **1969** 3667.
8. Ramey, K. C. and Messick, J. *Tetrahedron Letters* **1965** 4423.
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. Nader, F. W. and Eliel, E. L. *J. Am. Chem. Soc.* **92** (1970) 3050.
12. Eccleston, G., Pettrick, R. A., Wyn-Jones, E., Hamblin, P. C. and White, R. F. M. *Trans. Faraday Soc.* **66** (1970) 310.
13. Eliel, E. L. *Accounts. Chem. Res.* **3** (1970) 1.
14. Hamblin, P. C., White, R. F. M. and Wyn-Jones, E. *J. Mol. Struct.* **4** (1970) 275.

Received March 27, 1972.