Chemistry of the S=O Bond. Part III.[1] Nuclear Magnetic Resonance and Infrared Studies on Phenylethylene Sulphites

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The 100 MHz ^1H n.m.r. spectra of phenylethylene sulphites have been examined for solutions in several solvents. Interpretation of the ^1H n.m.r. spectra together with an i.r. study of the S=O stretching frequency in a number of solvents suggests the existence of a basically similar conformation in solution for each of these sulphites, as suggested for the methylethylene sulphites.

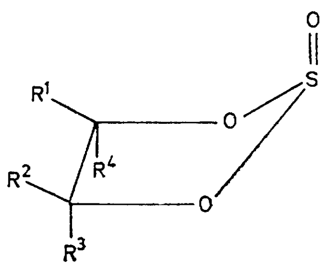
THERE is very little recorded data of ^1H n.m.r. and i.r. spectra of phenylethylene sulphites. In 1965, Thompson *et al.*[2] tentatively assigned the ^1H n.m.r. and $\nu_{S=O}$ band of the two isomers of the sulphite of *meso*-dihydrobenzoin using the conclusions of previous workers on similar studies of ethylene[3] and trimethylene sulphites.[4,5] Thus, comparing both isomers, the methylene protons at lowest field in the major isomer were assigned *cis* to the exocyclic S=O bond. Also, experimental values for $\nu_{S=O}$ of 1220 for the major, and of 1230 cm^{-1} for the minor sulphite were assigned to conformers containing an axial and equatorial S=O bond respectively. No details of concentrations, solvents, *etc.* for the i.r. spectra were given so these assignments must be considered tentative.

The object of this study was to complement the investigation of the complete series of methylethylene sulphites[1] by a similar study of the ^1H n.m.r. and i.r. spectra of the complete series of phenyl-substituted ethylene sulphites.

I.r. Spectra.—The results are summarised in Table 1. The greater size and electronegativity of the phenyl groups relative to methyl give, as expected, higher values of $\nu_{S=O}$.[6] Nevertheless, it is apparent from Table 1 that the solvent and dilution behaviour of $\nu_{S=O}$ for phenylethylene sulphites is similar to that of the methylethylene sulphites.[1] Tetraphenylethylene sulphite has the highest $\nu_{S=O}$ values yet recorded for an ethylene sulphite derivative. The interaction about the C(4)–C(5) bond and the sulphite group may reach a sufficient proportion with the full substitution of phenyl groups into the ring for the tetraphenyl derivative to have a distorted ring geometry.

Shoulders about $\nu_{S=O}$ (solid) are observed for all compounds, particularly for the tetraphenyl derivative; these are not observed in solution.

N.m.r. Spectra.—Analysis of the 100 MHz ^1H n.m.r. spectra of the phenylethylene sulphites are summarised in Table 2. A similar ring geometry to methylethylene sulphites being assumed (as suggested by the above i.r. results), the assignment of chemical shifts follows.



(I) $R^1 = R^2 = R^3 = R^4 = H$
(II) $R^1 = R^2 = R^3 = H;\ R^4 = Ph$
(III) $R^1 = Ph,\ R^2 = R^3 = R^4 = H$
(IV) $R^2 = R^3 = H,\ R^1 = R^4 = Ph$
(V) $R^2 = R^4 = H,\ R^1 = R^3 = Ph$
(VI) $R^1 = R^2 = H,\ R^3 = R^4 = Ph$
(VII) $R^1 = R^2 = Ph,\ R^3 = R^4 = H$
(VIII) $R^1 = R^2(R^4) = R^3 = Ph,\ R^4(R^2) = H$
(IX) $R^1 = R^2 = R^3 = R^4 = Ph$
(X) $R^1 = R^4 = Ph,\ R^2 = H,\ R^3 = Me$
(XI) $R^1 = R^4 = Ph,\ R^2 = Me,\ R^3 = H$

Chemical shifts. It has been shown that the equations derived for the methylethylene sulphites[1] can also be

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used as a basis for assignments of ring protons in phenylethylene sulphites.[8] These calculations also confirm some unusual assignments of geminal *cis*- and *trans*-protons. For example, by considering the difference in chemical shifts of the ring protons in the two isomers of 2-methyl-1,1-diphenylethylene sulphite calculations indicate that the proton *cis* to the S=O bond in 1,1-diphenylethylene sulphite resonates to higher field than the *trans*-proton. Further, as with isomer 2 of 1-methylethylene sulphite the *gem*-methylene protons of isomer 2 of 1-phenylethylene sulphite are similarly assigned for carbon tetrachloride solutions although the order reverts to normal for benzene solutions. This unusual shielding is also found in other systems. Studies on diphenylcyclopentanes[9] have shown that a cyclopentane hydrogen atom which lies *cis* to an adjacent phenyl group is shielded relative to one which is *trans*. For example the α-proton signal in *trans*-1,2-diphenylcyclopentane is at higher field than the α-proton signal in the *cis*-isomer.

TABLE 1

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

	Ethylene sulphite			1-Phenylethylene sulphite, isomer 1			1-Phenylethylene sulphite, isomer 2			1,1-Diphenyl-ethylene sulphite			(±)-1,2-Diphenyl-ethylene sulphite		
Solvent	A	B	Δ	A	B	Δ	A	B	Δ	A	B	Δ	A	B	Δ
C_6H_{12}	1221	1229	+8	1225	1228	+3	1220	1224	+4	1221	1226	+5	—	—	—
CCl_4	1214	1220	+6	1217	1223	+6	1214	1220	+6	1215	1221	+6	1214	1218	+4
PhMe	1212	1218	+6	1215	1220	+5	1211	1216	+5	1214	1217	+3	1214	1218	+4
CS_2	1214	1219	+5	1217	1222	+5	1213	1218	+5	1215	1218	+3	1213	1215	+2
PhH	1213	1219	+6	1216	1221	+5	1211	1216	+5	1214	1219	+5	1213	1217	+4
Dioxan	1208	1213	+5	1211	1216	+5	1209	1214	+5	1214	1216	+2	1211	1214	+3
MeCN	1204	1210	+6	1210	1212	+2	1204	1209	+5	1211	1215	+4	1208	1212	+4
$PhNO_2$	1203	1209	+6	1208	1213	+5	1208	1213	+5	1208	1212	+4	1207	1209	+2
CH_2Cl_2	1203	1209	+6	1207	1213	+6	1207	1212	+5	1207	1213	+6	1207	1210	+3
Neat (liquid)		1199		Solid											
(vapour)		1246	(KBr) disc)		1190			1202			1209			1190	

	1,2-Diphenyl ethylene sulphite, isomer 1			1,2-Diphenyl-ethylene sulphite, isomer 2			1,1,2-Triphenyl-ethylene sulphite (isomeric mixture)			1,1,2,2-Tetra-phenyl-ethylene sulphite			2-Methyl-1,1-diphenyl-ethylene sulphite (isomeric mixture)		
Solvent	A	B	Δ	A	B	Δ	A′	B′	Δ	A′	B′	Δ	A	B	Δ
C_6H_{12}	—	—	—	—	—	—	—	—	—	—	—	—	—	1227	—
CCl_4	1221	1221	0	—	1220	—	1222	1222	0	1233	1234	+1	1217	1222	+5
PhMe	1214	1220	+6	—	—	—	1219	1221	+2	1232	1233	+1	1218	1221	+3
CS_2	1220	1221	+1	—	1221	—	1220	1220	0	1231	1232	+1	1216	1220	+4
PhH	1217	1220	+3	—	1220	—	1220	1221	+1	1232	1232	0	1216	1219	+3
Dioxan	1214	1218	+4	—	—	—	1221	1220	−1	1230	1230	0	1214	1216	+2
MeCN	1211	1214	+3	—	1212	—	1214	1215	+1	1225	1228	+3	1211	1211	0
$PhNO_2$	1210	1213	+3	—	—	—	1212	1214	+2	1225	1229	+4	1208	1209	+1
CH_2Cl_2	1208	1214	+6	—	1213	—	1213	1215	+2	1225	1228	+3	1210	1210	0
Solid (KBr disc)		1207						1210		1223m and 1232s				1206	

Concentration A = 0·330 — 0·350M. Concentration B = 0·052 — 0·054M. Concentration A′ = 0·160 — 0·180M. Concentration B′ = 0·029 — 0·031M. — Indicates insufficient solubility. Values are quoted to ± 1 cm^{-1}.

By analogy, the signal of the proton *cis* to the S=O bond in (±)-1,2-diphenylethylene sulphite ought to lie to higher field than the proton resonance for isomer 2 of this sulphite, and this was found to be the case.

Clearly, the average orientation of the phenyl group with respect to the ring protons in these sulphites has a pronounced effect on the chemical shifts, in view of the nature of shielding in aromatic rings. Whatever the degree of restricted rotation that may occur about the bond joining the phenyl group to the ring, this ought to be the same for all those compounds where there is one phenyl group per carbon atom. Geminal phenyl groups, as in 1,1-diphenylethylene sulphite, do not appear to have completely free rotation because of a mutual repulsive interaction of the *ortho*-protons with consequent restricted rotation which is initiated or changed relative to monophenyl derivatives.

Coupling constants. Values (averaged over the four solvents used) are summarised in Table 3, together with the average values (in parentheses) of the corresponding methyl derivatives. The three types of couplings for the phenylethylene sulphites are somewhat higher than those of the methylethylene sulphites with J_{vic} (*trans*) showing the greatest change. One of the reasons for this must be the increased electronegativity of the phenyl group although increased steric interaction between substituents and the atoms of the ring may be another factor. The magnitude of coupling constants has also been described in terms of an equilibrium of pseudorotational conformers resulting from restricted rotation about the ring carbon–carbon bond.[8] This will be discussed in detail in a later paper.

TABLE 2

Chemical shifts [δ (p.p.m.)] and coupling constants (J/Hz) of some ethylene sulphites *

Compound	Solvent †	R^1	R^2	R^3	R^4	12	13	14	23	24	34
Ethylene sulphite [7] (I)	1	4·810	≡R^1	4·447	≡R^3	7·00	6·58	≡23	−8·15	≡13	≡12
	3	4·082		3·538		6·74	6·56		−8·23		
	4	4·846		4·497		6·88	6·70		−8·42		
Phenylethylene sulphite, isomer 1 (II)	1	5·834	4·861	4·074	7·29	6·56	7·12		−8·30		
	2	5·597	4·563	3·806	7·18‡	6·46	7·18		−8·31		
	3	5·429	4·266	3·527	7·07‡	6·40	7·08		−8·49		
	4	5·900	4·913	4·169	7·35	6·44	7·30		−8·53		
Phenylethylene sulphite, isomer 2 (III)	1	7·34	4·355	4·636	5·296				−8·98	10·45	6·62
	2	7·22‡	4·240	4·377	5·085				−9·03	10·43	6·56
	3	7·10‡	4·051	3·838	4·695				−9·01	10·03	6·86
	4	7·43	4·438	4·717	5·391				−9·13	10·45	6·58
1,1-Diphenylethylene sulphite (IV)	1	7·32	4·875	5·109	7·28				−9·35		
	2	7·20‡	4·733	4·835	7·20‡				−9·46		
	3	7·13‡	4·617	4·702	7·13‡				−9·48		
	4	7·37	4·955	5·137	7·35				−9·38		
(±)-1,2-Diphenylethylene sulphite (V)	1	7·33‡	5·275	≃R^1	5·059					9·79	
	2	7·20‡	5·561		4·955					9·77	
	3	7·08‡	5·648		4·920					9·83	
	4	7·35‡	5·683		5·185					9·78	
1,2-Diphenylethylene sulphite, isomer 1 (VI)	1	6·097	≡R^1	6·98	≡R^3						
	2	5·902		6·82							
	3	5·757		6·76							
	4	6·142		7·04							
1,2-Diphenylethylene sulphite, isomer 2 (VII)	1	7·06‡	≡R^1	5·739	≡R^4						
	2	6·90‡		5·473							
	3	6·95‡		5·153							
	4	7·13‡		5·827							
1,1,2-Triphenylethylene sulphite (isomers 1 and 2) (VIII)	1										
	2	← 6·70 (All protons) 7·80 →									
	3										
	4										
1,1,2,2-Tetraphenylethylene sulphite (IX)	1										
	2	← 6·80 (All protons) 7·70 →									
	3										
	4										
2-Methyl-1,1-diphenylethylene sulphite, isomer 1 (X)	1	7·30‡	5·586	1·238	≃R^1				6·37		
	2	7·25‡	5·568	1·079					6·39		
	3	7·20‡	5·564	0·911					6·35		
	4	7·33‡	5·735	1·263					6·40		
2-Methyl-1,1-diphenylethylene sulphite, isomer 2 (XI)	1	7·31‡	1·275	5·444					6·71		
	2	7·27‡	1·216	5·311					6·75		
	3	7·20‡	1·189	5·133					6·75		
	4	7·33‡	1·333	5·570					6·82		

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

TABLE 3

Average coupling constants (J/Hz)

Compound	Geminal	*cis*-Vicinal	*trans*-Vicinal
Ethylene sulphite	8·27	6·87	6·61
1-Phenylethylene sulphite, isomer 1	8·41 (8·24)	6·47 (6·11)	7·17 (6·91)
1-Phenylethylene sulphite, isomer 2	9·04 (8·60)	6·66 (6·12)	10·36 (9·14)
1,1-Diphenylethylene sulphite	9·42 (8·50)		
(±)-1,2-Diphenylethylene sulphite			9·79 (8·83)

EXPERIMENTAL

The ^1H n.m.r. and i.r. spectra were recorded under conditions identical to those previously described.[1]

Preparation of Sulphites.—All sulphites were prepared by the method and techniques previously described.[1]

1-*Phenylethylene sulphite, isomers* 1 *and* 2. The sulphite was prepared using commercial 2-phenylethane-1,2-diol (Kodak) and resolved on a 1·5 ft column of 25% Carbowax (400M) on Chromosorb P. A gas flow of 153 ml min^{-1} at 178·5 °C gave retention times of 16·6 min for isomer 1 and 13·4 min for isomer 2. After ' topping and tailing,' each isomer was isolated with an isomeric purity of at least 90% and a second resolution achieved an isomeric purity of at least 99·5%. Isomer 2 was a semi-solid at room temperature and exhibited a double m.p.; isomer 1, m.p. 45 °C and isomer 2, m.p. 28—30, 37—38 °C [Found (isomeric mixture): C, 52·4; H, 4·3; S, 25·9. Calc. for $C_8H_8O_3S$: C, 52·2; H, 4·4; S, 26·1%].

1,1-*Diphenylethylene sulphite*. The required diol, 1,1-

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diphenylethane-1,2-diol, was prepared by the reduction of benzilic acid [10] and the pure sulphite was obtained in 57% yield, m.p. 67—68 °C (Found: C, 64·7; H, 4·75; S, 12·4. Calc. for $C_{14}H_{12}O_3S$: C, 64·6; S, 12·3%).

1,2-*Diphenylethylene sulphite, isomers* 1 *and* 2. *meso*-Dihydrobenzoin was prepared according to a previous procedure.[10,11] From the diol a 93% yield of crude sulphite was obtained with an isomer 1 : isomer 2 ratio of *ca.* 9 : 1, as indicated by ^1H n.m.r. spectra. Several recrystallisations from diethyl ether finally gave pure isomer 1, m.p. 129—130 °C (lit., 130—131,[2] 127—129 °C [12]). The combined mother liquors contained a mixture of isomers 1 and 2 (^1H n.m.r. spectra indicated *ca.* 45% isomer 2). Separation of the mixture was effected by t.l.c. on Kiesegel $HF_{254+366}$ (Merck) using benzene–light petroleum (b.p. 40—60°) (3 : 1) as solvent; isomer 2, R_F 0·532 and isomer 1, R_F 0·457. By this method pure isomer 2 was isolated, m.p. 129—130 °C (lit.,[12] 129—130 °C).

(±)-*Diphenylethylene sulphite.* Using (±)-dihydrobenzoin [10] a 65% yield of pure sulphite was obtained, m.p. 85—86 °C (lit.,[12] 85—86 °C).

1,1,2-*Triphenylethylene sulphite, isomeric mixture.* Using pure triphenylethylene glycol [13] a 60% yield of crude sulphite was obtained. Recrystallisation (twice) from diethyl ether–light petroleum (b.p. 60—80°) gave a 20% yield of pure sulphite, m.p. 124—125 °C. The sulphite decomposed on the column at the high temperature required for preparative g.l.c. analysis. T.l.c. could not resolve the mixture nor could ^1H n.m.r. spectra indicate the isomeric composition of the sulphite. Analysis and molecular weight determination yielded the anticipated values [Found (isomeric mixture): C, 71·1; H, 4·75; S, 9·5%; *M*, 335·5 ± 0·5. Calc. for $C_{20}H_{16}O_3S$: C, 71·45; H, 4·75; S, 9·55%; *M*, 336·0].

Tetraphenylethylene sulphite. Preparation from commercial benzpinacol (B.D.H.) gave a 17% yield of pure sulphite, m.p. 137·5—138·5 °C (Found: C, 75·55; H, 4·9; S, 7·7%; *M*, 412·05 ± 0·5. Calc. for $C_{26}H_{20}O_3S$: C, 75·75; H, 4·85; S, 7·75%; *M*, 412·5).

2-*Methyl*-1,1-*diphenylethylene sulphite.* An 83% yield of crude sulphite was obtained from the appropriate diol.[14] Recrystallisation from ether–light petroleum (b.p. 60—80°) gave the sulphite (58%), m.p. 106 °C, whose ratio ^1H n.m.r. spectra indicated to be isomer 1 : isomer 2 5 : 1. Decomposition occurred at the temperatures required to separate the isomers using preparative g.l.c. and t.l.c. also proved to be ineffective in resolving the two isomers (Found: C, 65·55; H, 5·0; S, 11·75. Calc. for $C_{15}H_{14}O_3S$: C, 65·7; H, 5·1; S, 11·7%).

C. H. G. thanks the S.R.C. for a research studentship.

[3/1179 *Received, 7th June*, 1973]

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