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Proton Magnetic Resonance, Structure and Stereoisomerism in Cyclic Sulfites

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The proton magnetic resonance spectra and structure of ethylene sulfite, ethylene sulfate, isobutylene sulfite and the two stable, geometrically isomeric species of propylene sulfite are discussed. The isomerism in the propylene sulfite system is demonstrated for the first time; the isomers are characterized *via* vapor chromatography, infrared spectrum and refractive index; and a structural assignment is given from an analysis of the proton spectra. The value of 3.74 Debye units for the dipole moment of the ethylene sulfite molecule in benzene solution at 25° is reported.

It is well known that the configuration about the sulfur atom in molecules of the type OSX_2 is pyramidal. Thus, electron diffraction studies have shown thionyl chloride to be pyramidal, with Cl–S–Cl and O–S–Cl angles of *ca.* 114 and 106°, respectively.[1] The sulfite ion may be thought of as being derived from thionyl chloride by replacement of the two chlorine atoms by oxygen anions. Resonance of the charges among the three oxygens then produces a symmetrical distribution. Indeed, the sulfite ion is known to be pyramidal with C_{3v} symmetry both in the crystalline state[2] and as a free ion in aqueous solution.[3] The pyramidal grouping, as opposed to a planar configuration about the sulfur atom, gives rise to isomerism in certain organic molecules. There have been isolated previously two stable, geometrical isomers of 1,4-dithian disulfoxide (and also of related compounds).[4] These isomers are presumably the bi-equatorial and axial-equatorial, chair-form structures I and II,[4] the isomerism depending specifically on non-coplanarity of the oxygen and carbon atoms in each sulfoxide moiety. This type of isomerism has been corroborated through the reported resolution of 4-amino-4′-methyldiphenyl sulfoxide into optical isomers.[5]

From analogy with the above systems, we should expect alkyl sulfites to have a pyramidal structure about the sulfur atom since the R–O radicals should behave as typical monovalent groups; hence suitable sulfites should show isomerism. There have been isolated previously two stable isomers of 2-chloropropane-1,3-diol-*cyclic* sulfite, which are thought to have the structures III and IV, the sulfoxide group being equatorial in both.[6] However, the possibility of additional isomers adds some uncertainty to the exact structural assignments.[6]

Given that the sulfite group in organic molecules is pyramidal, the *cyclic* sulfites derived from suitably substituted 1,2-diols, as for example V and VI, should be *cis* and *trans* isomers. It is the purpose of this paper to demonstrate this type of isomerism,

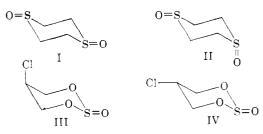(1) K. J. Palmer, *J. Am. Chem. Soc.*, **60**, 2360 (1938).

(2) W. H. Zachariason and H. E. Buckley, *Phys. Rev.*, **37**, 1295 (1931).

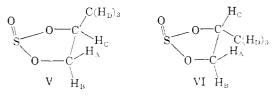(3) A. Simon and K. Waldmann, *Z. physik. Chem. (Leipzig)*, **204**, 235 (1955).

(4) E. V. Bell and G. M. Bennett, *J. Chem. Soc.*, 1798 (1927); 15 (1929).

(5) P. W. B. Harrison, J. Kenyon and H. Phillips, *ibid.*, 2079 (1958).

(6) P. B. D. de la Mare, W. Klyne, D. J. Miller, J. G. Pritchard and D. Watson, *ibid.*, 1813 (1956).

largely through proton magnetic resonance (p.m.r.) spectroscopy, and to consider in some detail the structure of ethylene sulfite and its derivatives by substitution of hydrogen.

Results and Discussion

P.m.r. Spectrum of Ethylene Sulfite.—The spectrum of ethylene sulfite at 40 Mc.p.s. is shown in Fig. 1 and is centered symmetrically at 5.57 p.p.m. on a scale in which internal tetramethylsilane is at 10.0 p.p.m.[7] Its complexity immediately shows that the protons in ethylene sulfite (VII) are not all equivalent magnetically. In contrast, the spectrum given by ethylene sulfate (VIII) consists of a single sharp line at 5.32 p.p.m. (CCl_4–$CHCl_3$ solution) so that in this case the protons are all equivalent magnetically, as is consistent with an average structural symmetry of C_{2v} for this molecule. These results demonstrate that the sulfite group does not execute a thermal vibration which rapidly inverts its configuration. The extended, symmetrical p.m.r. spectrum of ethylene sulfite is consistent with average structural symmetry C_S for this molecule, and is of the complicated form usually exhibited by the A_2B_2 class of proton system having spin–spin coupling constants of the same order of magnitude as the chemical shift for the A and B protons.[8] The possibility that the ethylene sulfite molecule might have more than two sets of non-equivalent protons[9] is pre-

(7) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(8) *Cf.* J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw–Hill Book Co., Inc., New York, N. Y., 1959, Chap. 6.

(9) It has been proposed recently by H. Finegold, *Proc. Chem. Soc. (London)*, 283 (1960), that the proton magnetic resonance spectra of dialkyl sulfites demonstrate a "fundamental skewness" of the sulfite
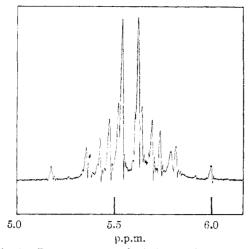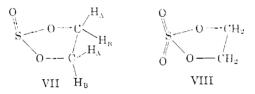
Fig. 1.—P.m.r. spectrum of ethylene sulfite at 40 Mc.p.s. on the scale in which tetramethylsilane as internal standard is at 10.0 p.p.m.[7]

cluded by our observation that the spectrum at 60 Mc.p.s. (not shown) retains the symmetry of the 40 Mc.p.s. spectrum. A complete analysis of these spectra is in progress.

VII   VIII

P.m.r. Spectrum of Isobutylene Sulfite.—The substitution of two methyl groups on one of the carbon atoms in ethylene sulfite, giving isobutylene sulfite (IX), leads to a relatively simple spectrum for the remaining ring protons since spin–spin coupling in the molecule is restricted essentially to the single term J_{AB}. The ring protons give a quadruplet centered at 5.75 p.p.m. and the two methyl groups give singlets at 8.40 and 8.66 p.p.m. (Fig. 2). The chemical shift calculated for the A and B protons $\pm(\nu_A - \nu_B)$ is 0.155 p.p.m., or 6.2 c.p.s. at 40 Mc.p.s., and the coupling constant

group and hence a non-equivalence of the two alkoxy groups. However, the observed spectra of the methylene protons in these *noncyclic* sulfites are more reasonably explained by non-equivalence of the two protons in *each* methylene group, which is an expected consequence of the stable pyramidal configuration of the sulfite group. A particular case of this general phenomenon was discovered some time ago by P. M. Nair and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 4565 (1957). The effect does not require high potential barriers to rotation but is a general consequence of the molecular asymmetry, as was pointed out by J. A. Pople, *Mol. Phys.*, **1**, 3 (1958). The most important contributing factors are probably a difference in the chemical shifts of the two protons in each methylene group and differences in the average populations of the different rotational conformations of these groups.

We have examined the spectrum of the methylene protons of diethyl sulfite, as a 10–15% solution in benzene, under high resolution at 60 Mc.p.s. and find that there are presently eight weak bands in addition to the eight distinct bands demonstrated by H. Finegold (ref. above). The positions and intensities of all sixteen resolved bands are consistent with an analysis for the AB part of an ABC₃ spectrum with $J_{AB} = 10.3$ c.p.s. (details of this study will be reported later, elsewhere).

A reinterpretation similar to that given above may be made for the H¹ and P³¹ spectra of O,O'-diethyl methylphosphonothionate, also reported by H. Finegold, *J. Am. Chem. Soc.*, **82**, 2641 (1960). As in the sulfite case, additional weak lines should be found in the spectrum if our interpretation is correct.
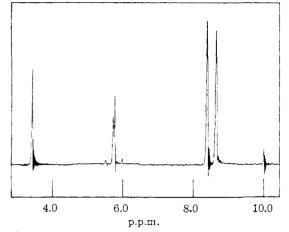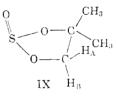
Fig. 2.—P.m.r. spectrum of isobutylene sulfite at 40 Mc.p.s., including the reference bands from benzene as external standard (3.42 p.p.m. at far left) and tetramethylsilane as internal standard (10.0 p.p.m. at far right).[7]

$\pm J_{AB}$ is 8.5 c.p.s. Again, the non-equivalence of H_A and H_B, and of the two methyl groups, demonstrates the non-coplanarity of the oxygen atoms. The pronounced asymmetry in the two parts of the isobutylene sulfite spectrum is accurately reproducible as in Fig. 2 and may be attributed to slightly dissimilar spin–spin coupling of protons A and B with those of the two methyl groups.[9] This may arise from a slight permanent puckering of the five-membered ring, caused by mutual interaction of the terminal oxygen atom and the *cis* methyl group.

IX H_B

The Propylene Sulfites.—We find that a typical, pure propylene sulfite sample may be completely separated into two isomeric components by vapor phase chromatography at 160°. (The slower-moving component will be termed i and the faster ii.) The two forms are produced in the ratio *ca.* 1:2 in our preparations and may be collected in quantity from the chromatograph. They have a refractive index difference $(\Delta n^{25}D)$ of 0.0012 and do not slowly interconvert when isolated in a pure state at room temperature. Only very minor differences in the infrared spectra were observed (see Experimental) as is consistent with the great structural similarity of the isomers as far as thermal vibrations are concerned. The greatest differences $(\Delta\nu$ *ca.* 40 cm.$^{-1})$ occur for two bands in the 440–510 cm.$^{-1}$ region, which are almost certainly due to bending motions of the five-membered rings. Isomer ii has three additional observable bands which presumably have very low intensity in i.

The propylene sulfite isomers are six-spin proton systems of the type ABCD₃ (*cf.* V and VI). The methyl protons (D) *in each isomer* give a well resolved doublet, centered at 8.46 p.p.m. for i and at 8.65 p.p.m. for ii with a separation J_{CD} of 6.0
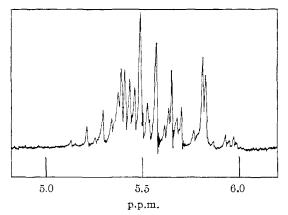
Fig. 3.—P.m.r. spectrum for the ring protons of propylene sulfite isomer i at 60 Mc.p.s. on the scale in which tetra-methylsilane as internal standard is at 10.0 p.p.m.[7]

c.p.s. These doublets are in accord with expectation for the D proton spectrum of a CD_3 grouping in which the chemical shift of the C and D protons is large compared to the coupling between them: $\pm J_{CD}/(\nu_D - \nu_C) \ll 1$.

The p.m.r. spectra given by the ring protons (A, B and C) for the two isomers are not completely resolved at 40 Mc.p.s.; however, well resolved spectra for these may be obtained at 60 Mc.p.s. as displayed in Figs. 3 and 4. These spectra are positioned over the range ca. 5 to 6 p.p.m. and are thus removed from the spectra of the methyl protons by at least ca. 100 c.p.s. for 40 Mc.p.s. (cf. J_{CD}). If the CD_3 group of four protons were isolated from the others, a characteristic quartet of bands separated by J_{CD} and with intensities in the ratio 1:3:3:1 would be expected for the C proton spectrum. No such quartet is observed, and, in general, a very complex spectrum for the C protons would be expected as a result of spin–spin coupling of proton C with protons A and B in addition to D. The spectrum of the ring protons of isomer i is indeed exceedingly complex (Fig. 3) and may not be analyzed by inspection. The ABC proton spectrum of isomer ii, however, is singularly simple, with the lines falling into three distinct groups (Fig. 4). The sextet of broad bands to low field centered at 4.95 p.p.m. may plausibly be identified with proton C, since it is located next to a methyl group; then the two groups of four bands centered at 5.36 and 6.10 p.p.m. must be derived from the two protons A and B (which may not be distinguished). Hence, the chemical shifts between the A and B protons and between the C proton and the lower field member of the A and B pair are 0.74 and 0.41 p.p.m., respectively, or 44 and 25 c.p.s. at 60 Mc.p.s. The observed spectrum of Fig. 4 thus approximates reasonably to a first-order ABC spectrum,[8] and accordingly the values of the above shifts are large compared with the coupling constants between the protons ($\pm J/\Delta\nu < ca. \frac{1}{4}$). By inspection of the line splitting in the two quartets, the following parameters may be obtained: $\pm J_{AB} = ca. 8$ c.p.s., $\pm J_{AC} \approx \pm J_{BC}$, ≈ 6.0 c.p.s. The latter two coupling constants are approximately equal to each other and to $\pm J_{CD}$; hence, the C proton spectrum of isomer ii consists
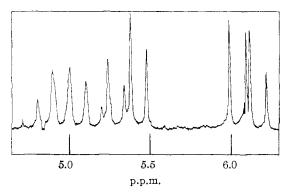

Fig. 4.—P.m.r. spectrum for the ring protons of propylene sulfite isomer ii at 60 Mc.p.s. on the scale in which tetra-methylsilane as internal standard is at 10.0 p.p.m.[7]

of a primary quartet derived from the CD_3 combination, each member of which is split twice over into two lines separated by 6.0 c.p.s., giving the observed sextet with mean separation 6 c.p.s. and intensities approximately in the ratio 1:5:10:10:5:1.

The spectrum for the ring protons of isomer i is clearly not a first-order spectrum and the chemical shifts for these protons must be similar in magnitude to the coupling constants. Accordingly, inspection of Fig. 3 shows at least that the line positions for the three protons lie within the range ca. 5.4 to ca. 4.8 p.p.m. It is consistent with the structure of the propylene sulfite isomers that reversing the configuration of the sulfite group (going from isomer ii to i. for example) should move two ring protons (including H_C) to higher field and one ring proton to lower field while the methyl protons move to lower field, as is observed. The question of deciding which isomer has which configuration is attempted below through calculation of the effect of the S=O group on some of the proton chemical shifts in any one molecule. The two principal contributing effects considered are the electric field and diamagnetic anisotropy of the S=O bond.

Structure of Ethylene Sulfite.—A model for this molecule will now be constructed using bond angles and lengths assumed from related systems. Using the following mean bond lengths: C—C = 1.54,[10] C—O = 1.43,[10] S—O ≈ 1.65[10,11] and S=O ≈ 1.44 Å.,[12] the ethylene sulfite ring may be fitted together with angles OCC = 111° and SOC = 108° (values close to the tetrahedral angle) and OSO ca. 102°. Such an angle about sulfur probably would not involve much strain (cf. 105 ± 3° for CSC in dimethyl sulfide and 102 ± 3° for ClSCl in sulfur dichloride[13]), but the ring may possibly be slightly puckered in its equilibrium state in order to accommodate more nearly tetrahedral angles about the C and O atoms. Yet if this is so, the above p.m.r. results show that the whole molecule must retain effectively C_S symmetry through thermal vibrations. It will be assumed

(10) L. Pauling, "The Nature of the Chemical Bond." 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, Chap. 7.

(11) Pauling gives the sum of the *single* bond radii of oxygen and sulfur as 1.70 Å. (see ref. 10). A measured value, in potassium ethyl sulfate, is 1.60 Å.; J. A. J. Jarvis, *Acta Cryst.*, **6**, 327 (1953).

(12) *Cf.* A. Simon and H. Kriegsmann, *Z. physik. Chem.* (*Leipzig*), **204**, 369 (1955), and K. J. Palmer, *J. Am. Chem. Soc.*, **60**, 2360 (1938).

(13) *Cf.* ref. 10, p. 112.

below that the ring is planar. If the O=S—O angle in ethylene sulfite is taken as 106°, the same as O=S–Cl in thionyl chloride,[1] then the S=O bond should make an angle of 116° with the plane of the ethylene sulfite ring.

It may be shown that this model is consistent with the electric dipole moment of ethylene sulfite, the measurement of which was included in this study. The following mean bond moments may be derived from other systems: $\mu_{H-C} = 0.4$,[14,15] $\mu_{C-O} = 0.74$,[14,15] $\mu_{S=O} = 2.8$[14,16] and $\mu_{S-O} \approx 0.4$ D.[17] (the sense of the moments is positive to negative going left to right, as $^{\delta+}H—C^{\delta-}$). Vector addition of the bond moments using the angles assumed above gives a resultant molecular moment of magnitude 3.8 D. This value is quite insensitive to changes of 1 or 2° in the assumed angles. The observed value is 3.74 (see Experimental), and agreement with the calculated value to within ±0.1 is really more than can be expected of the nonetheless reasonably self consistent system of bond moments,[14] especially when in our case the value taken for μ_{S-O} is not too well established. However, the agreement of calculated and observed moments may be taken as support for the assumed model and argues that the S=O bond in alkyl sulfites is almost certainly very similar to those in related OSX₂ structures, with a bond moment of 2.8 D.[16]

Effect of S=O Electric Field on Chemical Shift.—It appears to be established now quite firmly that the sulfur–oxygen bond in sulfoxides, sulfones and thionyl halides is a p^2-pd hybrid double bond, with an electric moment corresponding to a charge separation on the atoms of ca. one-third of an electron in the sense $^{\delta+}S=O^{\delta-}$.[18-22] This

appears to have been first proposed by Sutton and his co-workers on the basis of the observed dipole moments of typical sulfones and sulfoxides.[18,19]

In calculating the effect of the electric field of the S=O dipole on the chemical shift of the A and B protons in the *cyclic* sulfite molecules ($\Delta\delta_{EI}$) it will be assumed that the positive charge associated with the sulfur atom affects the A and B protons equally. Then only the effect of the charge on the terminal oxygen atom need be evaluated. Adapting the formula derived recently by Buckingham[23] for the change in proton shielding in an X–H bond due to a neighboring dipole, eq. 1 is obtained for the situation in ethylene sulfite, where $\Delta\delta_{EI} = \delta_A - \delta_B$. The proton *cis* to the S=O

$$\delta \times 10^6 = 9.6\, e \times \cos\theta/R^2 - 23e^2/R^4 \quad (1)$$

bond is labeled A, and a positive δ means a shift to higher field; e is the pole strength in units of electronic charge and θ is the angle between the direction of the C–H bond and the line, of length R in Å. units, joining the oxygen and hydrogen atoms in question. From the assumed model of ethylene sulfite, $R_A = 3.72$, $R_B = 4.30$Å., $\theta_A = 62°30'$, $\theta_B = 27°00'$ and e is ca. $^1/_3$: whence $\Delta\delta_{EI} = 0.05 \times 10^{-6}$, or the A protons are shifted 0.05 p.p.m. to lower field from the B protons. This effect is ca. 30% of the shift observed in isobutylene sulfite and is therefore quite significant; however, it may now be assumed that the major contribution to the shift is from the magnetic anisotropy of the S=O bond.

Anisotropy of the S=O Double Bond.—In order to calculate the contribution made by the magnetic anisotropy of the S=O bond to the chemical shift of the A and B protons in the sulfites considered, some knowledge of the values of the three principal magnetic susceptibilities of the bond is required. At the present time, it is difficult to make even rough a priori estimates of these. However, if it is assumed that almost the entire shift for the A and B protons is due to the magnetic anisotropy effect, it is possible to calculate an approximate anisotropy back from the observed chemical shift provided certain simplifying assumptions are made. The plausibility of the magnitude and direction of the result may then be discussed.[24]

The principal susceptibilities for S=O will be defined as χ_{zz} down the axis joining the two atoms, χ_{yy} perpendicular to χ_{zz} in the plane of symmetry of the ethylene sulfite molecule (which is also the nodal plane of the p-(pd) π-bond[20]) and passing through the mid-point[25] between the two atoms,

(14) Cf. C. P. Smyth, "Dielectric Behavior and Structure," Mc, Graw–Hill Book Co., Inc., New York, N. Y., 1955, Chap. VIII.

(15) Wheland gives $\mu_{C-O} = 1.5$ based on the assumption $\mu_{H-C} = -0.4$; i.e., he assumes the HC bond is polarized in the sense $\delta^-H-C^{\delta+}$ in aliphatic compounds: see G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 207–209. It actually makes little difference to our calculation which "convention" is used. It appears very difficult to determine at present the exact magnitude and direction of CH dipoles in different situations, but the Smyth procedure seems preferable: see ref. 12, and also L. E. Sutton, in E. A. Braude and F. G. Nachod's "Determination of Organic Structures by Physical Methods," Academic Press Inc., New York, N. Y., 1955, pp. 386–390.

(16) C. W. N. Cumper and S. Walker, Trans. Faraday Soc., 52, 193 (1956).

(17) No value for the sulfur–oxygen single bond moment has been recorded previously, but considering that $2\mu_{C-O} \approx \mu_{C-Cl}$ (see ref. 14), it appears reasonable to assume that μ_{S-O} would be about half of μ_{S-Cl}, which has the value of 0.7 D. (ref. 14). Accordingly, we shall assume $\mu_{S-O} = 0.4$ D. Furthermore, this value may be supported by the following argument. Small changes in S=O bond order are brought about by substantial changes in electronegativity of the X groups in OSX₂ molecules: cf. W. E. Moffitt, ref. 20; H. J. Hofmann and K. Andress, Z. anorg. allgem. Chem., 284, 234 (1956). Thus, the stretching frequencies of S=O bonds are 1312, 1229, 1214 (ref. 8), 1209, 1055, 968 and 932 cm.⁻¹ for thionyl fluoride, thionyl chloride, ethylene sulfite, noncyclic alkyl sulfites, alkyl sulfoxides and sulfite ion (two), respectively (cf. ref. 12). Hence, the electronegativities of the group X in OSX₂ molecules are in the semiquantitative order: F >> Cl > OR >> R >>> O⁻ (R = alkyl). It is then very plausible that μ_{S-O} should be say 0.4 ± 0.2 when $\mu_{S-Cl} = 0.7$ and $\mu_{S-C} = -0.5$ (ref. 14).

(18) G. M. Phillips, J. S. Hunter and L. E. Sutton, J. Chem. Soc., 146 (1945).

(19) I. E. Coop and L. E. Sutton, Trans. Faraday Soc., 35, 505 (1939).

(20) W. E. Moffitt, Proc. Royal. Soc. (London), A200, 409 (1950).

(21) H. P. Koch and W. E. Moffitt, Trans. Faraday Soc., 47, 8 (1951).

(22) Cf. G. Cilento, Chem. Revs., 60, 147 (1960), and refs. therein cited.

(23) A. D. Buckingham, Can. J. Chem., 38, 300 (1960).

(24) This notion and the appropriate equations are well presented by P. T. Narasimhan and M. T. Rogers, J. Phys. Chem., 63, 1388 (1959). Unfortunately, the system they treat yields very poor results in detail. It may nevertheless be concluded that of the three principal susceptibilities for the carbonyl C=O bond, χ_{xx}, directed parallel to the axis of the atomic p orbitals forming the π-bond, has the greatest magnitude.

(25) We see no reason why the origin of the principal axes should not be close to the mid-point between the S and O nuclei, since although the S=O bond has a high dipole moment equivalent to a displacement of ca. $^1/_3$ of an electron from the S to the O, the non-

and χ_{xx} perpendicular to χ_{yy}. The chemical shift due to anisotropy, $\Delta\delta_{An} = \delta_A - \delta_B$ is related to the susceptibilities χ_{ii} through the equation

$$\delta = \frac{10^{24}}{3NR^3} \Sigma_i (1 - 3\cos^2\gamma_i)\chi_{ii} \qquad (2)$$

where N is the Avogadro number and the γ_i are the angles subtended at the axes i by the line, of length R in Å., joining each of the protons A and B to the origin of the principal susceptibilities.

The relative magnitudes of the χ_{ii} may be established quite definitely as follows. The calculations of Guy and Tillieu[26,27] have shown distinctly that for σ-bonds $\chi_{zz} < \chi_{yy} = \chi_{xx}$ and for the π-bond between carbon atoms $\chi_{xx} > \chi_{yy} > \chi_{zz}$. Then for the C=C double bond and doubtless for the C=O double bond[24] it may be asserted that $\chi_{xx} > \chi_{yy} > \chi_{zz}$. This is almost certainly true also for the S=O double bond since it is basically similar in structure to the simple types of double bond: the presence of a d orbital contribution makes the electron density distribution in the S=O π-bond somewhat asymmetric about the xy plane but symmetry about the zx and zy planes is retained.[20] (Compared to pure p orbital π-bonds, the electrons in the S=O π-bond should be more diffuse and therefore have higher negative values of magnetic susceptibility.)

Using the above assumption, we shall proceed with the calculation of an approximate anisotropy, $\Delta\chi = \chi_{xx} - \chi_{zz}$, with two alternative forms of simplification $\chi_{xx} > \chi_{yy} \approx \chi_{zz}$ and $\chi_{xx} \approx \chi_{yy} > \chi_{zz}$ for which the terms in Σ in eq. 2 reduce to $(1-3\cos^2\gamma_x)\Delta\chi$ and $(1 - 3\cos^2\gamma_z)\Delta\chi$, respectively. From our model for ethylene sulfite, R_A and R_B are 3.41 and 3.73 and the angles are for R_A: $\gamma_x = 70°40'$, $\gamma_z = 69°35'$; and for R_B: $\gamma_x = 72°25'$ and $\gamma_z = 41°40'$. The value of $\Delta\delta$ for the A and B protons in isobutylene sulfite will be used: 0.15 $\times 10^{-6}$. For the former simplification an absurdly high value of $\Delta\chi$ is obtained and may be rejected; but for the latter the acceptable value of $ca. +9 \times 10^{-6}$ cm.^{3} mole^{-1} is obtained. If the isobutylene sulfite ring should be puckered by a few degrees compared to ethylene sulfite, inspection of the data from the assumed model shows that the approximate magnitude and particularly the direction of the calculated value of $\Delta\chi$ would be unchanged.

The positive value of $\Delta\chi$ is to be associated with a shift in the resonance signals from the A protons (*cis* to the S=O group) to lower field compared to the B protons. Therefore, $\Delta\delta_{An}$ and $\Delta\delta_{El}$ act *in the same sense*. The calculated value of $\Delta\chi$ may now be corrected for the 30% contribution to the observed chemical shift from the electric field effect, giving the final, approximate value of $\Delta\chi$ as $+6 \times 10^{-6}$ cm.^{3} mole.$^{-1}$ This is a reasonable magnitude for the anisotropy of a double bond.[26,27] Our conclusion is that the direction of the chemical shift for the A and B protons in isobutylene sul-

bonding and the valence electrons about S together should contribute about as much as those about O to both susceptibility and anisotropy. The point-dipole assumption for calculating the anisotropy effect in these *cyclic* sulfites is reasonably justified since the protons are situated at least 3Å. away from the S=O bond.

(26) J. Guy and J. Tillieu, *J. Chem. Phys.*, **24**, 1117 (1956); *Compt. rend.*, **242**, 279 (1956).

(27) J. Baudet, T. Tillieu and J. Guy, *ibid.*, **244**, 2920 (1957).

fite may be correlated with the direction of the anisotropy of the S=O bond and the direction of the electric field effect in this molecule or at least a very closely related one. On this basis, therefore, we conclude, from the line positions of proton C, that propylene sulfite isomer ii may be assigned as structure VI, and i as V.

It is hoped that this work will stimulate action to determine the structure of these sulfites by other methods. It is perhaps worth noting finally that while ethylene sulfite consists of a single molecular species, isobutylene sulfite and the two propylene sulfite isomers should be *dl*-mixtures of, in principle, separable optical isomers.

Experimental

Materials.—Reagent grade diols, thionyl chloride and inorganic reagents were employed.

A commercial sample of **ethylene sulfite** was fractionated to give a product, b.p. 63°(13 mm.), n^{25}D 1.4446.[6]

Anal.[28] Calcd. for $C_2H_4O_3S$: C, 22.2; H, 3.7; S, 29.6. Found: C, 22.4; H, 3.8; S, 29.4.

A **propylene sulfite** mixture was prepared by the usual simple method.[6,29] A slight excess of thionyl chloride was added gradually to the diol after which the temperature of the mixture was raised almost to the boiling point to complete the reaction. Stirring facilitated the evaporation of hydrogen chloride gas. The product was extracted thoroughly with cold water, dried over a mixture of anhydrous sodium carbonate and sodium sulfate and fractionated under reduced pressure giving a product, b.p. 58° (12 mm.), n^{25}D 1.4353[6] (yield 55%).

Anal. Calcd. for $C_3H_6O_3S$: C, 29.5; H, 4.9; S, 26.2. Found: C, 29.5; H, 4.9; S, 26.3.

Isobutylene Sulfite.—The yield of this material obtained from the simple method was *ca.* 20%. Adoption of the technique of passing a stream of inert gas through the reaction mixture under reduced pressure (*ca.* 200 mm.) in order to remove hydrogen chloride almost immediately as it was formed,[30,31] and the use of benzene as a diluent, resulted in a yield close to 60% of material, b.p. 53° (10-mm.), n^{25}D 1.4292.

Anal. Calcd. for $C_4H_8O_3S$: C, 35.3; H, 5.9; S, 23.5. Found: C, 35.6; H, 5.9; S, 23.3.

Ethylene sulfate was prepared in very low yield from ethylene dibromide and silver sulfate.[32,33] The product was distilled from the reaction mixture and repeated recrystallization from isoöctane gave fine, white needles, m.p. 98° (lit. 99°,[32] 91–92°[33]).

Anal. Calcd. for $C_2H_4O_4S$: C, 19.4; H, 3.2; S, 25.8. Found: C, 19.6; H, 3.1; S, 25.6.

The sulfites were shown to be 99$^+$% pure *via* vapor phase chromatography. The following retention times were observed for 0.01-ml. samples on a 250 cm., 10 mm. inside diam. vertical column packed with 25% Carbowax on 30-60 mesh firebrick, with 95 ml./min. helium gas at 4.7 p.s.i. and 160°: ethylene sulfite, 51.0 min.; isobutylene sulfite, 31.0 min.; and for the propylene sulfite isomers, the first (minor) fraction i 39.0 min. and the second (major) fraction ii 42.3 min. Collected samples of i and ii had n^{25}D 1.4362 and 1.4350, respectively. The sulfites could be stored indefinitely without change in sealed ampoules under vacuum in the dark.

Spectroscopy.—The spectra recorded in Figs. 1 to 4 were obtained using Varian 4300 B and 4311 high-resolution n.m.r. spectrometers operating at 40 and 60 Mc.p.s., respectively, with Varian 12-inch electromagnets and flux

(28) Analyses were by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y., and by the Bernhardt Mikroanalytisches Laboratorium, Mulheim (Ruhr), Germany.

(29) *Cf.* "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 112.

(30) W. Gerrard, *J. Chem. Soc.*, 99 (1939); 218 (1940).

(31) L. P. Kyrides, *J. Am. Chem. Soc.*, **66**, 1006 (1944).

(32) W. Baker and F. B. Field, *J. Chem. Soc.*, 86 (1932).

(33) *Cf.* J. S. Brimacombe, A. B. Foster, E. B. Hancock, W. G. Overend and M. Stacey, *ibid.*, 201 (1960).

stabilizers. Normal operating conditions were employed. The samples were degassed and sealed, under vacuum in Pyrex tubes of *ca.* 5 mm. o.d., with *ca.* 2% of tetramethylsilane (TMS) as internal reference and a 1 mm. capillary tube containing degassed benzene as external reference (ethylene sulfate was dissolved in a CCl_4-$CHCl_3$ mixture). The position of the center of each multiplet in the spectra is reported in parts per million (± 0.01) on the scale in which internal TMS is at 10 p.p.m., or 400 c.p.s. at 40 Mc.p.s.[7] The internal TMS in ethylene sulfite solution is 263.0 c.p.s. removed from the external benzene. No corrections were applied for differences in bulk magnetic susceptibility of the sulfites and benzene.

The infrared spectra were recorded in conventional fashion on a Beckman IR-4 instrument equipped with sodium chloride and cesium bromide optics. The bands common to the two propylene sulfite isomers were in cm.$^{-1}$: *ca.* 2975m, *ca.* 1460m, 1393m, 1212s, (ν S=O), 1057m, 909w, 834s, 680m and 382m. The bands which were different were for isomer i: 1333w, 1110w, 968s, 723m, 466m and 444m; and for isomer ii: 1140w, 1103w, 980m, 952m, 736m, 710w, 505m, 487m and 415m (s = strong, m = medium. w = weak intensity). These data are in reasonable agreement with those infrared bands for a propylene sulfite mixture which have been recorded previously.[6]

Dipole Moment.—The dielectric constants of dilute solutions of ethylene sulfite in benzene (ϵ) were measured at 25° over the weight fraction (ω) range of 0 to 0.1, using a Wissenschaftlich-Technische Werkstatten Dipolemeter, type

DM 01 operating at a frequency of 2 Mc.p.s. The linear expression relating ϵ and ω, derived by the method of least squares, was $\epsilon = 2.25 + \alpha\omega$, where $\alpha = 13.96$. By conventional methods, the following expressions relating ω with the specific volume (v) and refractive index (n) of the solutions at 25° were found: $v = 1.1445 + \beta\omega$, where $\beta = -0.469$ and $n = 1.4977 + \gamma\omega$, where $\gamma = -0.0304$. The value 3.74 was calculated for the electric moment (μ) of ethylene sulfite by substitution of the derived parameters α, β and γ in the equation of Everard, Hill and Sutton[34] (M = mol.wt.)

$$10^4\mu^2 = M (92.0\alpha + 1.5\beta - 279\gamma + 1.7)$$

Benzene was of analytical grade redistilled under nitrogen. Contact of the solutions with the atmosphere was avoided as far as possible.

(34) K. B. Everard, R. A. W. Hill and L. E. Sutton, *Trans. Faraday Soc.*, **46**, 417 (1950).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LAWRENCE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY 4, CALIF.]

Electrical and Magnetic Properties of Organic Molecular Solids. III. Violanthrene and Some Other Donors with the Acceptors o-Chloranil, Iodine and Tetracyanoethylene[1]

BY DAVID R. KEARNS AND MELVIN CALVIN

A study of the electrical and magnetic properties (and how they are affected by illumination) of violanthrene as a donor matrix with a variety of acceptor layers is reported. The principal acceptor most thoroughly studied was o-chloranil. A reciprocal study also was made with o-chloranil as an acceptor matrix and phthalocyanine as donor in a laminated configuration. Kinetics of photo-induced transients, both in terms of conductivity and magnetic response, are reported. All of the results may be interpreted in terms of the transfer of electrons from the donor to the acceptor layer, giving rise to an orbital and electrostatically determined positive and negative ion and radical distribution on either side of the interface, respectively.

Introduction

Both the development of our knowledge of the electrical and magnetic properties of organic molecular electron donor–acceptor complexes[2-4] and the development of concepts for the function of such complexes in biological energy transformations, including photosynthesis[5] and muscle contraction,[6] have prompted a further investigation of a configuration of molecules more closely resembling the lamellar systems of biology.[2b,5a] We report here an investigation of the electrical,

(1) The work described in this paper was sponsored by the U. S. Atomic Energy Commission.

(2) (a) G. Tollin, D. R. Kearns and M. Calvin, *J. Chem. Phys.*, **32**, 1013 (1960); (b) D. R. Kearns, G. Tollin and M. Calvin, *ibid.*, **32**, 1020 (1960).

(3) (a) H. Akamatsu, H. Inokuchi and Y. Matsunaga, *Bull. Chem. Soc. Japan*, **29**, 213 (1956); (b) Y. Matsunaga, *ibid.*, **28**, 475 (1955), and *J. Chem. Phys.*, **30**, 855 (1959).

(4) See proceedings of conference on "Electronic Conductivity in Organic Solids," Duke University, April, 1960; to be published by Interscience Publishing Co., New York, N. Y., 1961.

(5) (a) Melvin Calvin, *Rev. Mod. Phys.*, **31**, 147 (1959); **31**, 157 (1959); (b) W. Arnold and R. K. Clayton, *Proc. Natl. Acad. Sci. U. S.*, **46**, 769 (1960).

(6) A. Szent-Gyorgyi, *Radiation Research Suppl.*, **2**, 4 (1960).

photoelectric, magnetic, photomagnetic and spectroscopic behavior of a variety of donor–acceptor systems in the laminated solid arrangement, that is, a donor layer in contact with an acceptor layer and a boundary established between them. A fundamental hypothesis underlying this work and deriving some support from it is: While the absorption of light in the charge transfer band by a donor–acceptor molecular complex in solution (or in the gas phase) might very well lead to the "effective" transfer of an electron from one of the components to the other, energy conversion or storage cannot be achieved in this way beyond that comprising an ordinary excited electronic molecular state. The return to the ground state (by emission or thermal decay) is too easy and rapid. If, however, the donor and acceptor components are each part of a solid and probably ordered array, charge separation may occur following the charge transfer act (resulting from light absorption) by a process of electron and/or hole migration with concomitant "trapping" in the two respective phases. Thus, the oxidized and reduced sites are not only long lived but widely separated so that relatively