Chemistry of the S=O Bond. Part I. Nuclear Magnetic Resonance and Infrared Studies on Trimethylene Sulphite

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The conformation of trimethylene sulphite has been studied by ^1H n.m.r. spectroscopy and by an i.r. investigation of the S=O bond stretching vibration in different solvents at two concentrations. From analysis of the n.m.r. spectrum, cross-ring couplings are evident, although not previously reported.† The i.r. studies are more comprehensive than those in previous reports and the interpretation of our data leads to different conclusions from those of others workers.

THE conformation of the cyclic ester, trimethylene sulphite, has been studied by a variety of physical techniques.[1-9] For example, Altona *et al.*[4] obtained *X*-ray data on crystalline material at −100 °C and concluded that the molecule is rigid and exists in a chair form with the exocyclic oxygen atom in an axial position (I). Investigation of the conformation of trimethylene sulphite as a neat liquid or in solution has led to conflicting conclusions. Initially, Arbuzov[1] suggested, from the results of dipole moment measurements, that the molecule existed as an equilibrium mixture of the two forms (I) and (II), with comparable amounts of both. But Van Woerden,[3,7,8] in a more detailed study of dipole moments and i.r. spectra of trimethylene (and substituted trimethylene) sulphites, concluded that the

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† *Note added in proof:* Since submission of this paper, an analysis of the 60 MHz ^1H n.m.r. spectrum of neat trimethylene sulphite has been published (P. Albriktsen, *Acta Chem. Scand.*, 1971, **25**, 478). The results are similar to the data we obtained from the analysis of the 100 MHz ^1H n.m.r. spectrum of a carbon tetrachloride solution of trimethylene sulphite (10% w/v).

[1] B. A. Arbuzov, *Bull. Soc. chim. France*, 1960, **27**, 1311.

[2] D. G. Hellier, J. G. Tillett, H. F. Van Woerden, and R. F. M. White, *Chem. and Ind.*, 1963, 1956.

[3] H. F. Van Woerden, Ph.D. Thesis, Leiden, 1964.

[4] C. Altona, H. J. Geise, and C. Romers, *Rec. Trav. chim.*, 1966, **85**, 1197.

[5] D. G. Hellier, Ph.D. Thesis, London, 1966.

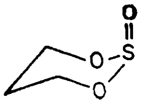
[6] G. Wood and M. Miskow, *Tetrahedron Letters*, 1966, 4433.

[7] H. F. Van Woerden and E. Havinga, *Rec. Trav. chim.*, 1967, **86**, 342.

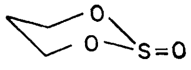
[8] H. F. Van Woerden and E. Havinga, *Rec. Trav. chim.*, 1967, **86**, 353.

[9] G. Eccleston, P. C. Hamblin, R. A. Pethrick, R. F. M. White, and E. Wyn-Jones, *Trans. Faraday Soc.*, 1970, **66**, 310.

molecule exists entirely in solution as the axial chair form (I). Recently, Wood and Miskow[6] adduced evidence for flexible forms in solution by reinterpretation of the

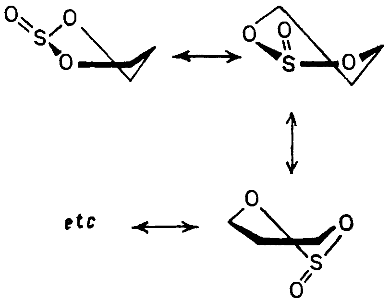


(I)



(II)

dipole moment data together with some n.m.r. measurements. Wyn-Jones and his co-workers[9,10] have used



(III)

the ultrasonic technique to study the conformation of trimethylene sulphite (and other ring sulphites). They conclude that the rigid chair form (I) is present in >90% proportion but in equilibrium with various twist forms. Unfortunately, these authors did not realise that cyclic sulphites are highly associated in solution. Evidence for association in cyclic sulphites has recently been published by Wood and Miskow,[11] and our own observations confirm that this is an important characteristic of the solution chemistry of sulphites. Despite this association the overall results of Wyn-Jones *et al.* are (probably fortuitously) not in great error. Since the ultrasonic relaxation observed for trimethylene sulphite occurs by a single relaxation mechanism both for a chloroform solution and for the neat liquid it seems most probable that their attribution of the relaxation to a conformational origin remains valid, as the large association now known to exist is both solvent- and concentration-dependent and any ultrasonic relaxation due to molecular association presumably lies outside the experimental frequency range (25—105 MHz) used in their work.

Anteunis[12] has introduced the term anancomeric to describe structures having virtually a single conformation because of an extreme position of the conformational equilibrium. This is the type of equilibrium suggested for trimethylene sulphite from results obtained by ultrasonic and other techniques. We have analysed the ^{1}H n.m.r. spectra of trimethylene sulphite to provide additional evidence for the anancomeric conformation in solution.

The 100 MHz proton spectrum of trimethylene sulphite (Figure 1) consists of four multiplets, (a), (b), (c), and (d), centred at δ *ca.* 4·92, 3·79, 2·54, and 1·61 p.p.m. From the magnitude of the couplings these may be assigned to

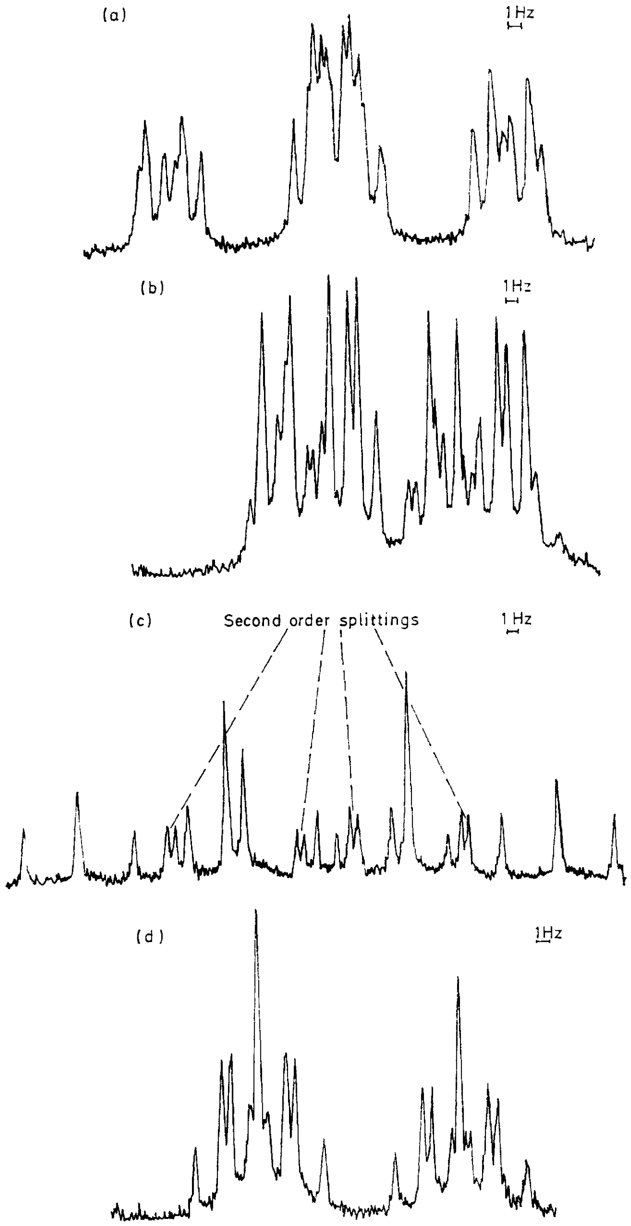


FIGURE 1 100 MHz ^{1}H N.m.r. spectrum of trimethylene sulphite [10% in in CCl_4 (w/v)]; (a) XX′ spectrum, (b) AA′ spectrum, (c) (R $\longrightarrow$ Y) spectrum, (d) M spectrum

equivalent axial protons at C-4 and C-6, equivalent equatorial protons at C-4 and C-6, the axial proton at C-5 and the equatorial proton at C-5. The signals may be analysed as an AA′XX′M(R $\longrightarrow$ Y) spin system (terminology of Diehl and Lustig[13]); this is similar to

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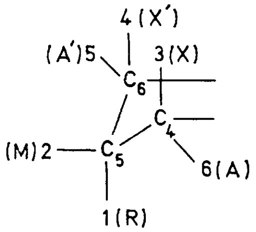
[10] P. C. Hamblin, R. A. Pethrick, R. F. M. White, and E. Wyn-Jones, *J. Mol. Structure*, 1968, **1**, 333.

[11] G. Wood and M. Miskow, *Tetrahedron Letters*, 1970, 1775.

[12] M. Anteunis, D. Tavernier, and F. Borremans, *Bull. Soc. chim. belges.*, 1966, **75**, 396.

[13] P. Diehl and E. Lustig, *J. Chem. Phys.*, 1966, **44**, 2974.

the AA′XX′MR spin system except that the R part of the spectrum [multiplet (c)] shows additional lines due to second-order splittings.*



The values of chemical shifts and coupling constants given in Table 1 were obtained as ' best-fit ' parameters using the iterative program LAOCOON III.[14] Although not shown, there is good agreement between the calculated and experimental spectra. The calculated values of the coupling constants are similar to those found for other carbocyclic systems.[4,12,15,16] The long-range ^4J coupling between the equatorial protons on C-4 and C-6 is the largest cross-ring coupling because these protons lie in a planar M arrangement.[17]

TABLE 1

Calculated chemical shifts and coupling constants of trimethylene sulphite *

Nucleus	δ/p.p.m. (from Me_4Si)	J/Hz	
R	δ(1) 2·541	−14·18 (1,2)	−0·27 (3,4)
M	δ(2) 1·618	12·77 (1,3)	−0·55 (3,5)
		12·77 (1,4)	−11·68 (3,6)
X	δ(3) 4·928	4·85 (1,5)	−11·68 (4,5)
X	δ(4)	4·85 (1,6)	−0·55 (4,6)
		2·64 (2,3)	−1·60 (5,6)
A	δ(5) 3·794	2·64 (2,4)	
		1·89 (2,5)	
A	δ(6)	1·89 (2,6)	

* Chemical shifts and coupling constants were obtained using a modified version of LAOCOON III with an r.m.s. error of 0·055 from assigning 145 (90%) of the 160 calculated lines with relative intensities > 0·02. Assignment of the remaining 15 lines was ambiguous because of the complexity of the AA′ spectrum (b). Chemical shifts are accurate to ±0·01 p.p.m. Coupling constants are considered accurate to ±0·1 Hz except the cross-ring couplings $J_{3.4}$, $J_{3,5} \equiv J_{4,6}$ and $J_{5.6}$, which are only accurate to ±0·2 Hz.

The differences between the chemical shifts of protons in cyclic sulphites have been interpreted as being largely due to the electric field effect and magnetic anisotropy of the S=O bond.[5,18] The shielding region of the S=O bond is shown in Figure 2; protons within the positive cone are shielded and those in the negative area are deshielded.

Assuming an axial chair form, it can be seen that both axial and equatorial protons of C-4 and C-6 lie well within the deshielding region. In particular, the axial protons of C-4 and C-6 lie in a *syn*-axial position with respect to the exocyclic S=O bond and are subject to maximum deshielding, confirming the assignment of these protons to the lowest field multiplet (a). The assignment of multiplet (b) to the equatorial protons on C-4 and C-6 is also in agreement with an axial chair form.[2,5]

For trimethylene sulphite the axial proton on C-5 has been shown to be less shielded than the equatorial proton. The C-5 methylene protons of (rigid) 1,3-dioxans have been given a similar assignment by Anteunis *et al.*[12] even though the axial protons at C-4 and C-6 absorb at higher field than the equatorial protons, analogous to what is found for cyclohexane. Anteunis attributes the anomalous chemical shift difference of the C-5 methylene protons in 1,3-dioxans to a lone-pair interaction of the 1,3-oxygen atoms with the equatorial proton on C-5. This type of interaction must be equally important in the origin of the chemical shift differences between the C-5 methylene protons for trimethylene sulphite (and derivatives). Anteunis has given a value of *ca.* 0·8 p.p.m. to the chemical shift difference between the C-5 methylene protons of rigid 1,3-dioxan. The chemical shift difference for C-5 methylene protons of trimethylene sulphite is *ca.* 0·9 p.p.m. (Table 1), indicating that the effect of the S=O bond on these chemical shifts is approximately the same or small. The chemical shift difference between the axial and equatorial proton on C-4 and C-6 must still be due principally to the electric field effect and magnetic anisotropy of the S=O bond,[18,19] mainly because of their close proximity to this bond, particularly for the axial protons.

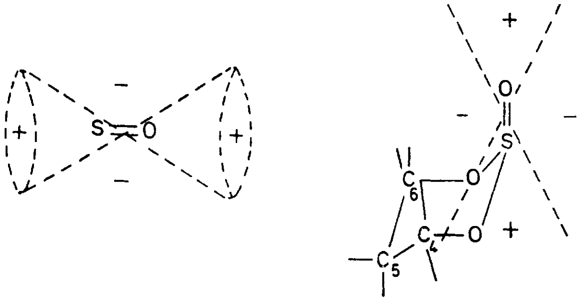


FIGURE 2

In addition to the n.m.r. spectral analysis of trimethylene sulphite we have studied the S=O stretching vibration of this cyclic ester in different solvents and at two concentrations in an attempt to obtain further in-

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* In ref. 13 Diehl and Lustig showed that the high and low field peaks of the central triplets are split by a factor $p \simeq J_{RX}{}^2/(\nu_R - \nu_X)$ Hz providing that $\nu_R - \nu_X$ is much greater than other coupling constants. The calculated value of p, 0·68 Hz, using the values given in Table 1, compare favourably with the experimentally observed value of 0·70 Hz.

[14] S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, 1964, **41**, 3863.

[15] For references see J. E. Anderson, *Quart. Rev.*, 1965, **19**, 434.

[16] For a review see H. Feltkamp and N. C. Franklin, *Angew. Chem.*, 1965, **77**, 804.

[17] J. Meinwald and A. Lewis, *J. Amer. Chem. Soc.*, 1961, **83**, 2769; J. Meinwald and Y. Meinwald, *ibid.*, 1963, **85**, 2514.

[18] (*a*) B. A. Arbuzov and Yu. Yu. Samitov, *Tetrahedron Letters*, 1963, 473; Yu. Yu. Samitov, *Doklady Akad. Nauk S.S.S.R.*, 1965, **164**, 347; J. G. Pritchard and P. C. Lauterbur, *J. Amer. Chem. Soc.*, 1961, **83**, 2105; (*b*) L. Cazaux and P. Maroni, *Tetrahedron Letters*, 1969, 3667.

[19] Yu. Yu. Samitov and R. M. Aminova, *Zhur. strukt. Khim.*, 1964, **5**, 538.

formation on conformation. The results are summarised in Table 2.

The presence of the band in the region of 1230 cm^{-1} in the i.r. spectrum of trimethylene sulphite and some 5-substituted trimethylene sulphites [3,5,7,8] has been assumed to indicate the presence of an equatorial S=O bond and/or ring conformation other than or in addition to a rigid chair conformation. Recently, investigation of 4,6-substituted trimethylene sulphites [18b,20] established that for some isomers in such ring strained systems the higher i.r. stretching vibration of *ca.* 1230 cm^{-1} was associated with an equatorial S=O bond and/or one in which the ring was so distorted that a true axial S=O bond was not possible.

TABLE 2

S=O Frequencies (cm^{-1}) of trimethylene sulphite in various solvents

Solvent	Concentration A i	Concentration A ii	Concentration B i	Concentration B ii	D1	D2	PA	PB	DAB
MeCN	1194	1233	1187	1235	−7	+2	21	14	7
CCl_4 (+10% phenol)	1194	1234	1190	1233	−4	+1			
C_6H_{12}	1198	1234	1200	1235	+2	+1	19	11	8
CCl_4	1190	1235	1196	1235	+6	0	17	10	7
CS_2	1190	1233	1192	1233	+2	0	18	11	7
C_6H_6	1189	1233	1194	1235	+5	+2	15	8	7
$PhNO_2$	1181	1233							
Neat (liquid)	1183	1233					28		
(vapour)	1212								
$NH_2\cdot[CH_2]_2\cdot NH_2$	1178	1232							
EtOH	1187	1233							

Concentration range A = 0·32—0·34M, D1 = i (B) − i (A). Concentration range B = 0·05—0·06M, D2 = ii (B) − ii (A). PA = Relative percentage of peak ii compared to peak i, concentration A. PB = Relative percentage of peak ii compared to peak i, concentration B.

Although the change of relative intensities of the two S=O bands from one solvent to another has been reported,[6] there appear to have been no systematic solvent–solvent, solvent–concentration i.r. studies of trimethylene sulphite solutions. Also Wood and Miskow [11] have recently reported that several cyclic sulphites, in particular trimethylene sulphite, are all highly associated in dilute solutions, but previous i.r. studies of trimethylene sulphite and substituted trimethylene sulphites have not considered or recognised the extensive molecular association now known to exist even at very low concentrations.

From the i.r. data of the S=O stretching vibrations one can note the following:

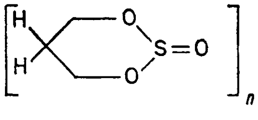
(*a*) The position of the band at higher wavenumber (*ca.* 1234 cm^{-1}) shows little or no variation with change in solvent or solute concentration. However, the intensity of the band relative to that at the lower wavenumber (*ca.* 1195 cm^{-1}) is dependent on both solvent and solute concentration. The relative change of intensity upon dilution is approximately the same (*ca.* 30%) for the five solvents used where sufficiently accurate data could be determined.

(*b*) The position of the band at the lower wavenumber gives comparable values for carbon tetrachloride, carbon disulphide, and benzene at the higher concentration, but solvent shifts upon dilution differ though all shifts are 'positive' (defined here as shifts to higher wavenumbers). 'Negative' shifts upon dilution occur only for polar solvents (CH_3CN or CCl_4–PhOH). Generally, for the solution of higher concentration, the greater the polarity and solvation power of the solvent the lower the stretching frequency (in cm^{-1}) of the main S=O band. This behaviour is similar to that found for sulphoxides.[21]

(*c*) The ν(S=O) band for the saturated vapour, and at lower pressures, gave a single sharp peak at 1212 cm^{-1} with rotational P and Q branch maxima at 1203 and 1217 cm^{-1}, respectively. There was no observable variation in these values with decrease of pressure.

For trimethylene sulphite the observation of the higher wavenumber band has been attributed to the presence of species (II) in the equilibrium and/or flexible forms [species (III), *etc*].[6]

Although intensity changes in such bands with change of solvent and upon dilution have usually been interpreted as changes in the position of the equilibrium, the amount of species (II)—(III) relative to species (I) deduced, on this assumption, from i.r. data for the higher concentration, is too high to agree with the ultrasonic relaxation results, which predict the presence of at least 90% of species (I) in a yet more highly concentrated solution and in the neat liquid. Another apparent inconsistency concerns the decreases in intensity of the band at 1234 cm^{-1} upon dilution. These decreases are approximately the same (*ca.* 30%) for solvents of a reasonable range of polarity and solvation power.



(IV)

The band at 1234 cm^{-1} cannot be attributed to non-monomeric species of the type (IV) since the value of *n* varies disproportionately from solvent to solvent if the

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[20] S. Sarel and V. Usieli *Israel J. Chem.*, 1968, **6**, 885; W. Wucherpfennig, *Annalen*, 1970, **737**, 144.

[21] D. Barnard, J. M. Fabian, and H. P. Koch, *J. Chem. Soc.*, 1949, 2442; T. Gramstad, *Spectrochim. Acta*, 1963, **19**, 829; T. Cairns, G. Eglinton, and D. T. Gibson, *ibid.*, 1964, **20**, 31.

band at *ca*. 1200 cm^{-1} band is assumed to be that of the solvated monomer. Combining our intensity measurements with Wood and Miskow's data, this would predict relative values of n of 40·5 (cyclohexane), 14·6 (carbon tetrachloride), and 2·5 (acetonitrile) for 1% solutions.

The work of Gillespie and Robinson has shown that the S=O bond is very sensitive to its environment.[22] By studying a large series of acyclic sulphites and sulphuryl and sulphate compounds they showed that the length of an S=O bond and the bond angle of an SO_2 group may be correlated with the S=O bond stretching vibration, and that this correlation can be extended to include many other compounds including neutral molecules and ions. They derived the relationships (1) and (2), where $\nu(S{=}O)$ = i.r. stretching frequency in cm^{-1}, $r(S{=}O)$ = bond length in Å, and $N(S{=}O)$ = bond order.

$$\nu(S{=}O)\, r(S{=}O)^{3·7} = 4·79 \times 10^3 \qquad (1)$$

$$N(S{=}O) = 15·65/r(S{=}O)^{7·4} + 0·7 \qquad (2)$$

Although equations (1) and (2) were originally applied to acyclic molecules they appear to hold for the S=O bond in trimethylene sulphite. From the equations the data in Table 3 can be calculated. The results of an *X*-ray analysis of crystalline trimethylene sulphite[4] gave an estimated bond length of 1·45 ± ·011 Å, equivalent to a calculated bond order of 1·70 ± 0·04.

TABLE 3

$\nu(S{=}O)$ (cm^{-1})	Bond length (Å)	Bond order
1180	1·460	1·652
1190	1·456	1·669
1200	1·453	1·685
1210	1·450	1·701
1220	1·447	1·718
1230	1·443	1·734

The calculations show that only very small changes in the S=O bond environment [with resultant change in $r(S{=}O)$] are required to produce changes in stretching frequencies of 0—50 cm^{-1}.

The solvent behaviour of the band at the lower wavenumber follows, on the whole, a predictable pattern. The greater the polarity and solvation power of the solvent, the greater the induced polarity of the S=O bond, the smaller the bond order, and the lower the related stretching frequency. Thus for solvents of high polarity, stretching frequencies of 1178 and 1181 cm^{-1} are observed, but vibrations at higher wavenumber are observed for solvents of lower polarity. For the vapour phase a highest value of 1212 cm^{-1} is noted. This presumably reflects the bond order of the molecule free from any solvent effects.

Dilution in solvents of low polarity effectively decreases the dielectric constant of the medium (and molecular association); ' positive ' shifts are therefore observed. Dilution with polar solvents produces more effective solvation and ' negative ' (lower wavenumber) shifts are observed for these.

In contrast, the band at 1234 cm^{-1} shows little change in frequency with changes in either solvent or solute concentration and is missing in the i.r. spectrum of the vapour. Thus, the behaviour of the band at 1234 cm^{-1} for trimethylene sulphite does not appear to be entirely consistent with that expected for the S=O bond stretching frequency for species (II) or (III). Since this band occurs in conjunction with that at lower frequency for trimethylene sulphite and in those isomers of the simple 5-substituted trimethylene sulphites that have been suspected of possessing flexible rings,[3,7,18b,20] another possible interpretation is that the flexibility is not so great as to cause ring inversion to any great extent, but sufficient to allow some ring distortion either by association with a polar solvent and/or by molecular association, which could give rise to additional $-CH_2-$ vibrations associated with the ring. Bands of varying intensity for other six-membered carbocyclic compounds such as cyclohexane[23] and 1,3-dioxan[24] are also found in the region 1220—1260 cm^{-1}, probably due to $-CH_2-$ twist vibrations. We have found from an extensive study of the i.r. spectrum of five-membered ring cyclic sulphites, such as ethylene sulphite,[25] that these only possess one S=O band, at *ca*. 1190 cm^{-1}, and the band at 1230 cm^{-1} is absent.

Our conclusions from the i.r. studies are as follows.

1. Ultrasonic relaxation techniques indicate that some relaxation process occurs. This can be due to (*a*) the equilibrium suggested or (*b*) the molecular association now known to exist. Since the relaxation occurs *via* a single (solvent-independent) mechanism, either process (*a*) or (*b*) is involved but not both. If the process is (*a*), then implicit in this statement is that the equilibrium must lie at least 90% in favour of the conformation with an axial S=O bond [species (I)]. However, if the band at 1234 cm^{-1} were due only to an S=O stretching vibration, the i.r. spectrum of the neat liquid would suggest that this percentage must not be greater than 72%.

2. Frequency changes with change in solvent and solute concentrations are observed for the band at *ca*. 1196 but not for that at 1234 cm^{-1}. However, the intensity of the latter is dependent upon solvent and solute concentration though dilution effects for different solvents are approximately the same.

3. Methylene vibrations for other carbocyclic compounds are also observed in the 1230 cm^{-1} region and these vibrations are probably present in trimethylene sulphite (and other six-membered ring sulphites).

It therefore seems likely that an exclusive and direct assignment of the band at 1234 cm^{-1}, for trimethylene sulphite and some of its substituted derivatives to an equatorial S=O bond or to an S=O bond in flexible conformers is an oversimplification and that another factor,

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[22] R. J. Gillespie and E. A. Robinson, *Canad. J. Chem.*, 1963, **41**, 2074.

[23] H. Fukushima, T. Miyazawa, T. Shimanouchi, and H. Takahashi, *J. Mol. Spectroscopy*, 1964, **13**, 43.

[24] R. Mecke and F. Langenbucher, 'Infra-red Spectra of Selected Chemical Compounds,' Heyden, vol. VII, London, 1970; H. Wunderlich, *Z. analyt. Chem.*, 1968, **241**, 234.

[25] Unpublished observations.

or combination of factors, is also probably involved. A similar i.r. investigation of a large number of 5-substituted trimethylene sulphite derivatives confirms our conclusions and we are also investigating the i.r. behaviour of the S=O bond of some 4,6-substituted derivatives, where ring distortion and flexible conformations are known to exist.

Summary.—The n.m.r. and i.r. data confirm the general conclusion that the conformation of trimethylene sulphite in solution is similar to that in the solid state and that despite an earlier claim,[6] it exists predominantly, if not exclusively, in a chair conformation with an axial S=O bond.

EXPERIMENTAL

The ^{1}H n.m.r. spectra were run on a Varian HA100 instrument for 10% (w/v) trimethylene sulphite solutions in carbon tetrachloride. Peak positions were calibrated by direct frequency count. At least three spectra were run (forward and reverse sweep) and the reproducibility of the line positions was ±0·05 Hz.

All i.r. measurements were obtained using the Perkin-Elmer 521 spectrophotometer. The trimethylene sulphite samples and all solvents were purified by standard techniques to a spectroscopically pure level. For solutions of trimethylene sulphite in six different solvents at the two concentration [0·33 and 0·05M (giving *ca.* 8 and *ca.* 1% solutions)] the i.r. spectra were recorded on a linearly expanded calibrated scale and are accurate to ±1 cm^{-1}. For the solvents ethanol, methylenediamine, and nitrobenzene, accurate measurements of absorption frequencies in the required region could only be made for solutions at the higher concentration, so the relative intensities of the 1234 and the 1200 cm^{-1} bands could not be measured with any certainty.

One of us (C. H. G.) thanks to the S.R.C. for a research studentship.

[1/263 *Received*, 12*th March*, 1971]