Chemistry of the S=O Bond. Part II.[1] Nuclear Magnetic Resonance and Infrared Studies on Ethylene Sulphites (1,3,2-Dioxathiolan 2-Oxides)

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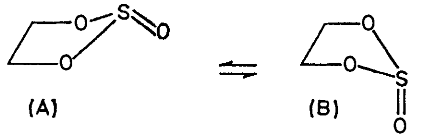
The 100 MHz ^{1}H spectra of methyl-substituted ethylene sulphites have been examined in several solvents. In all cases, the ^{1}H spectra have been fully analysed and it has been possible to establish a chemical shift additivity for a series of compounds. Interpretation of the ^{1}H spectra together with an i.r. study of the S=O stretching frequency of the sulphites in various solvents strongly suggests the existence of only a single (and basically similar) conformation in solution for each of these sulphites.

It is established [2,3] that organic sulphites give rise to medium or intense bands near 1210 cm^{-1} attributed to the S=O stretching vibration. In particular, the earliest studies [2,4] of $\nu_{S=O}$ in ethylene sulphites gave values in the range 1212—1216 cm^{-1} (liquid film) for ethylene sulphite and the isomeric mixture of propylene sulphite. Later studies of pure isomers and isomeric mixtures of ethylene sulphites have clearly shown the solvent-dependence of $\nu_{S=O}$ and has led to the suggestion by some workers of the presence of a variable conformational equilibrium (A) $\rightleftharpoons$ (B) in solution.


(A) (B)

^{1}H N.m.r. spectroscopy has also been used to investigate the stereochemistry of ethylene sulphites. The first n.m.r. studies were by Pritchard and Lauterbur [5] in 1961 who described the 40 MHz ^{1}H spectra of ethylene and 1,1-dimethylethylene sulphite and the 60 MHz spectra of the two isomers of propylene sulphite. No detailed analysis of the spectra was attempted, although they did conclude from a partial analysis and from calculations of the effect of the electric field and anisotropy of the S=O bond that the sulphites have similar structures.

Detailed analysis of the ^{1}H spectrum (60 MHz) of ethylene sulphite have been discussed by Finegold [6] and briefly by Haake *et al.*[7] in 1968. The former used first-order spectral analysis and the latter, computer analysis techniques. Finegold calculated the ^{1}H n.m.r. spectral parameters of ethylene sulphite and of a mixture of the two isomers of propylene sulphite in relation to studies of weak intermolecular forces and medium (solvent) effects. Although he postulated a stable non-inverting ring with a pseudo-axial preference of the S=O bond to the ring, he assigned protons *cis* to the S=O bond as resonating to higher field relative to the *trans*; this is opposite to the assignment of other workers including the analysis by Haake *et al.* of ethylene sulphite. There are also several misprints in this paper including some of the chemical shift values given for ethylene sulphite in various solvents.

With the exception of ethylene sulphite, no detailed n.m.r. and i.r. study on solutions of isomerically pure ethylene sulphites has been reported. The object of this study was to qualify the preliminary observations of previous workers on the structures of ethylene sulphites by examination of the complete series of methyl-substituted ethylene sulphites by ^{1}H n.m.r. and i.r. spectroscopy.

Nuclear Magnetic Resonance Spectra.—Complete analysis of the 100 MHz spectra of all the methyl-substituted ethylene sulphites was possible either by direct analysis or by interpolation of 220 MHz spectra. The results are summarised in Table 1.

Ethylene and propylene sulphites. The (corrected) results of Finegold [6] for ethylene sulphite (I) in terms of solution concentration are the nearest comparable with

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[1] Part I, C. H. Green and D. G. Hellier, *J.C.S. Perkin II*, 1972, 458.

[2] H. H. Szmant and W. Emerson, *J. Amer. Chem. Soc.*, 1956, **78**, 454.

[3] L. J. Bellamy, ' The Infrared Spectra of Complex Molecules,' 2nd edn., Methuen, London, 1958, p. 360.

[4] P. B. de la Mare, W. Klyne, D. J. Millen, J. G. Pritchard, and D. Watson, *J. Chem. Soc.*, 1956, 1813.

[5] J. G. Pritchard and P. C. Lauterbur, *J. Amer. Chem. Soc.*, 1961, **83**, 2105.

[6] H. Finegold, *J. Phys. Chem.*, 1968, **72**, 3244.

[7] P. Haake, J. P. McNeal, and E. J. Goldsmith, *J. Amer. Chem. Soc.*, 1968, **90**, 715.

the present study and are included in Table 1 for comparison. The ^{1}H spectra of isomer 1 of propylene sulphite (III) consists of four distinct sets of multiplets (Figure 1) and gave a straightforward analysis. In contrast, isomer 2 (IV) gave a complex ^{1}H spectrum in all solvents, a multiplet corresponding to the three ring protons and a high-field methyl resonance. Fortunately the 100 MHz spectra could be analysed by interpolation of the less complex 220 MHz spectra (Figure 2).

Dimethyl-substituted ethylene sulphites. The ^{1}H spectra of 1,1-dimethylethylene sulphite (II) consists of two high-field singlets and a lower-field AB quartet. Pritchard and Lauterbur[5] observed a pronounced asymmetry in both multiplets and they suggested that this might arise from a slight permanent puckering of the five-membered ring, caused by a mutual interaction of the exocyclic oxygen atom and the *cis*-methyl group. But expansion and decoupling of the spectrum indicates that the asymmetry is due to long-range CH_3–H and *gem*-dimethyl coupling. The lower half of the quartet is split into quartets with J *ca.* 0·6 Hz by coupling with the highest-field methyl group. The lower-field methyl is also split by a coupling of *ca.* 0·4 Hz.

In the ^{1}H spectrum of (±)-1,2-dimethylethylene sulphite (V) there are four resonances, two high-field methyls and two multiplets containing eight lines each. The latter arises out of the proton pair of an AM quartet coupling with their geminal methyl group. The spectra are virtually of the first order and it is noticeable that in contrast to 1,1-dimethylethylene sulphite, no long-range coupling was observed.

The ^{1}H spectra of isomers 1 (VI) and 2 (VII) of 1,2-dimethylethylene sulphite correspond to those of $AA'X_3X_3'$ systems which have been discussed in detail by Anet and others.[8,9] Thus the AA′ part of the spectrum of isomer 1 consists of a multiplet symmetrically placed about ν_A [Figure 3(a)], the relative values of the coupling constants being such that 12 lines are observed [28 theoretical transitions are possible for

TABLE 1

Chemical shifts and coupling constants of some ethylene sulphites *

		Chemical shifts (p.p.m.)				Coupling constants, J/Hz					
Compound	Solvent †	δ_1	δ_2	δ_3	δ_4	12	13	14	23	24	34
Ethylene sulphite (ref. 5)	1	4·810	$\equiv\delta_1$	4·447	$\equiv\delta_3$	7·00	6·58	−8·15	≡14	≡13	≡12
(I)	3	4·082		3·538		6·74	6·56	−8·23			
	4	4·846		4·497		6·88	6·70	−8·42			
1,1-Dimethylethylene sulphite	1	1·652	4·364	4·117	1·384			±0·42	−8·48	±0·58	
(II)	2	1·482	4·203	3·863	1·185			±0·37	−8·48	±0·51	
	3	1·226	3·989	3·507	0·888			±0·40	−8·56	±0·56	
	4	1·667	4·428	4·167	1·351			±0·40	−8·49	±0·56	
Propylene sulphite,	1	5·039	4·645	3·808	1·412	6·16	6·91	6·24	−8·21		
Isomer 1	2	4·827	4·405	3·551	1·179	6·11	6·88	6·17	−8·21		
(III)	3	4·504	4·036	3·121	0·753	6·07	6·88	6·16	−8·26		
	4	5·103	4·698	3·871	1·428	6·09	6·99	6·20	−8·29		
Propylene sulphite,	1	4·568	4·220	4·462	1·594	9·09	6·07	6·23	−8·56		
Isomer 2	2	4·201	3·967	4·043	1·359	9·09	6·13	6·23	−8·64		
(IV)	3	3·890	3·798	3·686	1·039	9·25	6·17	6·19	−8·60		
(±)-1,2-Dimethylethylene	1	4·027	4·572	1·429	1·520	8·85		6·11	−6·10		
sulphite	2	3·770	4·405	1·154	1·286	8·81		6·08	−6·09		
(V)	3	3·518	4·288	0·861	1·041	8·81		6·10	−6·10		
	4	4·100	4·635	1·447	1·535	8·87		6·14	−6·13		
1,2-Dimethylethylene sulphite,	1	4·953	1·273	$\equiv\delta_2$	$\equiv\delta_1$	6·34	−0·13	5·73		≡13	≡12
Isomer 1	2	4·702	0·997			6·44	−0·21	5·68			
(VI)	3	4·516	0·727			6·47	−0·16	5·70			
	4	5·002	1·297			6·42	−0·15	5·71			
1,2-Dimethylethylene sulphite,	1	4·601	1·490	$\equiv\delta_2$	$\equiv\delta_1$	6·62	−0·17	5·93		≡13	≡12
Isomer 2	2	4·305	1·294			6·71	−0·25	5·90			
(VII)	3	3·865	1·004			6·59	−0·19	5·88			
	4	4·662	1·514			6·64	−0·15	5·86			
1,1,2-Trimethylethylene	1	1·352	4·671	1·539	1·189	6·45					±0·43
sulphite, Isomer 1	2	1·181	4·590	1·403	1·052	6·45					±0·44
(VIII)	3	0·866	4·445	1·129	0·775	6·47					±0·45
	4	1·372	4·744	1·558	1·215	6·47					±0·45
1,1,2-Trimethylethylene	1	1·432	4·223	1·518	1·375	6·50					±0·45
sulphite, Isomer 2	2	1·291	4·047	1·422	1·218	6·53					±0·44
(IX)	3	1·006	3·713	1·242	0·900	6·54					±0·45
	4	1·456	4·281	1·549	1·403	6·50					±0·44
1,1,2,2-Tetramethylethylene	1	1·510	1·298	$\equiv\delta_2$	$\equiv\delta_4$	0·55					≡12
sulphite	3	1·224	0·887			0·55					
(X)	4	1·539	1·324			0·55					

* Chemical shifts and coupling constants were obtained either by first-order analysis or as r.m.s. error values by use of a modified version of LAOCOON III.[1] Chemical shifts are accurate to ±0·01 p.p.m. and coupling constants are considered accurate to ±0·10 Hz. † All solutions, except in solvent 2, were 10% (w/v). Solvent 1 was carbon tetrachloride, solvent 2 was carbon tetrachloride with 30% (v/v) of [$^2H_6$]benzene added. Solvent 3 was [$^2H_6$]benzene and solvent 4 was $CDCl_3$.

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[8] F. A. L. Anet, *J. Amer. Chem. Soc.*, 1962, **84**, 747.

[9] A. A. Bothner-By and C. Naar-Colin, *J. Amer. Chem. Soc.*, 1962, **84**, 743.

$J(X_3X_3') = 0$, $\delta(AX) \gg J(AX_3)$ and $J(AX_3')$] and for the X_3X_3' part six lines are observed (14 theoretical transitions) symmetrically placed about ν_X [Figure 3(b)]. As observed by Anet the spectrum of an $AA'X_3X_3'$ spin system can readily be solved if $J(AX_3')$ is small (or zero). This is applicable to the systems under consideration. Reasonably accurate values can be obtained for coupling $J(AX_3')$ since the relative spacings of several transitions of medium intensity in both parts of the multiplets of A and X contain a direct contribution from this parameter. A computer 'best-fit' analysis was performed to obtain r.m.s. error values.

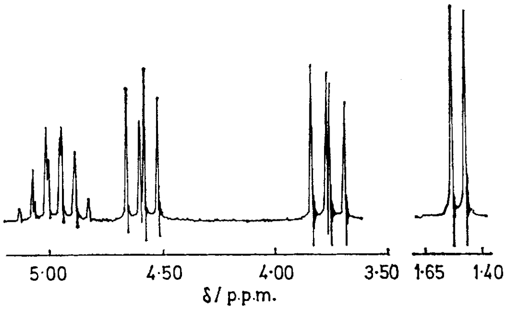


FIGURE 1 100 MHz ^{1}H N.m.r. spectrum of propylene sulphite, isomer 1 [10% (w/v) in CCl_4] (methyl doublet not to scale)

Tri- and tetra-methylethylene sulphite. Although isomer 1 (VIII) and isomer 2 (IX) of 1,1,2-trimethylethylene sulphite could not be separated the multiplets of each isomer are sufficiently resolved at 100 MHz to extract all parameters. The first-order spectra consist of four multiplets for each isomer, a low-field quartet and at higher field three sets of methyl resonances, one of which is split into a clean doublet (J *ca.* 6 Hz), and the remaining two into quartets with splittings of *ca.* 0·45 Hz each. *gem*-Methyl couplings are well resolved on both methyl groups but the low-field quartet and high-field methyl doublet show no sign of any additional long-range coupling.

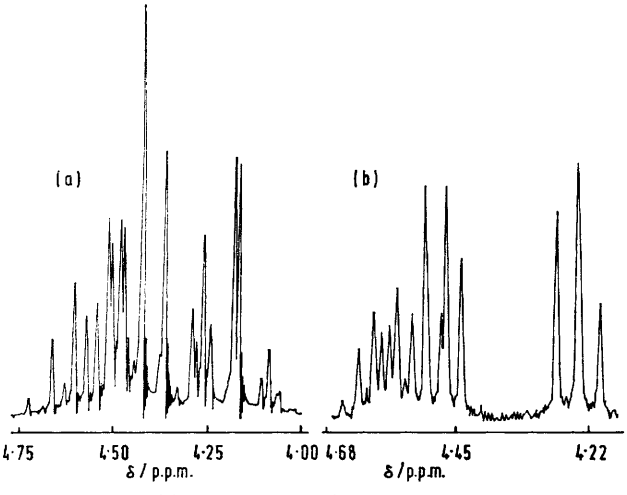


FIGURE 2 (a) 100 MHz and (b) 220 MHz ^{1}H spectra of propylene sulphite, isomer 2 [10% in CCl_4 (w/v)]

As expected, the spectrum of 1,1,2,2-tetramethylethylene sulphite (X) is relatively simple, consisting of two high-field methyl resonances from two non-equivalent methyl groups. The signals are broad and show marked signs of *gem*-dimethyl coupling.

The Assignment of Chemical Shifts.—For some of the spectra discussed above, chemical-shift assignment of geminal ring protons must be undertaken with care. A similar ring geometry being assumed, possible assignments of chemical shifts are given in Figure 4. Because of symmetry or the similarity in the values of vicinal coupling constants, it is not possible by direct analysis of the spectra to assign unambiguously which of the geminal ring protons are *cis* or *trans* to the S=O bond. For example, the geminal ring proton *cis* to the S=O bond in isomer 1 of propylene sulphite can be assigned to chemical shift δ_2 (IIIa) or δ_3 (IIIb), and *vice-versa* for the geminal proton *trans* to the S=O bond. [N.B. The notation (IIIa), (IIIb), *etc.* does NOT indicate other possible structural isomers or conformers.]

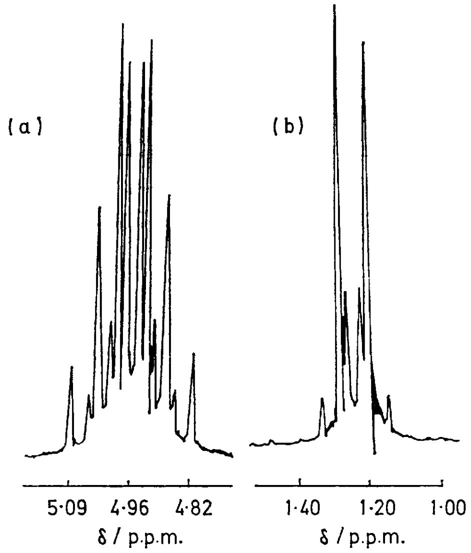


FIGURE 3 (a) AA′ and (b) X_3X_3' part of the 100 MHz ^{1}H spectrum of 1,2-dimethylethylene sulphite, isomer 1 [10% in CCl_4 (w/v)]

The data summarised in Table 1 can be used to calculate chemical-shift differences between ring protons by considerations of shielding or deshielding effects and provide a unique basis for the assignment of structures for the sulphites. Thus for ethylene sulphite, the chemical shift of the protons *cis* (β) and *trans* (α) to the S=O bond will be given by equations (1) and (2) where

$$\nu_\beta = (\Delta\sigma\mathrm{SO})\beta + \sum_{0}\Delta\sigma\beta \qquad (1)$$

$$\nu_\alpha = (\Delta\sigma\mathrm{SO})\alpha + \sum_{1}\Delta\sigma\alpha \qquad (2)$$

$(\Delta\sigma\mathrm{SO})\alpha,\beta$ are specific contributions to the average values of the screening tensors at α and β due to the diamagnetic anisotropy of the S=O bond susceptibility. $\sum_{1}\Delta\sigma\alpha$ and $\sum_{0}\Delta\sigma\beta$ are the summation of the several remaining average screening tensors that affect ν_α and ν_β. It can be shown that by symmetry $\sum_1 \Delta\sigma\alpha = \sum_0 \Delta\sigma\beta$, and therefore equation (3) follows. For the propylene sulphites

$$\nu_\beta - \nu_\alpha = (\Delta\sigma\text{SO})\beta - (\Delta\sigma\text{SO})\alpha \qquad (3)$$

each of the ring protons will experience an additional contribution from the methyl groups, and their chemical shift may be expressed as in equations (4) and (5), where

$$\nu_i = (\Delta\sigma\text{Me-}\textit{trans})i + (\Delta\sigma\text{SO})j + \Sigma\Delta\sigma j + \Sigma\Delta\sigma i \qquad (4)$$

$$\nu_k = (\Delta\sigma\text{Me-}\textit{cis})k + (\Delta\sigma\text{SO})j + \Sigma\Delta\sigma j + \Sigma\Delta\sigma k \qquad (5)$$

$i = a,b,c$ for isomer 1, $k = a',b',c'$ for isomer 2, $j = \alpha$ if i,k is *trans* to the S=O bond and $j = \beta$ if i,k is *cis* to the S=O bond. $\Sigma\Delta\sigma i,k$ are the terms for the effect on the screening tensors other than those due to the diamagnetic anistropy of the S=O bond susceptibility arising from the asymmetry introduced by replacement with a methyl group. By use of equations (1) and (2), (4) and (5) may be expressed in the form (6) and (7), *i.e.*, we obtain

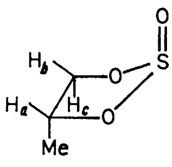
$$\nu_i = (\Delta\sigma\text{Me-}\textit{trans})i + \nu_j + \Sigma\Delta\sigma i \text{ (Isomer 1)} \qquad (6)$$

$$\nu_k = (\Delta\sigma\text{Me-}\textit{cis})k + \nu_j + \Sigma\Delta\sigma k \text{ (Isomer 2)} \qquad (7)$$

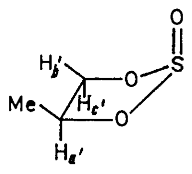
equations (8) and (9).

$$(\Delta\sigma\text{Me-}\textit{trans})i = \nu_i - \nu_j - \Sigma\Delta\sigma i \qquad (8)$$

$$(\Delta\sigma\text{Me-}\textit{cis})k = \nu_k - \nu_j - \Sigma\Delta\sigma k \qquad (9)$$



Isomer 1
(III)



Isomer 2
(IV)

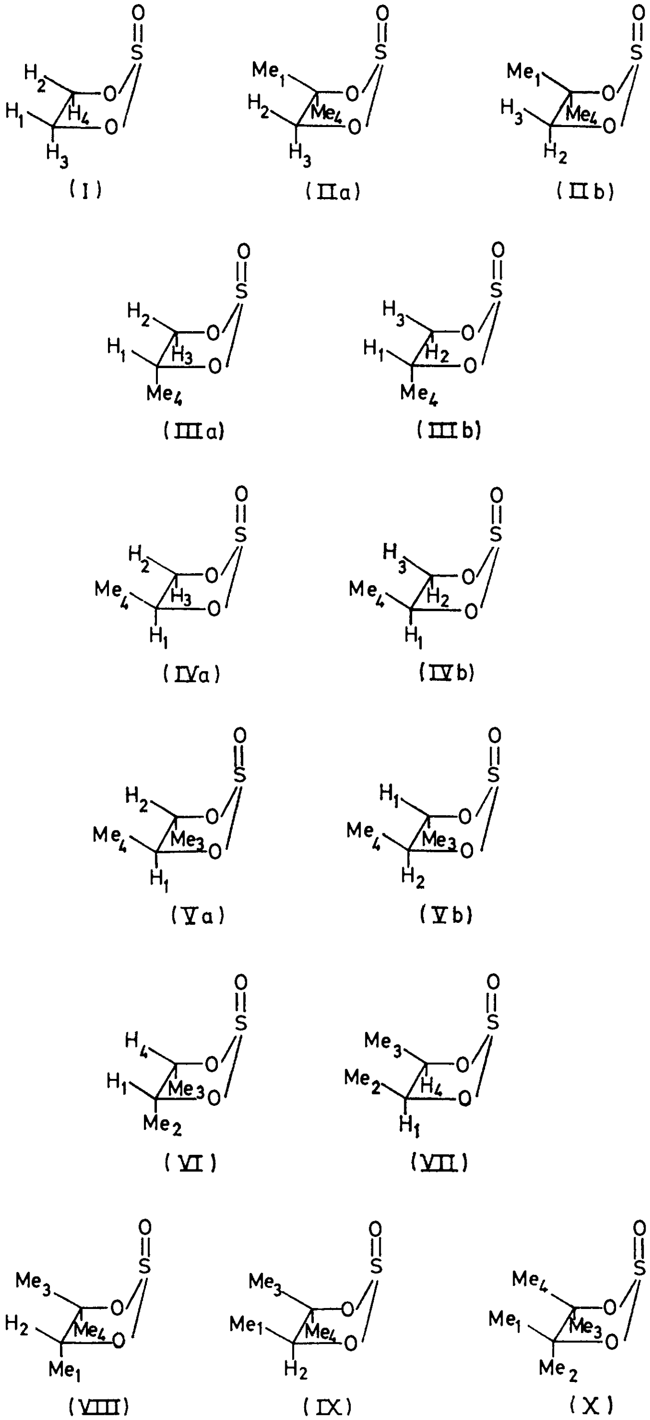
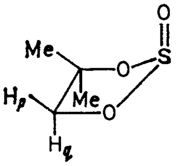


FIGURE 4 Possible chemical-shift assignments of the ring protons for ethylene sulphite and the methyl-substituted ethylene sulphites. The number adjacent to each proton or methyl group refers to the numbering of chemical shifts as in Table 1



(II)

Let us consider the chemical-shift difference of ring protons for 1,1-dimethylethylene sulphite (II). Here we have equation (10a), leading to (10b). $\Sigma\Delta\sigma p$ is defined in

$$\nu_p = (\Delta\sigma\text{Me-}\textit{cis})p + (\Delta\sigma\text{Me-}\textit{trans})p + (\Delta\sigma\text{SO})\beta + \Sigma\Delta\sigma\beta + \Sigma\Delta\sigma p \qquad (10a)$$

$$\nu_p = (\Delta\sigma\text{Me-}\textit{cis})p + (\Delta\sigma\text{Me-}\textit{trans})p + \nu_\beta + \Sigma\Delta\sigma p \qquad (10b)$$

the same terms as $\Sigma\Delta\sigma i,k$. From (8) and (9) we obtain (11a) and (11b), and similarly equation (12). Subtracting (12) from (11), and since $\Sigma\Delta\sigma p \simeq \frac{1}{2}(\Sigma\Delta\sigma b' + \Sigma\Delta\sigma b)$ and $\Sigma\Delta\sigma q \simeq \frac{1}{2}(\Sigma\Delta\sigma c' + \Sigma\Delta\sigma c)$, with $\Sigma\Delta\sigma p \simeq \Sigma\Delta\sigma q$ by symmetry, we obtain equations (13) and (14); the latter

$$\nu_p = (\nu_{b'} - \nu_\beta - \Sigma\Delta\sigma b') + (\nu_b - \nu_\beta - \Sigma\Delta\sigma b) + \nu_\beta + \Sigma\Delta\sigma p \qquad (11a)$$

$$\nu_p = v_{b'} + \nu_b - \nu_\beta - \Sigma\Delta\sigma b' - \Sigma\Delta\sigma b + \Sigma\Delta\sigma p \qquad (11b)$$

$$\nu_q = \nu_{c'} + \nu_c - \nu_\alpha - \Sigma\Delta\sigma c' - \Sigma\Delta\sigma c + \Sigma\Delta\sigma q \qquad (12)$$

$$\nu_p - \nu_q \simeq \nu_{b'} - \nu_{c'} + \nu_b - \nu_c - \nu_\beta + \nu_\alpha \qquad (13)$$

$$\delta_{pq} \simeq \delta_{b'c'} + \delta_{bc} - \delta_{\beta\alpha} \qquad (14)$$

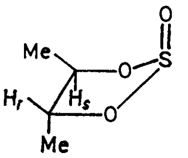
represents the difference in chemical shift between the protons *cis* and *trans* to the S=O bond in 1,1-dimethylethylene sulphite. The results of calculation δ_{pq} for 1,1-dimethylethylene sulphite by use of equation (14) are given in Table 2 for carbon tetrachloride and [$^2H_6$]benzene solutions. Only assignments (IIIa) and (IVa) predict values of δ_{pq} that are consistent with experimental values. Further, the positive sign indicates that the relative effects of $\Delta\sigma\mathrm{Me}_{cis/trans}$ upon the methylene protons are insufficient to reverse the effect of $\Delta\sigma\mathrm{SO}_{cis/trans}$, that is, the proton *cis* to the S=O bond resonates to lower field than the *trans*, so assignment (IIa) holds for 1,1-dimethylethylene sulphite.

TABLE 2

Assignments		Solvent CCl_4	 C_6D_6
		p.p.m.	
(IIIa)	δ_{bc}	*ca.* 0·84	*ca.* 0·91
(IIIb)	δ_{bc}	*ca.* −0·84	*ca.* −0·91
(IVa)	$\delta_{b'c'}$	*ca.* 0·24	*ca.* 0·11
(IVb)	$\delta_{b'c'}$	*ca.* −0·24	*ca.* −0·11
		δ_{pq} (calc)	δ_{pq} (calc)
(IIIa), (IVa)		*ca.* 0·23	*ca.* 0·48
(IIIa), (IVb)		*ca.* 0·71	*ca.* 0·26
(IIIb), (IVa)		*ca.* −1·44	*ca.* −1·35
(IIIb), (IVb)		*ca.* −0·96	*ca.* −1·58
	δ_{pq} (obs)	0·27	0·48

From Table 1: $\delta_{\beta\alpha}(CCl_4)$ = *ca.* 0·36 p.p.m. and $\delta_{\beta\alpha}(C_6D_6)$ = *ca.* 0·54 p.p.m.

Similarly, for (±)-1,2-dimethylethylene sulphite (V) $\nu_r = (\Delta\sigma\mathrm{Me}\text{-}cis)r + (\Delta\sigma\mathrm{Me}\text{-}trans)r + \nu_\beta + \Sigma\Delta\sigma r$, or



(V)

alternatively in the form (15a). Likewise, since $\nu_s =$

$$\begin{aligned}\nu_r &= (\Delta\sigma\mathrm{Me}\text{-}cis)b' + (\Delta\sigma\mathrm{Me}\text{-}trans)a + \nu_\beta + \Sigma\Delta\sigma r\\ &= \nu_{b'} - \nu_\beta - \Sigma\Delta\sigma b' + \nu_a - \nu_\beta - \Sigma\Delta\sigma a + \nu_\beta + \Sigma\Delta\sigma r\\ &= \nu_{b'} + \nu_a - \nu_\beta + \Sigma\Delta\sigma r - \Sigma\Delta\sigma b' - \Sigma\Delta\sigma a \qquad (15a)\end{aligned}$$

$\nu_c + \nu_{a'} - \nu_\alpha + \Sigma\Delta\sigma s - \Sigma\Delta\sigma c - \Sigma\Delta\sigma a'$ and $\Sigma\Delta\sigma r \simeq \Sigma\Delta\sigma b' + \Sigma\Delta\sigma a$ and $\Sigma\Delta\sigma s \simeq \Sigma\Delta\sigma c + \Sigma\Delta\sigma a'$, we obtain equation (15b) and then (15c). The results of calculating

$$\nu_r - \nu_s \simeq \nu_{b'} + \nu_a - \nu_\beta - \nu_c - \nu_{a'} + \nu_\alpha \qquad (15b)$$

$$\delta_{rs} \simeq \delta_{ac} + \delta_{b'a'} - \delta_{\beta\alpha} \qquad (15c)$$

δ_{rs} by use of (15c) are summarised in Table 3 for carbon tetrachloride and [$^2H_6$]benzene solutions.

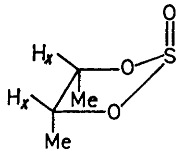
TABLE 3

Assignments		Solvent CCl_4	 C_6D_6
		p.p.m.	
(IIIa)	δ_{ac}	*ca.* 1·23	*ca.* 1·38
(IIIb)	δ_{ac}	*ca.* 0·40	*ca.* 0·47
(IVa)	$\delta_{b'a'}$	*ca.* −0·35	*ca.* −0·09
(IVb)	$\delta_{b'a'}$	*ca.* −0·11	*ca.* −0·21
		δ_{rs} (calc)	δ_{rs} (calc)
(IIIa), (IVa)		*ca.* 0·52	*ca.* 0·75
(IIIa), (IVb)		*ca.* 0·76	*ca.* 0·63
(IIIb), (IVa)		*ca.* −0·32	*ca.* −0·17
(IIIb), (IVb)		*ca.* −0·07	*ca.* −0·28
	δ_{rs} (obs)	0·55	0·74

From Table 1: $\delta_{\beta\alpha}(CCl_4)$ = *ca.* 0·36 p.p.m. and $\delta_{\beta\alpha}(C_6D_6)$ = *ca.* 0·54 p.p.m.

Only assignments (IIIa) and (IVa) predict values for δ_{rs} comparable with experimental values. As before, the positive sign indicates that the relative effects of $\Delta\sigma\mathrm{Me}_{cis/trans}$ on the ring protons enhances the effect of $\Delta\sigma\mathrm{SO}\alpha,\beta$, that is, the proton *cis* to the S=O bond still resonates to lower field than the *trans*, and (Va) is the correct assignment.

For 1,2-dimethylethylene sulphite Isomer 1 (VI) we have equation (16a). For $i = a,b$ we obtain equations



(VI)

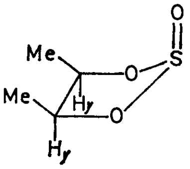
$$\nu_x = \sum_i(\Delta\sigma\mathrm{Me}\text{-}cis) + \nu_\beta + \Sigma\Delta\sigma x \qquad (16a)$$

(16b) and (16c). Similarly for the protons in Isomer 2

$$\nu_x = \nu_a - \nu_\beta - \Sigma\Delta\sigma a + \nu_b - \nu_\beta - \Sigma\Delta\sigma b + \nu_\beta + \Sigma\Delta\sigma x \qquad (16b)$$

$$\nu_x = \nu_a + \nu_b - \nu_\beta + \Sigma\Delta\sigma x - \Sigma\Delta\sigma a - \Sigma\Delta\sigma b \qquad (16c)$$

(VII) we obtain equation (17). The chemical-shift



VII

$$\nu_y = \nu_{a'} + \nu_{c'} - \nu_\alpha + \Sigma\Delta\sigma y - \Sigma\Delta\sigma a' - \Sigma\Delta\sigma c' \qquad (17)$$

difference can be obtained by subtracting equation (17) from (16c), leading to equation (17a), where C is given by

$$\nu_x - \nu_y = \nu_a - \nu_{a'} + \nu_b - \nu_{c'} - \nu_\beta + \nu_\alpha + \Sigma\Delta\sigma x - \Sigma\Delta\sigma y + C \qquad (17a)$$

$$C = -\Sigma\Delta\sigma a + \Sigma\Delta\sigma a' - \Sigma\Delta\sigma b + \Sigma\Delta\sigma c' \qquad (17b)$$

(17b). $\Sigma\Delta\sigma x$ and $\Sigma\Delta\sigma y$ are the changes in the average screening tensors *other* than that for the S=O bond brought about by changes in symmetry produced when two methyl groups are substituted *trans*/*trans* and *cis*/*cis* to the S=O bond. By symmetry $\Sigma\Delta\sigma x \simeq \Sigma\Delta\sigma y$ and hence equation (18) follows.

$$\nu_x - \nu_y \simeq \nu_a - \nu_{a'} + \nu_b - \nu_{c'} - \nu_\beta + \nu_\alpha + C \qquad (18)$$

For the protons geminal to methyl groups in the propylene sulphites we obtain equations (18a)—(18d)

$$\nu_a = (\Delta\sigma\text{Me-}\mathit{trans})a + \nu_\beta + \Sigma\Delta\sigma a \qquad (18a)$$

$$\nu_{a'} = (\Delta\sigma\text{Me-}\mathit{cis})a' + \nu_\alpha + \Sigma\Delta\sigma a' \qquad (18b)$$

$$\nu_a - \nu_\beta = (\Delta\sigma\text{Me-}\mathit{trans})a + \Sigma\Delta\sigma a = +0{\cdot}23 \text{ p.p.m. } (\mathrm{CCl_4}) \qquad (18c)$$

$$\nu_{a'} - \nu_\alpha = (\Delta\sigma\text{Me-}\mathit{cis})a' + \Sigma\Delta\sigma a' = +0{\cdot}12 \text{ p.p.m. } (\mathrm{CCl_4}) \qquad (18d)$$

(see Table 1). If we assume that the inductive effect of the methyl group on the proton geminal to it is the same whether the methyl group is substituted *cis* or *trans* to the S=O bond, then equations (19a) and (19b) follow,

$$\Sigma\Delta\sigma a' - \Sigma\Delta\sigma a \simeq \nu_{a'} - \nu_\alpha - \nu_a + \nu_\beta \qquad (19a)$$

$$\Sigma\Delta\sigma c' - \Sigma\Delta\sigma b \simeq \nu_{c'} - \nu_\alpha + \nu_\beta \qquad (19b)$$

which lead to equation (19c). Substituting (19c) into

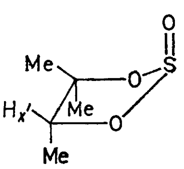
$$C \simeq \nu_{a'} - \nu_a + \nu_{c'} - \nu_b + 2(\nu_\beta - \nu_\alpha) \qquad (19c)$$

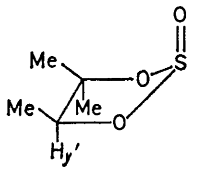
(18) and eliminating we obtain equation (20a) and thus (20b).

$$\nu_x - \nu_y \simeq \nu_\beta - \nu_\alpha \qquad (20a)$$

$$\delta_{xy} \simeq \delta_{\beta\alpha} \qquad (20b)$$

By similar arguments to those above, equation (21) can be derived for the trimethyl derivatives. For carbon tetrachloride solution the observed values are $\delta_{xy} = 0{\cdot}35$ p.p.m.; $\delta_{\beta\alpha} = 0{\cdot}36$ p.p.m. and $\delta_{x'y'} = 0{\cdot}45$ p.p.m.; $\delta_{aa'} = 0{\cdot}47$ p.p.m. By use of equations (20b) and (21) and by comparing the predicted values of δ_{xy} and $\delta_{x'y'}$ for benzene solutions, the observed values are $\delta_{xy} \simeq 0{\cdot}65$ p.p.m.; $\delta_{\beta\alpha} \simeq 0{\cdot}54$ p.p.m. and $\delta_{x'y'} \simeq 0{\cdot}73$ p.p.m.; $\delta_{aa'} \simeq 0{\cdot}61$ p.p.m. This indicates a discrepancy of *ca.* 0·11 p.p.m. for each value. The discrepancy arises from the fact that the relative upfield shift produced for *trans*-protons (Δ) increases with increasing substitution in the ring. If μ_a and μ_β are the upfield shifts in benzene relative to carbon tetrachloride solution, then $\Delta = \mu_\alpha - \mu_\beta$, where α designates the proton *trans* to the S=O bond and β designates the proton *cis* to the S=O bond. Values for the methyl-substituted derivatives are given in Table 4; the largest Δ values occur where a methyl group *cis* to the S=O bond is lying *trans*-vicinal to a ring proton.


Isomer 1
(VIII)


Isomer 2
(IX)

$$\delta_{x'y'} \simeq \delta_{aa'} \qquad (21)$$

For 1,2-dimethylethylene sulphite the proton *trans* to the S=O bond relative to that in ethylene sulphite shifts an additional (0·30 − 0·18) = 0·12 p.p.m. Similarly for the proton geminal to the methyl group for the isopropylene and trimethyl-substituted sulphites, there is an additional shift of (0·28 − 0·14) = 0·14 p.p.m. Thus an additional factor of *ca.* 0·13 p.p.m. has to be taken into account for these sulphites.

The structures of isomers 1 and 2 of 1,2-dimethylethylene sulphites can be deduced from purely stereochemical principles. The substitution of methyl groups into the ethylene sulphite ring is always preferred for the position *trans* to the S=O bond. This is also suggested from the relative amounts of *cis*/*trans*-isomers that are present on preparation and in greater detail by equilibration experiments. This preference probably arises from the stereoelectronic and electrostatic repulsive interactions experienced between the protons of the methyl group and the S=O bond which only occur for a *cis*-position of the methyl group relative to the S=O bond. The observed shift for $\delta_{\beta\alpha}$ is also positive, providing further evidence that protons *cis* to the S=O bond in ethylene sulphite resonate to lower field than the *trans*.

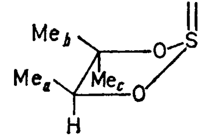
TABLE 4

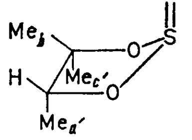
Δ Values for methyl-substituted ethylene sulphites

	Δ/p.p.m.
Ethylene sulphite	0·18
Propylene sulphites (tertiary proton)	0·14
Propylene sulphite (methylene protons, isomer 1)	0·09
Propylene sulphite (methylene protons, isomer 2)	0·35
1,1-Dimethylethylene sulphite	0·23
(±)-1,2-Dimethylethylene sulphite	0·19
1,2-Dimethylethylene sulphite (isomers 1 and 2)	0·30
1,1,2-Trimethylethylene sulphite isomers 1 and 2)	0·28

The additivity of the chemical shifts for the methyl groups can be shown in an exactly analogous manner as for the ring protons by commencing with tetramethylethylene sulphite and considering ' loss ' of methyl groups as ' increasing ' substitution of protons. To avoid repetition we shall only consider the calculation for 1,1-dimethylethylene sulphite.

The chemical shifts in Table 1 for the methyl groups in tetramethyl ethylene sulphite are $\delta_{\beta\alpha}(\mathrm{CCl_4}) = $ *ca.* 0·21 p.p.m. and $\delta_{\beta\alpha}(\mathrm{C_6D_6}) = $ *ca.* 0·33 p.p.m., where β now refers to the methyl groups *cis* to the S=O bond and α to methyl groups *trans* to the S=O bond. In the case of the trimethyl derivatives there are two structures (C) and (D) and, for each of these, two possible assignments exist for the *gem*-methyl resonances, that is (VIIIa) or (VIIIb) for Isomer 1 and (IXa) or (IXb) for Isomer 2. For 1,1-dimethylethylene sulphite, the chemical-shift difference between the *cis* (p) and *trans* (q) methyl groups

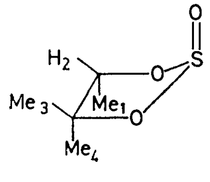

(C)


(D)

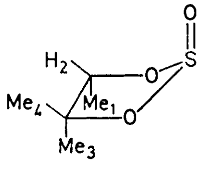
will be (22) as given as in Table 5 by equation (14).

$$\delta_{pq} \simeq \delta_{bc} + \delta_{b'c'} - \delta_{\beta\alpha} \qquad (22)$$

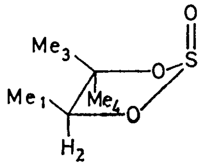
From the calculations given in Table 5, only assignments (VIIIa) together with (IXa) will predict values of the same order, for both solvents, to those observed experimentally.



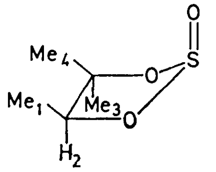
(VIIIa)



(VIIIb)



(IXa)



(IXb)

TABLE 5

Assignments		Solvent	
		CCl_4	C_6D_6
		p.p.m.	
(VIIIa)	$\delta_{b'c'}$	*ca.* 0·35	*ca.* 0·35
(VIIIb)	$\delta_{b'c'}$	*ca.* −0·35	*ca.* −0·35
(IXa)	δ_{bc}	*ca.* 0·14	*ca.* 0·34
(IXb)	δ_{bc}	*ca.* −0·14	*ca.* −0·34
		δ_{pq} (calc)	δ_{pq} (calc)
(VIIIa), (IXa)		*ca.* 0·28	*ca.* 0·36
(VIIIa), (IXb)		*ca.* 0·00	*ca.* −0·33
(VIIIb), (IXb)		*ca.* −0·42	*ca.* −0·35
(VIIIb), (IXb)		*ca.* −0·71	*ca.* +1·03
	δ_{pq} (obs)	0·27	0·34

Also, the positive sign predicted indicates that for isobutylene sulphite the methyl group *cis* to the S=O bond is to be found to lower field than the *trans*.

In an analogous procedure to the above, chemical-shift additivity of methyl groups can be established for the other methyl-substituted ethylene sulphites.

General Characteristics of the ^1H *Spectra Data.—Chemical shifts.* The calculations above show that, first, within an error of *ca.* 0·03 p.p.m., chemical shifts are additive to a remarkably good approximation along the whole series of methyl-substituted ethylene sulphites and, secondly, it confirms all assignments of proton sets. Inherent in the former statement is that if additivity is exhibited, then the relative effects of the S=O bond anisotropy must be reasonably constant; this suggests a similar S=O bond configuration (presumably with the S=O bond axially orientated to the ring) for all members of this series.

For virtually all cases, shifts in benzene relative to carbon tetrachloride solution are greater for substituents *trans* to the S=O bond than those substituted *cis*. It has also been observed that for both mono-substituted derivatives where the substituent is *trans* to the S=O bond (Isomer 1), the relative shifts produced by benzene for the *cis*/*trans* *gem*-methylene protons are invariably much smaller than in the other sulphites.

Coupling constants. Values of coupling constants for the sulphites, averaged over the solvents used, are summarised in Table 6. The *cis*-vicinal coupling constants show a small decrease in value (*ca.* 0·8 Hz) upon substitution of one methyl group into the ring; further substitution of a second methyl group produces a smaller decrease (*ca.* 0·3 Hz). For the propylene sulphites the value of this parameter is the same for both isomers whereas for isomers 1 and 2 of 1,2-dimethylethylene sulphite it is slightly larger when the protons are *trans* to the S=O bond.

Variations in geminal coupling constants (*ca.* 0·4 Hz) are smaller than *cis*-vicinal couplings with practically the same value for ethylene sulphite, isomers 1 and 2 of propylene sulphite, and 1,1-dimethylethylene sulphite.

trans-Vicinal coupling constants show the largest variation between compounds (2·5 Hz) with a maximum value of 9·20 Hz for Isomer 2 of propylene sulphite. Relative to ethylene sulphite the change is small but significant for Isomer 1 of propylene sulphite (+0·3 Hz) with larger increases for Isomer 2 of propylene sulphite and for the (±)-1,2-dimethylethylene sulphite.

Geminal CH_3–H coupling shows a variation of *ca.* 0·5 Hz over the range of compounds. An abrupt increase takes place when the methyl group involved in the coupling is placed *cis*-vicinal to another methyl group and the largest value is where the two methyl groups in question are *cis* relative to the S=O bond.

Methyl–H (J^4) long-range coupling occurs *trans* across the ring which is to be expected from the work of Davis *et al.*[10] on specifically deuteriated 1,2-dibromo-2-phenylpropanes. This parameter is only observed in three sulphites (see Table 6) despite the possibility of its being exhibited in others; the largest value is observed for 1,1-dimethylethylene sulphite.

Geminal methyl coupling occurs in all compounds with geminal methyl groups. Values vary from 0·44 to 0·55 Hz, which are of the same order as the coupling reported for the geminal methyl groups of *cis*-2,2,4,5-tetramethyl-1,3-dioxan.[11]

Infrared Spectra.—Compared with six-membered cyclic sulphites (the trimethylene sulphites [12-14]) few i.r. studies of ethylene sulphites have been reported.[15,16] The known solvent- and concentration-dependence of the

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[10] D. R. Davis, R. P. Lutz, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1961, **83**, 246; D. R. Davis and J. D. Roberts, *ibid.*, 1962, **84**, 2252.

[11] F. A. L. Anet, *J. Amer. Chem. Soc.*, 1962, **84**, 747.

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

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

[14] H. F. Van Woerden and E. Havinga, *Rec. Trav. chim.*, 1966, **86**, 342.

[15] K. L. Dorris, *Appl. Spectroscopy*, 1970, **24**, 492.

[16] J. Szafranek, *Roczniki Chem.*, 1970, **44**, 517.

$\nu_{S=O}$ band[1,17] makes cross-correlation of the available experimental data difficult, as solutions of similar concentrations (where solution concentrations have been stated) have not been studied for many sulphites. The data in Table 7 represent the first systematic study of the $\nu_{S=O}$ band in ethylene and methyl-substituted ethylene sulphites; $\nu_{S=O}$ was measured for each sulphite in a variety of solvents at two different concentrations in each solvent.

TABLE 6

Average coupling constants/Hz

Compound	*cis*-Vicinal	Geminal	*trans*-Vicinal	Geminal CH_3–H	$J^4(CH_3$–H)
Ethylene sulphite	6·87	8·27	6·61		
Propylene sulphite, Isomer 1	6·11	8·24	6·91	6·12	
Propylene sulphite, Isomer 2	6·12	8·60	9·14	6·12	
1,2-Dimethylethylene sulphite, Isomer 1	5·71			6·42	0·19
1,2-Dimethylethylene sulphite, Isomer 2	5·89			6·64	0·16
1,1-Dimethylethylene sulphite		8·50			0·40
(±)-1,2-Dimethylethylene sulphite			8·83	6·11	
Trimethylethylene sulphite, Isomer 1				6·46	
Trimethylethylene sulphite, Isomer 2				6·52	

TABLE 7

$\nu_{S=O}$ Values (cm^{-1}) for ethylene sulphite and methyl-substituted ethylene sulphites

	Ethylene sulphite			Propylene sulphite, Isomer 1			Propylene sulphite, Isomer 2			1,1-Dimethylethylene sulphite			(±)-1,2-Dimethylethylene sulphite		
Solvent	*A*	*B*	Δ	*A*	*B*	Δ	*A*	*B*	Δ	*A*	*B*	Δ	*A*	*B*	Δ
C_6H_{12}	1221	1229	+8	1221	1227	+6	1219	1227	+8	1219	1225	+6	1218	1223	+5
CCl_4	1214	1220	+6	1213	1219	+6	1215	1219	+4	1214	1219	+5	1211	1216	+5
PhMe	1212	1218	+6	1212	1218	+6	1212	1218	+6	1213	1218	+5	1211	1215	+4
CS_2	1214	1219	+5	1212	1219	+7	1212	1217	+5	1213	1218	+5	1210	1214	+4
PhH	1213	1219	+6	1213	1218	+5	1213	1218	+5	1213	1217	+4	1211	1214	+3
Dioxan	1208	1213	+5	1208	1212	+4	1208	1212	+4	1207	1212	+5	1208	1211	+3
MeCN	1204	1210	+6	1206	1210	+4	1203	1208	+5	1203	1208	+5	1202	1206	+4
$PhNO_2$	1203	1209	+6	1204	1208	+4	1204	1208	+4	1204	1209	+5	1203	1207	+4
CH_2Cl_2	1203	1209	+6	1204	1208	+4	1203	1208	+5	1205	1209	+4	1201	1205	+4
Neat (liquid)	1199			1200			1200			1204			1201		
Vapour	1246			1241			1242			1242			1242		

	1,2-Dimethylethylene sulphite, Isomer 1			1,2-Dimethylethylene sulphite, Isomer 2			1,1,2-Trimethyl ethylene sulphite (isomers 1 and 2 mixture)			Tetramethylethylene sulphite		
	A	*B*	Δ	*A*	*B*	Δ	*A*	*B*	Δ	*A*	*B*	Δ
C_6H_{12}	1216	1223	+7	1219	1225	+6	1218	1223	+5	1224	1228	+4
CCl_4	1212	1216	+4	1216	1219	+3	1211	1216	+5	1217	1223	+6
PhMe	1211	1215	+4	1215	1219	+4	1211	1215	+4	1217	1223	+6
CS_2	1211	1214	+3	1213	1218	+5	1209	1215	+6	1216	1221	+5
PhH	1210	1214	+4	1214	1217	+3	1213	1216	+3	1216	1220	+4
Dioxan	1206	1209	+3	1209	1215	+6	1210	1213	+3	1212	1215	+3
MeCN	1202	1206	+4	1202	1208	+6	1202	1206	+4	1206	1211	+5
$PhNO_2$	1203	1207	+4	1203	1210	+7	1200	1208	+8	1208	1212	+4
CH_2Cl_2	1200	1204	+4	1205	1209	+4	1202	1205	+3	1205	1210	+5
Neat (liquid)	1200			1201			1200					
Vapour	1241			1242								
Solid (KBr disc)											1212	

Concentration *A* = 0·330—0·350M. Concentration *B* = 0·052—0·054M. Δ = $\nu_{S=O}(B) - \nu_{S=O}-(A)$ cm^{-1}. Values are quoted to ±1 cm^{-1}.

The range of $\nu_{S=O}$ for the sulphites spans *ca.* 25 cm^{-1} and follows the trend observed for trimethylene sulphite, that is, with increasing polarity of solvent a decrease in wavenumber is displayed. Also, dilution shifts are positive (to higher wavenumber) for all solvents.

The very similar solvent and solute concentration behaviour of $\nu_{S=O}$ for the sulphites suggests that no overt change has occurred about the sulphite moiety with substitution of methyl groups in all the possible positions relative to the S=O bond.

In an i.r. study of ethylene sulphite Dorris[15] observed shoulders on $\nu_{S=O}$ (neat liquid) and band doubling (methanol solution) which he interpreted as evidence for an equilibrium involving axial and equatorial S=O species. However, it is well established[18,19] that similar but more marked doubling or shoulders about $\nu_{S=O}$ is exhibited in the i.r. spectra of the higher members of acyclic dialkyl sulphites (neat liquids and solids) which is attributable to rotational isomerism. Szafranek[16] also observed $\nu_{S=O}$ band splittings for dimethyl sulphite in methanolic solutions.

It therefore seems unlikely that the assignment of shoulders and splitting of $\nu_{S=O}$ in ethylene sulphite to

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[17] G. Wood and M. Miskow, *Tetrahedron Letters*, 1966, **4433**; H. F. Van Woerden and E. Havinga, *Rec. Trav. chim.*, 1967, **86**, 341.

[18] J. Szafranek, *Roczniki Chem.*, 1967, **41**, 405.

[19] S. Detoni and D. Hadzi, *Spectrochim. Acta*, 1957, **11**, 601.

conformational equilibria is valid, particularly as they are only resolved in solvents which are capable of providing a high degree of hydrogen bonding and, under such conditions, energy barriers of rotational isomers will be heightened. For an equilibrium involving equatorially orientated S=O bond conformers then, in order for the i.r. data to be compatible with this supposition, the equilibrium position must lie far enough in one direction so that equatorial S=O bond species make an insignificant contribution to relative i.r. parameters or, somewhat unlikely, to be completely parallel in all ten systems.

The $\nu_{S=O}$ values for the ethylene sulphites are higher than those observed for most trimethylene sulphites. A similar trend has been found for the 1,3-dioxolan-2-ones (five-membered cyclic carbonates) which show a higher C=O stretching frequency in their i.r. spectra compared with the six-membered cyclic carbonates.[20,21] Bellamy[22] has described the increase in stretching frequency of X=O in five-membered rings compared with six-membered rings (for a variety of elements X including C and S) in terms of both the size of the ring and the size of X.

Conclusion.—The establishment of a chemical-shift additivity relationship between the sulphites together with the similar solvent- and concentration-dependence of the $\nu_{S=O}$ band for the sulphites strongly suggests that the ethylene sulphites studied possess a similar and stable conformation in solution.

EXPERIMENTAL

The ^1H n.m.r. spectra were run on a Varian HA100 instrument. Peak positions were calibrated by direct frequency count. At least two spectra were run (forward and reverse sweep) and the reproducibility of the line positions was better than 0·1 Hz.

The i.r. spectra were recorded in solution cells (with KBr windows) of width 0·05 mm on a Perkin-Elmer 521 spectrophotometer with a linearly expanded calibrated scale. Frequency absorptions could be quoted to at least ± 1 cm^{-1} except where peak broadening occurred. Solutions of the two concentrations were made up by direct weighing of the sulphites and all solvents were purified by standard techniques.

Preparation of Sulphites.—Of the various methods of preparation of cyclic sulphites,[23] best yields were obtained by essentially the procedure given below. All reactions were carried out in a system kept under a flow of dry nitrogen and precautions were taken to exclude atmospheric moisture.

To the diol (1 equiv.) dissolved in anhydrous diethyl ether (10—15% w/w of solute to solvent) was added anhydrous pyridine (2 equiv.) in one portion. The solution was cooled to 0—5 °C and then purified thionyl chloride (1·05 equiv.) (5% in excess), dissolved in solvent, was added dropwise with constant stirring. After addition was complete the system was left for a period, with further stirring, and allowed to attain room temperature. The precipitated pyridine hydrochloride was filtered off, washed with solvent, and the washings added to the bulk of the filtrate. The filtrate was washed with 5% sodium hydrogen carbonate solution to remove excess of thionyl chloride, followed by saturated sodium chloride solution, and then allowed to dry ($MgSO_4$) for 24 h. Finally the solvent was removed by distillation at reduced pressure over a water-bath to give the crude sulphite.

Individual yields and the purification of the sulphite concerned are discussed with the particular sulphite. Overall yields and purity of the crude products are greatly affected if the reactants are not pure. Purification of commercial thionyl chloride[24] and pyridine[25] is essential. The former always contains quantities of other sulphur derivatives (formed either during the manufacture and/or by subsequent decomposition of the chloride) which cannot be removed by simple distillation and the latter invariably contains water.

Purification and Separation Methods.—The crude sulphite was purified by distillation under reduced pressure. Where the sulphite exists in two or more isomeric forms, separation in all cases was achieved by preparative g.l.c. with a Pye Model 105 Gas Chromatograph. The instrument was operated under normal conditions with glass columns at below 220 °C, with nitrogen as carrier gas and a hydrogen flame ionisation detector. The column support used was Chromosorb P, mesh size 60—85BS (Pye). Before addition of the stationary phase the support was subjected to silizane treatment[26] as described.[27]

The stationary phase was put on the support in stages of 5% until the desired percentage of stationary phase to column support was reached. This was performed by dissolving the stationary phase in a suitable solvent, adding the support, and slowly removing the solvent by heating over a water-bath under reduced pressure. This was then dried in an oven at 110 °C for several hours. When the desired percentage composition was reached, the last drying period was extended for an additional 10—12 h. The glass column of required length was filled with the packing and preheated at 110 °C in the Gas Chromatograph with a moderately fast gas flow rate through the column, for *ca.* 6 h, after which time the temperature was gradually increased and the column was baked at just above the limit allowed for the stationary phase for 48 h. On allowing the column to cool and 'tapping,' to insure a homogeneous distribution of the packing along the whole length of the column, the column was ready for use.

Preparations.—Ethylene sulphite. By the procedure described above, with 0·30 mol of diol, a 75% yield of the crude sulphite was obtained. Fractional distillation gave a sample (0·15 mol, 50% yield) of pure sulphite, b.p. 59 °C/10 mmHg, $n_D^{25} = 1{\cdot}4454$ (lit.,[5] 63 °C/13 mmHg, $n_D^{25} = 1{\cdot}4446$).

Propylene sulphites, isomers 1 *and* 2. Following the standard procedure, with commercial propane-1,2-diol (0·61 mol) (Kodak), an 80% yield of the crude sulphite was obtained with an isomeric composition of isomer 1 to

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isomer 2 of *ca.* 2·20. This was purified by distillation under vacuum to give 0·37 mol of pure sulphite (60% yield), b.p. 63 °C/15 mmHg, $n_D^{25} = 1·4374$ (lit.,[5] 58 °C/12 mmHg, $n_D^{25} = 1·4353$).

The isomers were separated by preparative g.l.c. For a 7 ft column of 22% Montan Wax on Chromosorb P at 160·4 °C, gas flow 101 ml min^{-1}, retention times of 16·9 min for isomer 2 and 19·2 min for isomer 1 were obtained. Resolution, though optimised, was not complete so the mixture was topped and tailed; this gave an isomeric purity of 98% for isomer 1 and 94% for isomer 2. A second session resolved each isomer in at least 99·5% isomeric purity and gave isomer 1, $n_D^{25} = 1·43650$, with isomer 2, $n_D^{25} = 1·43634$. The mass spectrum gave a molecular ion of 122 for both isomers.

1,1-*Dimethylethylene sulphite*. 2-Methylpropane-1,2-diol was prepared as follows (in a system kept under a flow of dry nitrogen): To a suspension of lithium aluminium hydride (10·0 g) in anhydrous diethyl ether (400 ml) at 0 °C was added dropwise, during 2 h, α-methylethyl lactate (27·8 g) in anhydrous diethyl ether (250 ml). After addition was complete, the system was allowed to attain room temperature and left with stirring for several hours. The mixture was recooled to −5 °C, the alumino-complex was decomposed with 10% NaOH (16 ml) and distilled water (20 ml), and the system left at room temperature for *ca.* 7 h with continuous stirring, by which time the sodium aluminate had become granular. This was filtered off and washed with ether, and the washings were combined with the filtrate. The latter was washed with 5% sodium hydrogen sulphite solution, to remove any excess of sodium hydroxide. The washed ether solution was then allowed to dry ($MgSO_4$) for 24 h. Removal of the solvent by distillation at reduced pressure over a water-bath gave 10·8 g (57%) of crude diol. ^{1}H N.m.r. spectra indicated that the crude diol was at least 95% pure so the sulphite was prepared directly from this sample. From 0·12 mol of diol, 0·082 mol (69%) of crude sulphite was obtained by the standard procedure. Distillation of 0·05 mol gave 0·024 mol of pure sulphite, b.p. 72 °C/15 mmHg, $n_D^{25} = 1·4301$ (lit.,[5] b.p. 58 °C/10 mmHg, $n_D^{25} = 1·4292$).

1,2-*Dimethylethylene sulphite, isomers* 1 *and* 2 *and the* (±)-*isomer*. Following the standard procedure with a commercial sample (Kodak Limited) of butane-2,3-diol (a mixture of *meso* and (±) (1·11 mol), crude sulphite (0·772 mol; 70%) was obtained. Distillation yielded the pure sulphite, with different isomeric proportions in different fractions: fraction I, b.p. 86—88 °C/12 mmHg, $n_D^{25} = 1·4330$; fraction II, b.p. 88—90 °C/12 mmHg, $n_D^{25} = 1·4338$. Fraction I was found to contain a greater proportion of the (±)-isomer than the sum of isomers 1 and 2, but the proportions were reversed for fraction II. ^{1}H N.m.r. spectra indicated that isomer 2 was in least proportion in any fraction.

Fractions I and II were combined and separation was achieved by g.l.c. in two stages. (1) The (±)-isomer was separated from the mixture of isomers 1 and 2. By use of a 5 ft column of 30% Apiezon L on Chromosorb P at 156 °C, gas flow 82 ml min^{-1}, isomers 1 and 2 were eluted together with the following retention times: (±)-isomer, 8·76 min; isomers 1 and 2, 14·20 min. The column was very efficient and injection samples of 120 μl could easily be loaded with no decrease of column efficiency. In this way 12 g each of the (±)-isomer and the mixture of isomers 1 and 2 were obtained. (2) The sample of isomers 1 and 2 free from the (±)-isomer obtained above was resolved on a 15 ft column of 27% Montan Wax on Chromosorb P. Retention times of 30·65 min for isomer 2 and 33·26 min for isomer 1 were obtained at 160·5 °C, gas flow 98 ml min^{-1}. Peak resolution was not complete but topping and tailing gave an isomeric purity of 96% for isomer 1 and 80% for isomer 2. A second session yielded an isomeric purity of at least 99·5% for isomer 1 and 96% for isomer 2: isomer 1, $n_D^{25} = 1·4320$; isomer 2, $n_D^{25} = 1·4407$; (±)-isomer, $n_D^{25} = 1·4302$ [Found (isomeric mixture): C, 35·5; H, 5·7; S, 23·3. Calc. for $C_4H_8O_3S$: C, 35·3; H, 5·9; S, 23·5%].

1,1,2-*Trimethylethylene sulphite, isomers* 1 *and* 2. 3-Methylbutane-1,2-diol was prepared by the action of a methyl Grignard derivative upon ethyl lactate as follows. The Grignard reagent was prepared by standard methods from magnesium turnings (21·07 g) and methyl iodide (123 g) in anhydrous diethyl ether. To this reagent was added dropwise of ethyl lactate (28·4 g) in ether. After addition the reaction mixture was refluxed for 2 h whereupon the Grignard complex was decomposed by careful addition of acetic acid. The mixture was extracted with ether and the ether solution washed with 5% sodium hydrogen carbonate solution to remove excess of acid, followed by saturated sodium chloride solution, and dried ($MgSO_4$) for 24 h. Removal of the solvent by distillation over a water-bath gave 4·4 g of crude product (18%). ^{1}H N.m.r. spectra indicated this to be *ca.* 90% pure and the cyclic sulphite was prepared from this sample.

Following the standard procedure, the diol (0·042 mol) gave a yield of 87% of crude sulphite. Distillation gave a fraction of 0·03 mol at 120—124 °C/20 mmHg, which g.l.c. showed to be 96% pure. The impurity was removed by preparative g.l.c. on a 5 ft column of 20% Apiezon L on Chromosorb P at 170 °C, gas flow 120 ml min^{-1}, to give 0·021 mol (51%) of pure sulphite. ^{1}H N.m.r. spectra showed this sample to consist of a mixture of isomers 1 and 2 in the proportion 5 : 3 respectively, with $n_D^{25} = 1·4341$.

Attempts to separate the isomers on a wide variety of stationary phases and supports failed. The best results were obtained from a 15 ft column of 27% Montan Wax on Chromosorb P at 155 °C, gas flow 50—60 ml min^{-1}, which was sufficient just to resolve peak tops, but only for injection samples of less than 3 μl (Found: C, 39·8; H, 6·6; S, 21·2. Calc. for $C_5H_{10}O_3S$: C, 40·0; H, 6·7; S, 21·4%).

Tetramethylethylene sulphite. This compound was donated by Nicolas Research Institute Limited, Slough, Bucks.[28]

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