

NMR and IR Studies on Cyclic Sulfites. VIII. Sulfites Substituted at the Axial Position of Carbon Atom 5

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NMR and IR studies on three cyclic sulfites substituted at carbon 5 with the substituent occupying the *axial* position have been performed. The conformation is discussed on the basis of the spectral properties, examining the molecules in both a polar and a non-polar solvent. For these molecules an equilibrium is proposed between two chair forms (axial and equatorial S=O bond) and a twisted one.

NMR, IR, and dipole moment measurements on trimethylene (TM) sulfites substituted at carbon 5 have been reported.¹⁻⁹ It has been found that the equatorially substituted sulfites exist in the chair conformation with preferentially axial S=O group.⁶ The axially substituted 5-methyl- and 5-*tert*-butyl-TM sulfites have been examined^{2,6} and found to exist in an equilibrium between two chair conformations with the S=O bond situated in the axial or equatorial position. The preference for the S=O axially as compared to the S=O equatorially oriented is estimated to be 3.5 kcal/mol.^{2,3}

SPECTRAL ANALYSIS

The 5-phenyl- and 5-*tert*-butyl-TM sulfites constitute an [AB]₂C system with respect to the aliphatic ring protons. The appearances of the two spectra seem very similar (Fig. 1). Three main regions are due to the protons in position 4 and 6 (bands A and B, respectively), and the protons in position 5 (band C). The

proton in equatorial position 5 comes to resonance at lower frequency for the 5-*tert*-butyl substituted sulfite as compared to the 5-phenyl substituted one due to the difference in the shielding effects of the two substituents.

The protons in 4 (or 6) position are differently shielded by the S=O group. The lower field region is assigned to the axial protons. From the quartet structure of band A and B one large coupling constant (~ 12.0 Hz) is assigned to the 2J_4 (2J_6) coupling.

The fully computer analyzed 60 and 100 MHz spectra, with CCl₄ as solvent, and 60 MHz with CH₃CN as solvent resulted in good correlation between calculated and experimental spectra. The final r.m.s. values obtained were better than 0.06 when 7 to 9 of the 9 possible parameters were allowed to vary and about 40 transitions were fitted.

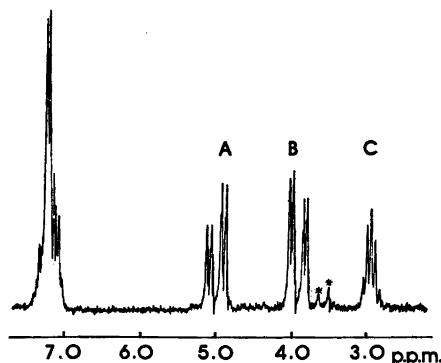
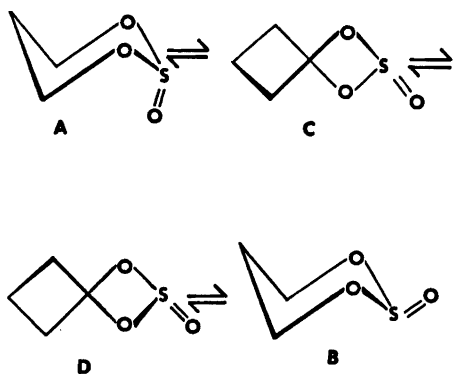


Fig. 1. The 60 MHz spectrum of axial 5-phenyl-trimethylenesulfite. (Solvent: CCl₄). An asterisk indicates impurity.

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RESULTS AND DISCUSSION

TM sulfite and some 5 equatorially substituted TM sulfites have been shown to exist in the chair conformation with the S=O group occupying the axial position in the ring.^{5,6} Other substituted cyclic sulfites are found to exist in non-chair conformations^{3,7,10} or in chair conformation with the S=O group in the equatorial position.¹⁰ Albriktsen⁶ has suggested that 5-methyl-TM sulfite with axial substituent exists in an equilibrium between two chair conformations with ax. and eq. S=O group, in which at most 2 % of the conformer with equatorial S=O group exists.



An NMR and IR study has been reported³ for 5-*tert*-butyl-TM sulfite with axial substituent. It has been concluded that the molecule exists in an equilibrium between two chair conformers A and B. Albriktsen⁶ has found that J_{4esa} is in the range 4.2–4.6 Hz in chair

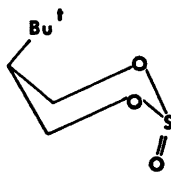
forms with an axial S=O group. Supposing an equilibrium as reported³ we will have A→B ($J_{4esa} \rightarrow J_{4ase}$) and excluding substituent effects on the coupling constants, a 4a5e coupling of 4.6 Hz for 5-*tert*-butyl-TM sulfite is possible for conformer B alone (Table 1).

Wucherpennig¹⁰ has calculated the dihedral angles for the conformers C and D. Applying Karplus plot, he calculated the corresponding coupling constants for the 4a5e coupling to be 6–7 Hz. From Table 1, it is evident that an equilibrium involving only the forms A and B is not probable.

Changing the solvent from a nonpolar to a polar one, J_{4ase} increases with only 0.15 Hz; the J_{4ese} , however, is increasing with approximately 2.1 Hz. The latter will have contribution from J_{4asa} (~12 Hz in conformer B) by an A→B transition. This comparatively small increase in J_{4ase} and the great increase in J_{4ese} may then be suggestive of a comparatively greater contribution from conformer B in a more polar medium, as anticipated from the dipole moment values for the different conformers,¹⁰ Table 2. Dipole moment measurements which have been performed¹¹ are also suggestive of a conformational equilibrium. The most probable equilibrium will consequently be one with contribution from all the symmetric forms; A, B, C, and D.

Looking at Table 3 concerning 5-phenyl-TM sulfite, no significant change in J_{4ase} is observed when changing the solvent. J_{4ese} , however, is changed from 3.2 to 4.5 Hz when increasing the polarity of the solvent. This suggests

Table 1. Spin-spin coupling constants (Hz) calculated from 60 and 98 MHz spectra of 5-*tert*-butyl-TM sulfite.



Solvent	2J_4	${}^3J_{4ese}$	${}^3J_{4ase}$	${}^4J_{4ese}$	${}^4J_{4asa}$	${}^4J_{4esa}$
CH ₃ CN ^a	–12.02	6.80	5.10	1.73	–0.20	–0.07
CCl ₄ ^b	–12.21	4.74	4.95	1.45	–0.15	–0.01

^a 60 MHz. ^b 98 MHz.

Table 2. Calculated dipole moment values for the different conformers of TM sulfite.¹⁰

Conformer	μ (D)
A	3.55 exp.
B	5.22 exp.
C	4.5 calc.
D	4.5 calc.

a conformational equilibrium, when the concentration of species with equatorial S=O bond grows increasing the polarity of the solvent.

If an equilibrium $S=O(a) \rightleftharpoons S=O(e)$ exists, the observed coupling constants can be expressed by eqn. 1

$$J_{4e5c}^{obs} = nJ_{4e5c} + (1-n)J_{4a5a} \quad (1)$$

By assuming ⁵ $J_{4e5c} = 2.73$ and $J_{4a5a} = 12.08$ and excluding substituent effects, we find that 5 % of conformer B is present in CCl_4 and 19 % in CH_3CN . The magnitude of J_{4a5a} may suggest contribution from the twisted conformers C and D in the equilibrium. The effect from the equatorial S=O bond may be the reason why J_{4a5a} is comparatively great since this coupling constant is 2.61 Hz in unsubstituted TM sulfite.⁶

It is known that the orientation of the electrons of a β -substituent may cause changes in a geminal coupling.¹² It is possible that such an effect also influences the vicinal coupling. The *gem*-coupling ³ J_4 decreases from -11.50 Hz in CCl_4 as solvent, to -12.22 Hz in CH_3CN .

However, the change in J_{4a5c} from unsubstituted TM sulfite to the molecule in discussion, is so large that we cannot exclude the participation of twisted forms in the equilibrium.

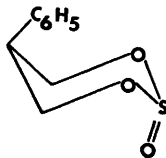
INFRARED SPECTRA

Several cyclic sulfites have been examined by IR spectroscopy.^{2-4,10,13} TM sulfite shows a strong absorption at 1190 cm^{-1} , and this frequency has been assigned to an *axial* S=O stretching vibration in a 6-membered ring.² *trans*-4,6-Dimethyl-TM sulfite has been proposed to exist in chair conformation with equatorial S=O bond.¹⁰ This molecule has a S=O absorption at 1240 cm^{-1} . This absorption has then been assigned an *equatorial* S=O bond in a 6-membered ring. Maroni and Tisnes⁹ have found an IR absorption at 1218 cm^{-1} for 4,5,6-trimethyl-TM sulfite. Furthermore, an absorption at 1224 cm^{-1} for *cis*-4,6-dimethyl-TM sulfite has been reported.⁹ These were assigned to a *twisted* conformer.

The nature of the solubility mechanism implies that polar conformers are to be favoured in a polar medium. The IR spectra of all the three molecules, 5-methyl-, 5-phenyl-, and 5-*tert*-butyl-TM sulfite with axial substituent show considerable changes at approximately 1200 cm^{-1} when changing the solvent from a nonpolar to a polar one (Fig. 2).

The intensity of the absorption at $\sim 1230\text{ cm}^{-1}$ is greatly increased at the expense of the one at $\sim 1200\text{ cm}^{-1}$ in the polar medium. This may also be suggestive of a conformational

Table 3. Spin-spin coupling constants (Hz) calculated from 60 and 98 MHz spectra of 5-phenyl-TM sulfite.



Solvent	² J_4	³ J_{4e5c}	³ J_{4a5c}	³ J_{4e5c}	³ J_{4a5a}	³ J_{4e5a}
CH_3CN	-12.22	4.50	3.80	1.83	-0.66	-0.16
CCl_4	-11.48	3.22	3.79	1.58	-0.20	-0.25
CCl_4^a	(-11.59)	(3.15)	(3.85)	(1.49)	(-0.21)	(-0.31)

^aNumbers in parentheses refer to 98 MHz spectra.

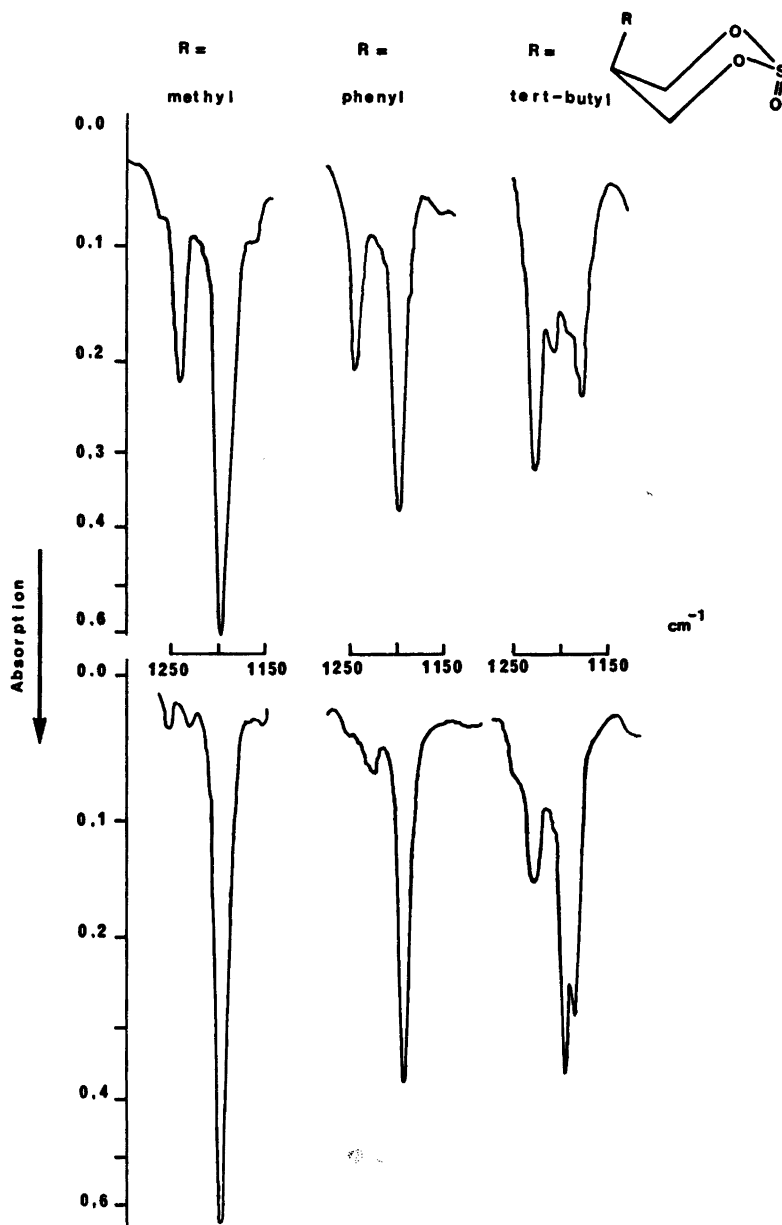


Fig. 2. The IR spectra of axial 5-substituted TM sulfites. (Solvents: Acetonitrile, upper spectra; 1,1,2,2-tetrachloroethane, lower spectra).

equilibrium with participation of a conformer with equatorial S=O bond.

In all cases examined (neat and in the two solvents) the IR spectra of 5-*tert*-butyl-TM sulfite with axial substituent show an absorp-

tion at $\sim 1210\text{ cm}^{-1}$. A weak shoulder is found at 1205 cm^{-1} in the spectrum of 5-phenyl-TM sulfite in acetonitrile as solvent. These absorptions are probably due to twisted conformers. Both the 1210 and the 1230 cm^{-1} peaks of

5-*tert*-butyl-TM sulfite are stronger in the more polar solvent which was to be expected due to the higher dipole moment of both the chair form with eq. S=O bond and the twisted ones. From the IR spectra it also seems conceivable that the contribution from the chair conformer with eq. S=O bond increases more than the contribution from the twisted conformer when changing to the more polar solvent.

EXPERIMENTAL

The 2-substituted 1,3-propane-diols were all prepared from the corresponding diethylmalonates by reduction with lithium aluminium hydride according to the method of Eliel *et al.*¹³

The cyclic sulfites were prepared according to the following method: The appropriate diol was dissolved in dry chloroform (ca. 20 % w/w) with two equivalents of pyridine. 1.02 equivalents of thionyl chloride, dissolved in three times its volume of chloroform, was added dropwise under stirring. The temperature was kept at 0 °C for about 3 h. The reaction mixture was filtered, and the filtrate was washed with a 2 % NaHCO₃ solution, 0.1 N HCl and water, respectively. The solution was dried over MgSO₄ prior to distillation.

The purity of the compounds was checked by NMR spectra and GLC analyses. The isomers of 5-methyl-TM sulfite (92 % S=O (a) 8 % S=O (e)) were separated by GLC on an Aerograph Autoprep A-700 with a 2.1 m × 6.0 mm column packed with 10 % PDEAS and 10 % Carbowax on Chromosorb W, OMCS A/W, 45/60 Mesh. The isomers of 5-phenyl-TM sulfite [84 % S=O (a) and 16 % S=O (e)] were separated by dissolving the crude product in ethanol. Since the isomer with axial phenyl group was negligibly soluble, it was filtered off at ca. 0 °C and recrystallized from ethanol as long white needles. (M.p. 60–62 °C). The isomers of 5-*tert*-butyl-TM sulfite (57 % S=O (a) and 43 % S=O (e)) were separated by cooling the crude product to -10 °C. The isomer with the axial substituent was then purified by GLC.

The NMR spectra were recorded in 5 mm O.D. sample tubes, and a small quantity of TMS was added to serve as reference and locking substance. The solvents used were CCl₄ and CH₃CN of spectroscopic purity. Dry nitrogen was bubbled through the solution to remove traces of oxygen.

The spectra were recorded by a JEOL JNM-C-60H instrument operating at 60 MHz (ca. 27 °C) and on a Varian HA-100 operating at 98 MHz (ca. 35 °C). All spectra were recorded in an internal lock mode with frequency sweep at 1.5 Hz/cm and calibrated every 5 Hz using a frequency counter. The counters were accurate

to 0.1 Hz for a 10 s count. The line position was taken as average of several spectra and is assumed to be accurate to about 0.05 Hz.

The IR spectra were recorded on a Unicam SP 200G instrument. Polystyrene was used for calibration. The spectra were recorded as 0.1 M solutions in CCl₄ and CH₃CN using cells with 0.1 mm path length.

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