ACTA CHEMICA SCANDINAVICA 26 (1972) 1783–1793

NMR Experiments on Cyclic Sulfites

II.* Analysis of the High Resolution NMR Spectra of Trimethylene Sulfite Substituted at Carbon Atom 5

PER ALBRIKTSEN

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

The high resolution proton magnetic resonance spectra of 5-methyl-, 5,5-dimethyl-, 5-phenyl-, and 5-*tert*-butyl-trimethylene sulfite have been completely analysed. The sulfites are found to exist in the chair conformation with axial S=O group. The axial preference of the S=O group is predicted from barrier to rotation in analogous systems. The long range coupling, $^4J_{ee}$, is found to become more positive upon substitution on carbon 5. The $^4J_{ee}$ is 1.6, 1.8, and 2.6 Hz for unsubstituted, 5-methyl-, and 5,5-dimethyl-trimethylene sulfite, respectively.

Recently the NMR sprectrum of trimethylene sulfite [1] has been analysed and the ring is found to exist in a rigid chair form with an axial S=O group. IR, NMR, and dipole measurements on the substituted trimethylene sulfites [2] suggest that symmetrical substituted sulfites exist in a chair conformation with either axial or equatorial S=O group. Conformational studies of sulfites substituted at carbon 5 have been reported.[3] The conformational energy of substituents at carbon 5 in trimethylene sulfite are found to be comparable to values obtained for substituted 1,3-dioxanes.[4] Dipole moment measurements and infrared analysis [5] indicate that cyclic sulfites substituted at carbon 5 exist in a chair form and the S=O group preferentially occupies the axial position. X-Ray analyses of trimethylene sulfite [6] and 5,5-dichloro-trimethylene sulfite [7] at −100°C suggest that the sulfites exist in a chair conformation with axial S=O group. Recently Wood *et al.*[8] studied the conformational behaviour of cyclic six-membered sulfites by dipole measurement and they concluded that the chair form is common for most cyclic sulfites substituted at carbon 5. The conformational energy [9] of the axial S=O group in *trans*-1,3,2-dioxathiadecaline-2-oxide is estimated to 1.9 kcal/mol.

This paper reports the NMR analysis of various cyclic sulfites substituted

* Part I: Ref. 1.

at carbon 5. The conformation is discussed on the basis of the spectral properties. The NMR spectra analysed are fully analysable and can be explained by a rigid chair conformation or by an equilibrium between different chair conformations with the existence of almost entirely one conformer.

EXPERIMENTAL

The 2-substituted 1,3-propane-diols were all prepared from the corresponding diethylmalonate by reduction with lithium aluminium hydride according to the method of Eliel *et al.*[4]

The cyclic sulfites were prepared according to the following method: The appropriate diol was dissolved in chloroform (*ca.* 20 % w/w). The thionylchloride, dissolved in an equivalent volume of chloroform was added dropwise under stirring. The temperature was kept at *ca.* 30°C for about 2 h. Dry nitrogen was then bubbled through the reaction mixture for half an hour and the mixture was then refluxed on a water bath for 2 – 3 h. The crude product obtained after evaporation of solvent was distilled. The yield obtained was 80 – 90 %.

NMR spectra and GC-analysis were taken as evidence of purity. The isomers of 5-*tert*-butyl-TM* sulfite were separated and purified according to van Woerden and Havinga.[5] The 5-phenyl-TM sulfite appeared to exist predominantly in one conformer, only 3 % of the other isomer was detected on GC. The isomers of 5-methyl-TM sulfite were not separated. GC-analysis showed that the mixture contained less than 3 % of impurities. The NMR signals due to the impurities were well separated from the sulfite signals and did not interfere with signals of interest for the analysis.

The compounds were introduced into 5 mm o.d. sample tubes and a small quantity of TMS was added to serve as NMR locking and reference substance. The NMR spectra of all compounds were measured as neat liquid, except 5-*tert*-butyl-TM sulfite, which was measured as a concentrated solution in CCl_4. All samples were degassed by the freeze-thaw-pump technique and the tubes were sealed under vacuum.

The spectra were determined at ambient temperature on a JEOL JNM-C-60H spectrometer (*ca.* 27°C), and on a Varian HA-100 spectrometer (*ca.* 35°C) operating at 60 and 100 MHz, respectively. All spectra were recorded in internal lock mode with frequency sweep at 50 Hz sweep width and calibrated every 5 Hz using a frequency counter. The counters were accurate to 0.1 Hz for a 10 sec count. The line position for the 60 MHz spectra is taken as the average of several spectra and is assumed to be accurate to about 0.05 Hz. Only one 100 MHz spectrum of each compound was measured. The computation was carried out using an IBM 360/50 computer and the graphical output was obtained using a Calcomp Plotter.

SPECTRAL ANALYSIS

The spectra of 5-mono-substituted-trimethylene sulfite can be divided into two main classes according to the spin systems. The 5-phenyl- and 5-*tert*-butyl-TM sulfite constitute an $[AB]_2C$ system with respect to the aliphatic ring protons and the 5-methyl-TM sulfite is an $[AB]_2CD_3$ spin system. The appearance of the spectrum of 5-*tert*-butyl-TM sulfite is different from that of 5-phenyl-TM sulfite. The difference is due to change in relative chemical shift between the proton in position 5 in the ring as compared to the protons in positions 4 and 6. H_5 in the 5-phenyl-TM sulfite is shifted to low field due to the effect of the phenyl group and resonates close to the protons in positions 4 and 6. It has been shown that the appearance of the signals due to nuclei C in an $[AB]_2C$ spin system is affected by the chemical shift difference between nuclei A and B.[10] The coupling constants between nuclei C and A

* TM = trimethylene

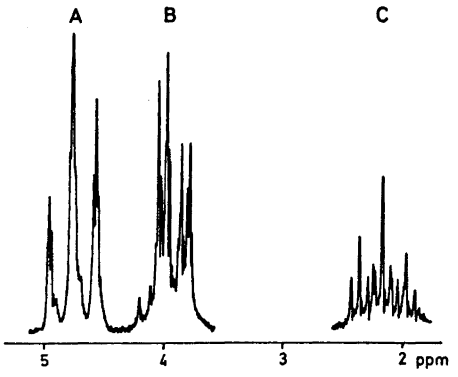


Fig. 1. 60 MHz NMR spectrum of 5-*tert*-butyl-trimethylene sulfite; ring protons only are shown.

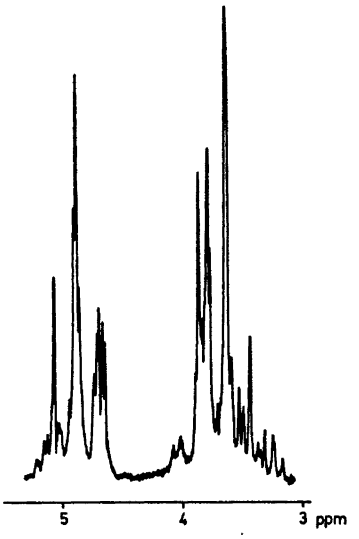


Fig. 2. 60 MHz NMR spectrum of 5-phenyl-trimethylene sulfite. The phenyl group is not recorded.

and B cannot be determined by simple inspection, unless the chemical shift between A and B is at least ten times the largest coupling constant involved. The spectrum of *5-tert*-butyl-TM sulfite consists of three main regions (Fig. 1) due to the protons in positions 4 and 6 (bands A and B) and the protons in position 5 (band C). From the triplet structure of band A, two large coupling constants (*ca.* 11.0 Hz), together with a fine structure due to long range coupling it is reasonable to assign the band to the axial protons at the α-carbons to the ring oxygens. The triplet structure arises as the trans coupling is comparable to the geminal coupling in magnitude. Band B is assigned to the equatorial proton in positions 4 and 6, and band C is accordingly assigned to the methine proton in position 5. The methine proton apparently occupies the axial position, due to the appearance of two large coupling constants in band A. Band C, a triplet of triplets, suggests that two large (*ca.* 12 Hz) and a smaller coupling constant (*ca.* 3.0 Hz) are involved. The 60 and 100 MHz spectra were fully analysed according to an $[AB]_2C$ spin system. The RMS obtained on calculated transitions was 0.1 when all parameters were allowed to vary. The probable errors were less than 0.02 Hz when 60 transitions were fitted.

The spectrum of the aliphatic protons of 5-phenyl-TM sulfite (Fig. 2) can be divided into two main regions. The low field region consists of a triplet with spacing about 11 Hz with each peak further split. This band is assumed to arise from the axial protons in positions 4 and 6. Apparently the axial nuclei A ($[AB]_2C$ spin system) in positions 4 and 6 are equally coupled to the nuclei B and C, $J_{gem} \simeq {}^3J_{aa} \simeq 11$ Hz. The high field band is very complex

due to the small chemical shift difference between the equatorial α-protons to the ring oxygen and the methine proton in position 5. The appearance of a second large coupling in the low field band indicates that the methine proton occupies the axial position, and hence the phenyl group is situated in the equatorial position. The fully computer analysed 60 and 100 HMz spectra resulted in a good fit between calculated and experimental spectra. The final RMS value obtained was 0.1 when all parameters were allowed to vary. The probable errors in the parameters were less than 0.02 Hz when 55 transitions were fitted.

The spectrum of the isomer mixture of 5-methyl-TM sulfite appeared to be fully analysable without any separation of the two isomers. The relative chemical shift for the various protons appears to be the same as for trimethylene sulfite.[1]

$$H_{4a(6a)} < H_{4e(6e)} < H_{5a} < H_{5e} < TMS$$

The assignment of different bands to the appropriate isomers was straight forward because one isomer was in great excess. The appearance of the bands

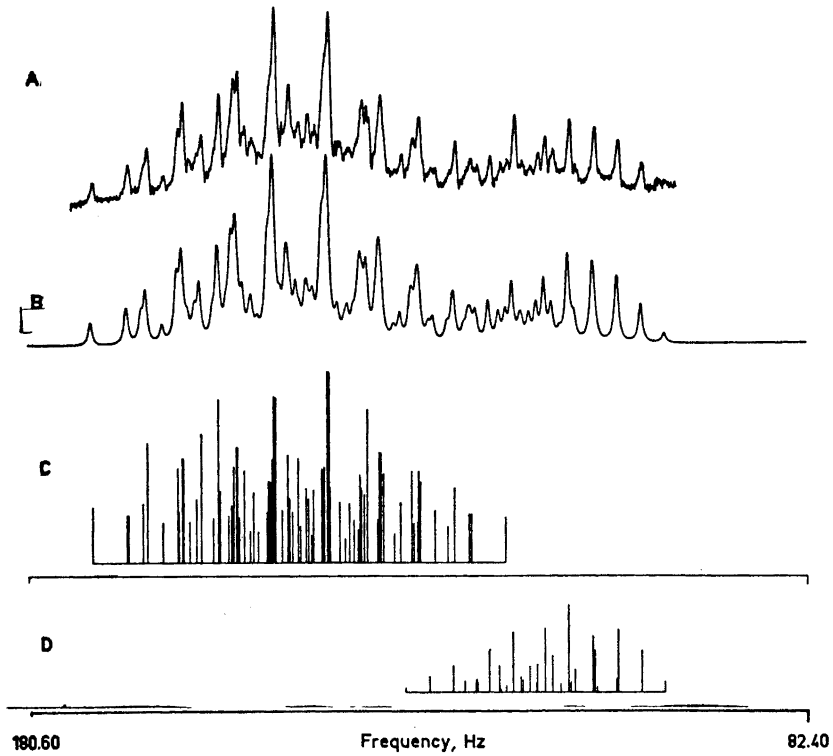


Fig. 3. Spectrum of protons H_{5e} and H_{5a} of the isomer mixture of 5-methyl-trimethylene sulfite at 60 MHz; A, observed; B, computed with parameters of tables (with a common half-width). The plot is of a mixture with 77 % of conformer with equatorial methyl group; C, stick plot of H_{5a} of 5-*eq*-methyl-trimethylene sulfite; D, stick plot of H_{5e} of 5-*ax*-methyl-trimethylene sulfite. C and D are scaled according to plot B.

assigned to the major isomer was similar to that of 5-*tert*-butyl-TM sulfite, apart from the high field band which was further split due to coupling to the methyl group. The triplet structure of the low field band of the major isomer suggests that this compound is the isomer with an equatorial methyl group. The low field band of the minor isomer, $H_{4a(6a)}$, is a doublet of doublets, $J_{gem} \simeq 10$ Hz and $^3J \simeq 3$ Hz, clearly shows that this isomer exists with an axial methyl group. The 60 MHz NMR spectrum of the methine protons in the two isomers is shown in Fig. 3. The final RMS values obtained were 0.07 (eq-CH_3) and 0.08 (ax-CH_3) when all parameters were allowed to vary. Probable errors obtained were less than 0.01 Hz for both isomers when 370 to 380 transitions were fitted. The spectra were analysed using the iterative computer programs LACX [11] and LAOCN3,[12] the latter with some modifications [13] to accomodate eight coupled nuclei. The core requirement using LAOCN3 8 spin version on an IBM 360/50 computer is about 166 K.

RESULTS AND DISCUSSION

Trimethylene sulfite has been shown to exist in the chair conformation [1] with the S=O group occupying the axial position in the ring. Substituted cyclic sulfites, however, are found to exist in non-chair conformations [8] or in chair conformation with the S=O group in the equatorial position.[5,14] The conformation of the 5-substituted trimethylene sulfites can be deduced from the appearance of the NMR spectra.

The compounds studied in this work all have spectra which are fully analysable on the basis of a symmetrical spin system, as either $[AB]_2C$ or $[AB]_2CX_3$. The spin systems indicate that the compounds studied exist in a rigid chair conformation or in an equilibrium between possible chair conformations.

The relative chemical shifts of axial and equatorial protons of carbon 4 and 6 are the reverse of those observed for dioxanes [15] but the same as found for trimethylene sulfite [1] and phosphorinanes.[16] The relative chemical shift difference as compared to dioxanes is taken as evidence for an axial oriented S=O group. In phosphorinanes [16] the swapping of chemical shifts compared to dioxanes is assumed to be due to an axial electronegative group attached to the phosphorus atom. The chemical shift data (Table 1) for the compounds studied indicate an axial S=O group in all compounds or an equilibrium between an axial and equatorial situated S=O group, with predominantly axial S=O.

For the 5-substituted TM sulfites variation in $^3J_{aa}{}^{obs}$, as regards the unsubstituted sulfite, might indicate an equilibrium between two chair conforma-

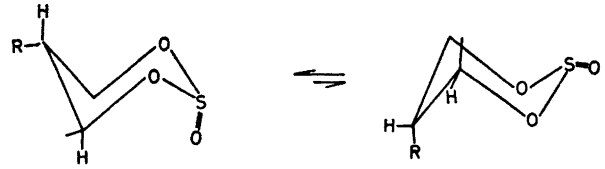


Table 1. Spin spin coupling constants[a] calculated from 60 and 100 MHz spectra.

R_1,R_2	$^2J_4$	$^3J_{4asa}$	$^3J_{4esa}$	$^3J_{4ase}$	$^3J_{4ese}$	$^4J_{4ese}$	$^4J_{4esa}$	$^4J_{4asa}$	$^3J_{Me,H_5}$	$^4J_{Me,4a}$	RMS
1. H,CH_3	−11.34	–	–	3.06	3.07	1.83	−0.28	0.01	7.07	0.49	0.07
	(−11.47)	–	–	(3.13)	(3.06)	(2.01)	(−0.18)	(0.0)	(7.09)	(0.46)	(0.08)
2. CH_3,H	−11.11	11.63	4.55	–	–	2.04	−0.37	−0.16	6.84	–	0.09
	(−11.22)	(11.59)	(4.54)	–	–	(2.12)	(−0.43)	(−0.22)	(6.83)	–	(0.09)
3. Bu^t,H	−11.15	11.84	4.21	–	–	2.23	−0.42	−0.33	–	–	0.1
	(−11.15)	(11.86)	(4.23)	–	–	(2.41)	(−0.36)	(−0.14)	–	–	(0.08)
4. Ph,H	−11.11	11.98	4.52	–	–	2.20	−0.36	−0.22	–	–	0.08
	(−11.11)	(12.05)	(4.57)	–	–	(1.97)	(−0.43)	(−0.28)	–	–	(0.09)
5. CH_3,CH_3	−11.03	–	–	–	–	2.57	−0.14	−0.04	–	–	0.06
6.[b] H,H	−11.38	12.08	4.63	2.61	2.73	1.58	−0.52	−0.04	–	–	–

[a] Numbers in parentheses are obtained from 100 MHz spectra. Spin spin coupling constants in Hz.
[b] Ref. 1.

tions. For the trimethylene sulfite, which has been shown to exist in a chair conformation with S=O axial,[1] the $^3J_{aa}$ is found to be 12.1 Hz. Substantial variation or decrease in the magnitude of this coupling constant might indicate an equilibrium where $^3J^{obs}$ can be expressed by $^3J^{obs} = n\,^3J_{aa} + (n-1)\,^3J_{ee}$. There are disadvantages in considering the vicinal coupling constants $^3J_{aa}$ and $^3J_{ee}$ from unsubstituted molecules in the calculation of the equilibrium, because of the dependence of ^3J on the electronegativity [18] of substituents at the carbon atoms holding the coupled nuclei. The lower observed values for $^3J_{aa}$ in compounds 2, 3, and 4 (11.6, 11.8, and 12.0 Hz, respectively) as compared with trimethylene sulfite (12.1 Hz) is probably due to a substituent effect. In 4-methyl-trimethylene sulfite [18] the two trans coupling constants are $^3J_{4a5a} = 11.6$ Hz and $^3J_{5a6a} = 12.9$ Hz. The decrease in $^3J_{4a5a}$ compared to $^3J_{a56a}$ is expected to be a substituent effect rather than a distortion of the ring. The R value [17] for this compound (2.07) is not significantly different from that calculated for trimethylene sulfite (2.05). In chlorophosphites [19] a similar change in $^3J_{aa}$, upon substitution at position 5 in the ring, is found ($^3J_{aa} = 11.5$ Hz in 5-methyl-, 11.9 Hz in 5-phenyl-, and 12.9 Hz in the unsubstituted 2-chloro-1,3,2-dioxaphosphorinane). The variation of $^3J_{aa}$ in the phosphites is believed to be due to substituent effects rather than an equilibrium between different chair conformations. The observation that $^3J_{P5He}$ (*ca.* 10.9 Hz) in 5-methyl- and 5-phenyl-chloro-phosphite and the unsubstituted compound is of the same magnitude does support the assumption that variation in $^3J_{aa}$ is due to substituent effects as the $^3J_{PH}$ is shown to be dependent on dihedral angles.[16]

Calculation of the equilibrium constant for the equilibrium $S=O_{(a)} \rightleftharpoons S=O_{(e)}$ in compound 2, assuming that there is no substituent effect operating on $^3J_{aa}$, indicates that the major isomer with axial S=O group exists in approximately 95 % (calculated from $^3J_{aa}$ and $^3J_{ee}$ in trimethylene sulfite [1]). Taking into account the substituent effects on ^3J it is reasonable to conclude that, at most, one or two per cent of isomers with equatorial S=O group exist. The conformational free energy for a methyl group in trimethylene sulfite, about 0.7 kcal/mol,[3] might not be large enough to give any significant amount of the isomer with the S=O group equatorial. The observed coupling constants for the equilibrium $S=O_{(a)} \rightleftharpoons S=O_{(e)}$ can be expressed by

$$J_{4a5e}{}^{obs} = nJ_{4a5e} + (n-1)J_{4e5a}$$

$$J_{4e5e}{}^{obs} = nJ_{4e5e} + (n-1)J_{4a5a}$$

The fact that $^3J_{4a5e}$ and $^3J_{4e5e}$ for the 5-axial-methyl substituted sulfite are nearly equal in magnitude (Table 1) suggests that this sulfite exists in a conformational equilibrium between the two chair forms, with the conformational equilibrium to the side with axial substituent.

The four-bond coupling constant between the equatorial protons in positions 4 and 6 is found to vary upon substitution in the ring. Substitution at C_5 in the systems studied would hardly effect the separation between the "rear lobes" of the hybrid orbitals which are bonded to the coupled nuclei, and thereby have negligible or no effect on the direct coupling mechanism. The positive shift in $^4J_{ee}$ upon substitution at C_5 in unstrained cyclic sulfites

Table 2. Chemical shift for the ring protons.[a]

Comp.	$H_{4e(6e)}$	$H_{4a(6a)}$	H_{5e}	H_{5a}
1	3.64	4.92	1.93	–
2	3.78	4.43	–	2.45
3	3.89	4.71	–	2.16
4	3.74	4.85	–	3.46
5	3.36	4.60	–	–
6	3.90	4.85	1.70	2.45

[a] ppm from TMS.

(Table 1) assumes that the indirect mechanism contributes to the coupling. MO description [20] of the substituent effect suggests a positive shift in the magnitude of $^4J_{ee}$ with either inductive or hyperconjugative substituents at C_5. Through-bond coupling in saturated systems does not depend on the dihedral angles of the system [21] and comparison of $^4J_{ee}$ in 5-methyl-substituted TM sulfite, phosphorinane, and siloxane, 1.83, 1.87, and 1.80, respectively, suggests that the indirect mechanism gives substantial positive contribution to $^4J_{ee}$ in heterocyclic six-membered ring systems. General trends in the sign and magnitude which can be inferred from tables and references [16,19] are as follows:

(i) Four-bond coupling constants between equatorial protons in six-membered ring systems are in the range 1.5 to 2.7 Hz.

(ii) $^4J_{HH}$ between protons in equatorial and axial position in the ring lies within the range 0.15 to 0.5 Hz and the sign is probably negative.

(iii) The coupling, $^4J_{HH}$, between axial protons probably has a negative sign and is in the range 0.0 to 0.4 Hz.

The effect of substitution:

(a) Substitution of one methyl group at C_5 increases $^4J_{ee}$ by 0.4 to 0.5 Hz.

(b) Geminal methyl groups at C_5 increase $^4J_{ee}$ by 1.0 to 1.2 Hz, as compared to unsubstituted ring systems.

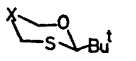
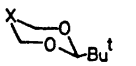
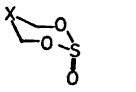
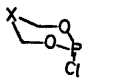
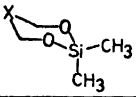
(c) A tertiary butyl or phenyl group increases the coupling, $^4J_{ee}$, about 0.6 to 0.8 Hz.

The freely rotating axial methyl group in position 5 in trimethylene sulfite is coupled to the axial protons, ^4J, in positions 4 and 6 by 0.5 Hz. Values obtained for dioxanes are in the range 0.3 to 0.7 Hz and are apparently dependent on the substituents.[22] The coupling found for the sulfite, $^4J_{Me} = 0.5$ Hz, is reasonable when compared to values obtained for dioxanes and to an average of $^4J_{ee}$ and $^4J_{ea}$ obtained for the 5-equatorial-methyl-trimethylene sulfite,

$$^4J_{HH}{}^{av} = \tfrac{1}{3}(^4J_{ee} + 2\ \ ^4J_{ea}) = 0.4_2 \quad \text{Hz}.$$

The barrier to ring inversions is largely due to tortional energy required for rotation about the bonds involved.[23,24] Rotation about the C–C bonds in propane [25] is about 3.4 kcal/mol and the barrier to ring inversion in cyclohexane [26] of 10.3 kcal/mol are partly related to each other. The transition states for ring inversion might involve half-chair, twist, or other forms, but regardless of the transition states involved, rotation about single bonds must take place.

Table 3. $^4J_{4ese}$ in various heterocyclic systems substituted at carbon 5.

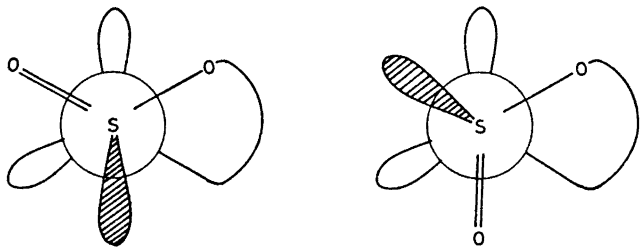
	X = CH_2	X = $CHCH_3$	X = $C(CH_3)_2$	
		2.0[e]		
			≃2.5[f]	Y = S=O 2.7[f]
				Y = $CHBu^t$ 2.5[f]
	1.58[a]	1.83(eq.CH_3) 2.04(ax.CH_3) 2.23[h] 2.20[i]	2.57	Y = $CHBu^t$ 2.25[f]
	1.40[b]	1.87(eq.CH_3)[d]	2.7[g]	
		≃1.80[e]		

[a] Ref. 1. [b] Ref. 16. [c] Ref. 33. [d] Ref. 19. [e] Ref. 34. [f] Ref. 35. [g] Ref. 36. [h] X = $CHBu^t$. [i] X = CHPh.

In a six-membered ring containing one or more single bonds with a higher barrier to rotation it is reasonable to expect a higher barrier to inversion as compared to cyclohexane. The barrier to rotation [27] about single bonds in systems containing adjacent electron pairs and polar bonds have been calculated and measured and are normally about 10 kcal/mol. This value is substantially higher as compared to values obtained for substituted ethanes.[28] The ring inversion for systems containing adjacent electron pairs and polar bonds is therefore expected to experience a considerably higher inversion barrier as compared to cyclohexanes. Analysis of the NMR spectra of 5-substituted sulfites has led to the conclusion that the sulfites exist in a rigid chair conformation when the substitutents are in the equatorial position. The conclusion that the S=O group occupies the axial position in all compounds studied can be explained from results obtained for various compounds containing the fragment X–C–O.[27] The least stable conformation is obtained when the polar C–X bond is placed between two electron pairs.

The energy to rotation about the single bond for fluoromethanol is about 12.6 kcal/mol.[27] Trans dihalogenated 1,4-dioxanes [29,30] and 1,4-dithianes [31,32] exist in the chair conformation with diaxial halogens. In the cyclic sulfites the S=O group exhibits a similar anomeric effect when the S=O group occupies the equatorial position.

The S=O group in cyclic sulfites is situated between two geminal electron pairs at the adjacent ring-atoms and is greatly destabilized in the equatorial position compared to the axial position. The axial S=O group experiences a minimum number of *gauche* interaction between the S=O group and lone pair electron orbitals which is assumed to be the most stable conformation [27] for similar systems. This interpretation leads to the same conclusion as proposed



(eq S=O) (ax S=O)

by other workers [8] based on the rotation barrier about the C–S bond in $HS(O)-CH_2^-$. Investigation of 1,2-oxathiane-2-oxide and its sulfur analogue by NMR suggested that the S=O bond adopts an axial configuration. They suggested that the strong preference for an axial S=O group resulted from dipolar interaction analogous to the anomeric effect suggested for the sulfites studied in this work. The unfavourable arrangement with the net dipole resulting from the non-bonded electrons oxygen nearly parallel to that of the S=O group is relieved with the S=O group adopting an axial configuration.

The author is indebted to Professor J. Dale at the Chemical Institute, University of Oslo, Norway, for the opportunity to use the VARIAN HA-100 spectrometer at his laboratory.

REFERENCES

1. Albriktsen, P. *Acta Chem. Scand.* **25** (1971) 478.
2. Wucherphennig, W. *Ann.* **737** (1970) 144.
3. van Woerden, H. F., Cerfontain, H., Green, C. H. and Reijerkerk, R. J. *Tetrahedron Letters* **1968** 6107.
4. Eliel, E. L. and Knoeber, M. C. *J. Am. Chem. Soc.* **90** (1968) 3444.
5. van Woerden, H. F. and Havinga, E. *Rec. Trav. Chim.* **86** (1967) 341.
6. Altona, C., Geise, H. J. and Romers, C. *Rec. Trav. Chim.* **85** (1966) 1197.
7. van Oyen, J. W. L., Hasekamp, R. C. D. E., Vershoor, G. C. and Romers, C. *Acta Cryst. B* **24** (1968) 1471.
8. Wood, G., McIntosh, J. M. and Miskow, M. H. *J. Can. Chem.* **49** (1971) 1202.
9. van Woerden, H. F. and de Vries-Miedema, A. T. *Tetrahedron Letters* **1971** 1687.
10. Gestblom, B. and Rodmar, S. *Acta Chem. Scand.* **18** (1964) 13.
11. Haigh, C. W. *Private communication.*
12. Castellano, S. and Bothner-By, A. A. *J. Phys. Chem.* **41** (1964) 3863.
13. Albriktsen, P. *Unpublished results.*
14. van Woerden, H. F. and Havinga, E. *Rec. Trav. Chim.* **86** (1967) 353.
15. Anteunis, M., Tavernier, D. and Borremans, F. *Bull. Soc. Chim. Belges* **75** (1966) 396.
16. Bergesen, K. and Albriktsen, P. *Acta Chem. Scand.* **25** (1971) 2257.
17. Lambert, J. B. *Accounts Chem. Res.* **4** (1971) 87, and references therein.
18. Albriktsen, P. *Unpublished results.*
19. Bergesen, K. and Albriktsen, P. *Acta Chem. Scand. To be published.*
20. Barfield, M. and Chakrabarti, B. *Chem. Rev.* **69** (1969) 757.
21. Barfield, M. and Grant, D. M. *Advan. Magn. Resonance* **1** (1965) 149.
22. Anteunis, M., Vandenbroucke, W. and Schamp, N. *Bull. Soc. Chim. Belges* **76** (1967) 552.
23. Hendrickson, J. B. *J. Am. Chem. Soc.* **83** (1961) 4537.
24. Harris, R. K. and Spragg, R. A. *J. Chem. Soc.* **1968** 684.

25. Scott, R. A. and Scheraga, H. A. *J. Chem. Phys.* **44** (1966) 3055, and references therein.
26. Anet, F. A. L. and Bourn, A. J. R. *J. Am. Chem. Soc.* **89** (1967) 760.
27. Wolfe, S., Rauk, A., Tel, L. M. and Csizmadia, J. G. *J. Chem. Soc. B* **1971** 136, and references therein.
28. Abraham, R. F. and Parry, K. *J. Chem. Soc.* **B 1970** 539.
29. Altona, C., Knoble, C. and Romers, C. *Rec. Trav. Chim.* **82** (1963) 1080.
30. Altona, C., Knoble, C. and Romers, C. *Rec. Trav. Chim.* **82** (1963) 1089.
31. Kalff, H. T. and Havinga, E. *Rec. Trav. Chim.* **85** (1966) 198.
32. Kalff, H. T. and Havinga, E. *Rec. Trav. Chim.* **85** (1966) 637.
33. Gelan, J. and Anteunis, M. *Bull. Soc. Chim. Belges* **77** (1968) 447.
34. Albriktsen, P. and Heggelund, S. *Unpublished results.*
35. Anderson, J. E. *J. Chem. Soc.* **B 1967** 712.
36. Katritzky, A. R., Nesbit, M. R., Michalski, J., Tulimowski, Z. and Zwierzak, A. *J. Chem. Soc.* **B 1970** 140.

Received August 25, 1971.