1012. *The Isomeric Pentane-2,4-diol Cyclic Sulphites.*

By P. C. LAUTERBUR, J. G. PRITCHARD, and R. L. VOLLMER.

It is shown that there exist two isomeric *meso*-pentane-2,4-diol cyclic sulphites, as a consequence of the pyramidal configuration of the sulphite group. The structures of these and the isomeric, racemic pentane-2,4-diol cyclic sulphite are discussed in the light of their nuclear magnetic resonance and infrared spectra.

SEVERAL examples of isomerism arising from the stable, pyramidal configuration of the sulphite and sulphoxide groupings are known.[1-3] As an additional example, the present paper describes the characteristics of the pentane-2,4-diol cyclic sulphite system, in which the sulphite portion engenders two forms with *meso*-symmetry. If structures having two adjacent, axial methyl groups are discounted as too unstable, the two *meso*-forms to be expected are (I) and (II), in which each configuration might exist as either the chair form or the flexible conformer, or a mixture. Each optical component of the racemic form could exist in three conformations, two of which are shown as (IIIc) and (IIIf) for one of the

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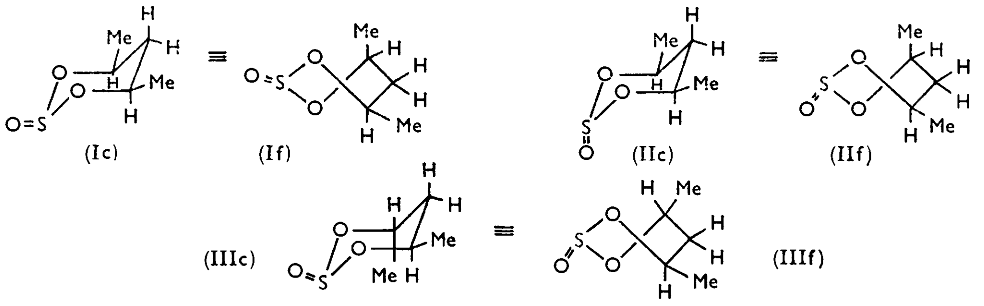
[1] Bell and Bennett, *J.*, 1927, 1798; 1929, 15; Harrison, Kenyon, and Phillips, *J.*, 1958, 2079.
[2] de la Mare, Klyne, Millen, Pritchard, and Watson, *J.*, 1956, 1813.
[3] Pritchard and Lauterbur, *J. Amer. Chem. Soc.*, 1961, **83**, 2105.

components. The third conformation would be the unlikely, chair form alternative to (IIIc) (equivalent to inverting the O=SO$_2$ configuration), in which the axial methyl group would experience severe repulsions both from an axial hydrogen atom and, more crucially, from the S=O oxygen atom.



(Ic) (If) (IIc) (IIf) (IIIc) (IIIf)

Three sulphites have been isolated from the reaction of thionyl chloride with a 2 : 1 mixture of *meso*- and racemic pentane-2,4-diol: two liquids (racemic and *meso*) and a solid at room temperature (*meso*) in 23%, 42%, and 2% yield, respectively. The features of the proton spectra and part of the infrared spectra of these products in different media are listed in the Tables and permit structural assignments to be made.

Nuclear Magnetic Resonance (*n.m.r.*) *Spectra.*—The symmetry of the products can immediately be diagnosed from the number of methyl doublets in their proton spectra. The *meso*-, chair-form structures (Ic) and (IIc) have planes of symmetry, so that the methyl groups in each form should have identical magnetic environments; and, if rapid vibrations of the rings be permitted in the flexible forms (If and IIf), the average magnetic environments for the methyl groups here should also be the same within each form. Thus, if we assume rapid interconversions of chair and flexible forms, the type of methyl resonance to be expected for each *meso*-sulphite would be a sharply defined, single doublet, with spin–spin splitting due to the (identical) neighbouring methenyl protons (at positions 2 and 4) as is observed for two of the products (cf. Table 1). With similar assumptions, the non-symmetrical racemic sulphite should have two distinct methyl resonances, each split into a doublet by distinct neighbouring methenyl protons, as observed for the remaining isomer. This diagnosis is confirmed by the resonance of the methenyl protons

TABLE 1

High-resolution proton magnetic resonance spectra at 60 Mc./sec. for pentane-2,4-diol cyclic sulphite isomers.*

Cyclic sulphite and condition	CH_3 resonance (τ)	CH resonance (τ)	CH_2 resonance (τ)
(A) Liquid sulphite (*meso*)			
Pure liquid	Doublet (8·76)	Sextet (approx.) (5·01)	Four main bands (8·1—8·4)
50% in benzene	Doublet (8·96)	Sextet (approx.) (5·14)	Five main bands (8·4—8·7)
20% in CCl_4	Doublet (8·78)	Sextet (approx.) (5·02)	Five bands (8·1—8·5)
(B) Solid sulphite, m. p. 45° (*meso*)			
20% in benzene	Doublet (9·01)	Complex multiplet (6·1)	At least 7 bands (8·6—9·8)
20% in CCl_4	Doublet (8·65)	Complex multiplet (5·47)	About 5 bands (8·1—8·4)
(C) Liquid sulphite (racemic)			
Pure liquid	Two doublets (8·48, 8·66)	Two sextets(5·01, 5·52)	Five bands (near triplet, 8·00)
50% in benzene	Two doublets (8·60, 8·84)	Two sextets (5·10, 5·76)	Five bands (near triplet, 8·27)
20% in CCl_4	Two doublets (8·47, 8·69)	Two sextets (5·03, 5·63)	Seven main bands (7·9—8·2)

* Chemical shifts (τ) are given in p.p.m. on the scale according to Tiers[4] in which tetramethylsilane is at 10·0 p.p.m. Where distinct multiplets are indicated, they are symmetrical, have the correct area distribution, and have peak separations *ca.* 6 c./sec. Where a number of bands is indicated, only the range of band positions is given.

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[4] Tiers, *J. Phys. Chem.*, 1958, **62**, 1151.

themselves. The racemic sulphite shows two distinct sextets chemically shifted by *ca.* 0·6 p.p.m. Each *meso*-isomer has a single multiplet, the one for isomer (A) in the different media being consistently at least 0·5 p.p.m. to lower field than that for (B).*

Of the three types of proton resonance in these molecules, only that for the methylene protons shows radical change of feature with change of medium. The CH_2 resonance for the racemic isomer as the pure liquid appears to be accidentally very close to a regular triplet with peak-separation *ca.* 6 c./sec.[5] However, the other methylene proton spectra defy even approximate analysis by inspection. This occurs because, for both possible forms of each sulphite, the magnetic environments of these two protons and the magnitude of their spin–spin coupling to the two methenyl protons are formally all different, producing complex, non-symmetrical spectra in general. Thus, the observed effects of the medium could be due either to changes in equilibria between c and f forms, or simply to dielectric effects on the chemical shifts for the one or for both conformers present (or to both causes). It is concluded that the nature of the medium has a comparatively modest effect on chemical shifts for the " liquid " sulphite isomers (A) and (C) but has a generally substantial effect for the " solid " isomer (B), particularly on the chemical shift between its methylene protons.

Infrared Spectra.—The most intense band in the spectrum of each sulphite isomer occurs in the region for S=O stretching vibrations ($\nu_{S=O}$),[6] at *ca.* 1190 cm.$^{-1}$ for two of the isomers and *ca.* 1230 cm.$^{-1}$ for the third (cf. Table 2). The spectra of the sulphites in carbon disulphide as diluent show improved resolution, compared with the pure liquids, only in the region of $\nu_{S=O}$ (as detailed in Table 2); outside this region the features of the spectra for each sulphite are essentially the same for the two media. Thus, the *meso*-sulphite (A) shows little change; the racemic sulphite (C) shows much better resolution but no change in feature; but the *meso*-isomer (B) shows better resolution, loss of two weak bands, and slight strengthening of the band at *ca.* 1190 cm.$^{-1}$, on dilution of the liquid phase in carbon disulphide. Hence, the infrared spectra appear consistent with the CH_2 proton resonance spectra in that only isomer (B) is much affected by changes in medium. The relative intensities of the bands at *ca.* 1190 and 1230 cm.$^{-1}$ for each sulphite offer no evidence that significant changes in equilibria between c and f forms take place with change of medium. Hence, we conclude that the observed changes in the spectra are due mostly to dielectric effects. The weak bands at *ca.* 1190 and 1230 cm.$^{-1}$ may, nevertheless, possibly be due

TABLE 2.

Infrared bands near to the frequency range for the S=O stretching vibration ($\nu_{S=O}$)[6] for pentane-2,4-diol cyclic sulphite isomers.

Cyclic sulphite and condition	$\nu_{max.}$ (cm.$^{-1}$)			
(A) Liquid sulphite (*meso*)				
Pure liquid	1272w	1230w	—	1188s
5% in CS_2	1272w	1231w	—	1188s
(B) Solid sulphite, m. p. 45° (*meso*)				
Crystalline solid	1272w	1230s, br	—	1192vw
Pure liquid (melted)	1272vw	1230s, br	1208 sh	1187vw
5% in CS_2	—	1240s	—	1194w
(C) Liquid sulphite (racemic)				
Pure liquid	1293w	1242 sh	1210 sh	1191s, br
5% in CS_2	1293w	1242w	1217m	1193s

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* There is no good correlation to be made between the similar shifts here for the racemic and the two *meso*-isomers, as the dispositions of the CH and S=O bond-directions do not all correspond in the three structures. The shift observed for the two *meso*-isomers is similar in magnitude to that for comparably placed protons in five-membered-ring sulphites (see ref. 3); but the detailed geometry of these systems is different from that of the present ones, so precluding useful deduction.

[5] Cf. Finegold and Kwart, *J. Org. Chem.*, 1962, **27**, 2361.

[6] Cf. Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen and Co. Ltd., London, 2nd edn., 1958, Ch. 22.

to the $\nu_{S=O}$ of small amounts of the alternative conformer in each case, as opposed to some other CH mode or combination tone. (We do not fully understand the significance of the weak bands at *ca.* 1210 and 1280 cm.$^{-1}$ that appear also to be associated with the motion of the S=O group.)

The strong bands at *ca.* 1190 cm.$^{-1}$ are consistent with previous observations for $\nu_{S=O}$ in 1,3-diol cyclic sulphite systems, and we assume that this frequency is associated with the more stable, chair conformations, as opposed to the flexible (boat) forms.[3] On this basis, the racemic isomer can be assigned as mostly (IIIc), and the *meso*-isomer (A) as mostly either (Ic) or (IIc). Our *meso*-isomer (B) is peculiar in that its $\nu_{S=O}$ is high, 1230—1240 cm.$^{-1}$ (higher even than has been observed for five-membered-ring and open-chain sulphites [2,7]); also, this isomer is formed in markedly lower yield than its *meso*-analogue and is metastable with respect to it at high temperature (see Experimental section). These characteristics are consistent with a flexible conformation in which the stretching motion of the S=O group could be coupled with ring-vibrations of higher frequency than is possible in the chair conformations.[8] As it appears reasonable to assume that repulsive interactions between the S=O group and the methenyl hydrogens would make form (IIc) unstable relative to (Ic), we suggest that our " solid " isomer (B) crystallizes in conformation (IIf), and that it may exist as an equilibrium mixture containing a small amount of form (IIc) in the liquid phase (as indicated above). The " liquid " *meso*-isomer (A) can then be assigned as (Ic).

EXPERIMENTAL

Fractional distillation of the products of reaction of thionyl chloride and a 2 : 1 mixture of *meso*- and racemic pentane-2,4-diols, giving liquid *meso*- and racemic pentane-2,4-diol cyclic sulphites, with b. p. 72°/12 and 82°/12 mm., and n_D^{20} 1·4403 and 1·4472, in 42% and 23% yield, respectively, has been reported.[9] Fractional freezing of the residue from the above distillation yielded 2·2% of a solid *sulphite* which, after recrystallization from ethanol, had m. p. 45° (Found: C, 40·0; H, 6·7; S, 20·9%; *M*, 173. $C_5H_{10}O_3S$ requires C, 40·0; H, 6·7; S, 21·3%; *M*, 150).

The isomeric purity of the sulphites was examined by vapour-phase chromatography on a 10-ft. column of internal diameter 0·4", packed with 8% by wt. of Carbowax (mol. wt. 9000) on 30—60 mesh fire-brick. For a flow of 570 ml./min. of helium gas at an inlet pressure of 40 lb./sq. in. on an F. and M. Scientific Corporation's model 500 instrument, with column temperature 135°, the retention times were 6·1, 4·2, and 18·9 min. for the racemic, " liquid " *meso*-, and " solid " *meso*-product, respectively. The racemic isomer, as prepared above, consistently contained about 2% of an impurity with retention time *ca.* 6·7 min., from which the pure racemic isomer could be separated by collection from the chromatograph in quantities suitable for the determination of spectra. The sulphites were reasonably stable at −10°. The " solid " *meso*-sulphite, when heated at 200° for 15 min., was converted for the most part into the " liquid " *meso*-isomer (no racemic isomer was detected), a process that could occur either through acid-catalyzed breaking and remaking of the ring or by thermal reversal of the $O=SO_2$ configuration.

The proton spectra were run on degassed samples in conventional fashion on a Varian A-60 instrument at the Mellon Institute. The infrared spectra were obtained on a Perkin-Elmer Corporation model 221 spectrophotometer.

MELLON INSTITUTE, PITTSBURGH, PENNSYLVANIA.
CHEMSTRAND RESEARCH CENTER, DURHAM, NORTH CAROLINA.
[Present addresses: (P. C. L.) DEPARTMENT OF CHEMISTRY,
THE STATE UNIVERSITY OF NEW YORK,
STONEY BROOK, N.Y., U.S.A.
(J. G. P.) RESEARCH DIVISION, HOFFMANN-LA ROCHE, INC.,
NUTLEY, N.J., U.S.A.]

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[7] Simon and Kriegsmann, *Z. phys. Chem. (Leipzig)*, 1955, **204**, 269; Chiurdoglu, de Groote, Masschelein, and van Risseghem, *Bull. Soc. chim. belges*, 1961, **70**, 342.

[8] Cole, Jones, and Dobriner, *J. Amer. Chem. Soc.*, 1952, **74**, 5571; Barton, Page, and Shoppee, *J.*, 1956, 331.

[9] Pritchard and Vollmer, *J. Org. Chem.*, 1963, **28**, 1545.