214. *Molecular Polarisability: the Anisotropy of the* C–S *Bond.*

By M. Aroney, R. J. W. Le Fèvre, and J. Saxby.

From measurements on dimethyl sulphide in carbon tetrachloride the longitudinal and transverse polarisabilities of the C–S bond are deduced as $0{\cdot}188 \times 10^{-23}$ and $0{\cdot}169 \times 10^{-23}$ c.c., respectively, an assumption being made that the C–S polarisability ellipsoid is one of revolution with $b_{\mathrm{L}}^{\mathrm{C-S}} \neq b_{\mathrm{T}}^{\mathrm{C-S}} = b_{\mathrm{V}}^{\mathrm{C-S}}$. These values are applied to investigate the conformations of diethyl and di-n-propyl sulphide and of diphenyl sulphide, and the structure of 1,3,5-trithian.

No estimate of the anisotropic polarisability of the C–S bond has yet been published. As explained in the discussion below, one set of values, appropriate to the C–S links in dimethyl sulphide, may be drawn from measurements now recorded of the dipole moment, molar Kerr constant, and refractivities of this substance. The longitudinal and transverse polarisabilities ($b_{\mathrm{L}}^{\mathrm{C-S}}$ and $b_{\mathrm{T}}^{\mathrm{C-S}}$) * so deduced, appearing applicable to 1,3,5-trithian, have therefore been used in a conformational analysis of diphenyl sulphide and the two simpler of the three di-n-alkyl sulphides also studied.

Experimental

Materials, Apparatus, etc.—Dimethyl sulphide, prepared from methyl iodide and sodium sulphide, was twice distilled from sodium, then having b. p. 37·5—38·5°. The higher sulphides were prepared and/or purified [1] to give: diethyl sulphide, b. p. 91·5—92·5°, di-n-propyl sulphide, b. p. 141—143°, and di-n-butyl sulphide, b. p. 186—188°. Diphenyl sulphide, b. p. 120—122°/3—4 mm., was prepared by Dougherty and Hammond's method.[2] Carbon tetrachloride, as solvent, was from a sulphur-free bulk supply which had been dried over anhydrous calcium chloride, fractionated through a 1-m. column packed with glass helices, then stored over fresh anhydrous calcium chloride. Symbols, headings, and methods of calculation used in the following Tables are explained in ref. 3, pp. 280—283. For carbon tetrachloride at 25°, $\varepsilon_1 = 2{\cdot}2270$, $d_1 = 1{\cdot}5845_4$, $(n_{\mathrm{D}})_1 = 1{\cdot}4575$, and $B_1 = 0{\cdot}070 \times 10^{-7}$ (Na light).

Previous Measurements.—Dipole-moment (D) determinations made before 1948 are listed by Wesson [5] in the M.I.T. Tables which give (solvent in each case, benzene; reference given in parentheses): dimethyl sulphide, 1·40 (6); diethyl sulphide, 1·61 (7), 1·58 (8); di-n-propyl sulphide, 1·55 (6); di-n-butyl sulphide, 1·57 (6), 1·56 (9); diphenyl sulphide, 1·47 (10), 1·565 (11), 1·50 (12). Since 1948 the following additional moments have been recorded (also in benzene): dimethyl sulphide, 1·45 (13); di-n-butyl sulphide, 1·61 (14). In comparing the

---

* Principal semi-axes of the polarisability ellipsoids of bonds, $b_{\mathrm{L}}^{\mathrm{XY}}$, $b_{\mathrm{T}}^{\mathrm{XY}}$, or $b_{\mathrm{V}}^{\mathrm{XY}}$, or of molecules, b_1, b_2, or b_3, are quoted throughout in 10^{-23} c.c. units.

[1] Vogel, " A Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1951, 2nd edn., p. 948.

[2] Dougherty and Hammond, *J. Amer. Chem. Soc.*, 1935, **57**, 117.

[3] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.*, 1955, **5**, 261.

[4] Calderbank and Le Fèvre, *J.*, 1949, 199.

[5] Wesson, " Tables of Electric Dipole Moments," Technology Press, M.I.T., 1948.

TABLE 1.

Incremental Kerr effects, refractive indexes, dielectric constants, and densities for solutions in carbon tetrachloride at 25°.

Solute: Dimethyl sulphide

10^5w_2	1059	2416	3804	6127
$10^7\Delta B$	0·004	0·008	0·012	0·022

whence $\Sigma 10^7\Delta B/\Sigma w_2 = 0{\cdot}334$.

10^5w_2	598	1059	1195	1883	2416	3152
$-10^4\Delta n$	—	—	—	5	—	6
ε^{25}	2·2732	2·3035	2·3171	2·3671	2·3943	2·4742
d_4^{25}	1·57624	1·57053	1·56833	1·55938	1·55468	1·54255

whence $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}023$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 7{\cdot}45$; $\Sigma\Delta d/\Sigma w_2 = -1{\cdot}315$.

Solute: Diethyl sulphide

10^5w_2	804	1578	2177	3931	8017	10,679
$10^7\Delta B$	−0·003	−0·006	−0·009	−0·016	−0·032	−0·048

whence $10^7\Delta B = -0{\cdot}357w_2 - 0{\cdot}793w_2^2$.

10^5w_2	3931	8017	10,679	12,527
$-10^4\Delta n$	0	0	1	2

whence $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}001$.

10^5w_2	146	411	537	584	956	1818	1888	2778
ε^{25}	2·2351	2·2507	2·2597	2·2620	2·2834	2·3325	2·3379	2·3894
d_4^{25}	1·5825	1·5790	1·5769	1·5767	1·5712	1·5600	1·5591	1·5474

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 5{\cdot}86$; $\Sigma\Delta d/\Sigma w_2 = -1{\cdot}36$.

Solute: Di-n-propyl sulphide

10^5w_2	1894	3566	4658	5936	6452	6872	8157
$10^7\Delta B$	−0·011	−0·021	−0·029	−0·036	−0·040	−0·043	−0·052
ε^{25}	2·3074	2·3810	2·4246	2·4759	2·5028	2·5198	2·5710
d_4^{25}	1·5594	1·5367	1·5228	1·5073	1·4989	1·4941	1·4785

whence $10^7\Delta B = -0{\cdot}568w_2 - 0{\cdot}826w_2^2$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 4{\cdot}25$; $\Sigma\Delta d/\Sigma w_2 = -1{\cdot}32$; $\Delta n = 0$ for all concentrations up to $10^5w_2 = 6872$.

Solute: Di-n-butyl sulphide

10^5w_2	1406	3378	4858	7749	8160	9325
$10^7\Delta B$	−0·009	−0·023	−0·033	−0·055	−0·058	−0·069
ε^{25}	2·2760	2·3434	2·3931	2·4844	2·4979	2·5391
d_4^{25}	1·5653	1·5387	1·5191	1·4839	1·4790	1·4632

whence $10^7\Delta B = -0{\cdot}623w_2 - 1{\cdot}17w_2^2$; $\Delta\varepsilon = 3{\cdot}47w_2 - 1{\cdot}61w_2^2$; $\Delta d = -1{\cdot}38_3w_2 + 0{\cdot}982w_2^2$; $\Delta n = 0$ for all concentrations up to $10^5w_2 = 9325$.

Solute: Diphenyl sulphide

10^5w_2	3364	3424	3679	4653	6129
$10^7\Delta B$	0·044	0·043	0·050	0·061	0·072

whence $\Sigma 10^7\Delta B/\Sigma w_2 = 1{\cdot}27$.

10^5w_2	1023	1628	2930	3284	3364	3747	3859
$10^4\Delta n$	26	40	—	—	82	93	—
ε^{25}	2·2591	2·2782	2·3190	2·3311	2·3324	2·3450	2·3480
d_4^{25}	1·57823	1·57449	1·56646	1·56421	1·56415	1·56191	1·56075

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}247$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 3{\cdot}14$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}613$.

TABLE 2.

Polarisations, dipole moments, and molar Kerr constants (from observations on solutions at 25°).

Solute	Solvent	$\alpha\varepsilon_1$	$-\beta$	$-\gamma$	$-\delta$	$_\infty P_2$ (c.c.)	R_D (c.c.)	μ (D) *	$10^{12}{}_\infty({}_mK_2)$
$(CH_3)_2S$	CCl_4	7·45	0·830	0·016	−4·77	69·7	19·0	1·56	1·4
$(C_2H_5)_2S$	,,	5·86 †	0·858 †	0·001	5·10	86·7	28·9	1·66	−4·1
$(n\text{-}C_3H_7)_2S$	,,	4·25 †	0·833 †	0	8·11	92·9	37·3	1·62	−7·3
$(n\text{-}C_4H_9)_2S$	,,	3·47 †	0·873 †	0	8·90	104·0	47·1	1·63	−9·5
$[\cdot CH_2\cdot S\cdot]_3$	C_6H_6	4·50 ‡	−0·491 ‡	−0·121 ‡	0 §	155·0 ‡	37·8 ‡	2·38 ‡	−18·1
$(C_6H_5)_2S$	CCl_4	3·14	0·387	−0·247	−18·1	109·1	60·0	1·50	24·7

* Calc. by assuming $_DP = 1{\cdot}05R_D$. † Measurements by M. Smith in 1957. ‡ From Calderbank and Le Fèvre, ref. 4. § Measurements by Dr. C. G. Le Fèvre.

above values with those listed in Table 2 it should be noted that ${}_{\mathrm{D}}P$ has not always been taken as $1{\cdot}05R_{\mathrm{D}}$ in refs. 6—14.

The Kerr constant B for liquid diethyl sulphide is cited in the International Critical Tables[15] as $+0{\cdot}106$ relatively to $B_{\mathrm{CS_2}}$ as unity.

DISCUSSION

Dimethyl Sulphide.—Molecular symmetry is such that the principal polarisability axes can be located as shown in Fig. 1, with b_1 (the dipole moment direction) and b_2 in the plane of the C–S–C triangle, and b_3 normal to this plane. If the assumption is made that the polarisability contributions of the sulphur " lone-pair " electrons can be included in the " effective " semiaxes for the C–S links and that the bond ellipsoids thus described are axially symmetric about the intercentre line, then b_1, b_2, and b_3 (and hence ${}_{\mathrm{E}}P^{\mathrm{Me_2S}}$, the electronic polarisation, and ${}_{\mathrm{m}}K^{\mathrm{Me_2S}}$) can be expressed in terms of the two unknowns $b_{\mathrm{L}}^{\mathrm{C\text{-}S}}$ and $b_{\mathrm{T}}^{\mathrm{C\text{-}S}}$:

$$
{}_{\mathrm{E}}P^{\mathrm{Me_2S}} = 4\pi\boldsymbol{N}(b_1 + b_2 + b_3)/9
$$

$$
{}_{\mathrm{m}}K^{\mathrm{Me_2S}} = 2\pi\boldsymbol{N}(\theta_1 + \theta_2)/9
$$

where

$$
\theta_1 = {}_{\mathrm{D}}P[(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2]/45\boldsymbol{k}T({}_{\mathrm{E}}P)
$$

$$
\theta_2 = \mu^2(2b_1 - b_2 - b_3)/45\boldsymbol{k}^2T^2
$$

and

$$
b_1 = 2b_{\mathrm{L}}^{\mathrm{C\text{-}S}}\cos^2\theta + 2b_{\mathrm{T}}^{\mathrm{C\text{-}S}}\sin^2\theta + 6b_{\mathrm{mean}}^{\mathrm{C\text{-}H}}
$$

$$
b_2 = 2b_{\mathrm{L}}^{\mathrm{C\text{-}S}}\sin^2\theta + 2b_{\mathrm{T}}^{\mathrm{C\text{-}S}}\cos^2\theta + 6b_{\mathrm{mean}}^{\mathrm{C\text{-}H}}
$$

$$
b_3 = 2b_{\mathrm{T}}^{\mathrm{C\text{-}S}} + 6b_{\mathrm{mean}}^{\mathrm{C\text{-}H}}
$$

Here, $\boldsymbol{N}$ is Avogadro's number, $\boldsymbol{k}$ is Boltzmann's constant, T the absolute temperature, and 2θ, the angle CSC, equals 98° 52′ according to an accurate and recent analysis[16] of the microwave spectrum of dimethyl sulphide. Each C–H link is regarded as isotropically polarisable (see ref. 17), with $b_{\mathrm{mean}}^{\mathrm{C\text{-}H}} = 0{\cdot}064$. ${}_{\mathrm{E}}P^{\mathrm{Me_2S}}$ is obtainable by addition of the C–S and C–H bond equivalents of Le Fèvre and Steel;[18] the values of ${}_{\mathrm{m}}K$ and μ are as listed for dimethyl sulphide in Table 2. Solution of the equations yields: $b_{\mathrm{L}}^{\mathrm{C\text{-}S}} = 0{\cdot}188$, $b_{\mathrm{T}}^{\mathrm{C\text{-}S}} = b_{\mathrm{V}}^{\mathrm{C\text{-}S}} = 0{\cdot}169$. If the dipole moment value of 1·50 D (reported by Pierce and Hayashi[16] from Stark-effect measurements) is used in the calculations, the C–S bond semiaxes thus derived differ negligibly (±0·001) from those above.

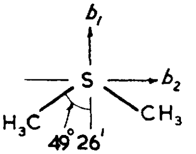
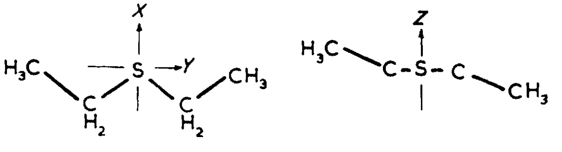


FIG. 1.



(a)

(b-d)

FIG. 2.

Diethyl Sulphide.—For the geometrical specification of the alkyl groups in diethyl and di-n-propyl sulphide, the angles CSC have been retained[16] at 98° 52′, and the angles CCS

---

[6] Hunter and Partington, *J.*, 1932, 2812.
[7] Sutton, New, and Bentley, *J.*, 1933, 652.
[8] Walls and Smyth, *J. Chem. Phys.*, 1933, **1**, 337.
[9] Jensen, *Z. anorg. Chem.*, 1935, **225**, 97.
[10] Bergmann, Engel, and Sandor, *Z. phys. Chem.*, 1930, *B*, **10**, 397.
[11] De Vries and Rodebush, *J. Amer. Chem. Soc.*, 1931, **53**, 2888.
[12] Hampson, Farmer, and Sutton, *Proc. Roy. Soc.*, 1933, *A*, **143**, 147.
[13] Lumbroso and Dumas, *Bull. Soc. chim. France*, 1955, 651.
[14] Boud and Smith, *J.*, 1956, 4507.
[15] International Critical Tables, 1930, Vol. VII, 1st edn., pp. 110—112.
[16] Pierce and Hayashi, *J. Chem. Phys.*, 1961, **35**, 479.
[17] Le Fèvre and Le Fèvre, *Chem. and Ind.*, 1955, 1121.
[18] Le Fèvre and Steel, *Chem. and Ind.*, 1961, 670.

and CCC regarded as 109·5°. Polarisability semiaxes for the C–C bond have been taken [19] as $b_{L}^{C-C} = 0{\cdot}099$, $b_{T}^{C-C} = b_{V}^{C-C} = 0{\cdot}027$. Fig. 2a represents a "planar" (*i.e.*, with the four carbon and one sulphur atoms lying in the same plane) zig-zag configuration for diethyl sulphide; structures 2b, 2c, and 2d are generated from 2a by rotating one C–CH_3 group, about its adjacent C–S bond as axis, up $\alpha°$ from the C–S–C plane, and the other down $\alpha°$ (cf. diethyl ether in ref. 20), so that they are "*trans*" with respect to the C–S–C plane. For each molecular model considered, a symmetric matrix defines the polarisability tensor referred to a system of Cartesian co-ordinate axes X, Y, Z (Fig. 2a). The matrix is not in general diagonal—the principal axes transformation which makes it so is effected *via* the Sydney University digitial computer SILLIAC, an eigenvalue–eigenvector programme being available in the computing library. Table 3 lists the principal polarisabilities and their locations with respect to X, Y, Z for configurations of diethyl sulphide corresponding to different values of $\alpha°$; and if $\mu_{\text{resultant}}$ is assumed to act along the X-direction, the molar Kerr constant is calculable for each structure.

The recorded $_{\infty}({}_{m}K_2)$ is $-4{\cdot}1 \times 10^{-12}$, *i.e.*, close to that deduced for the conformation in which α is *ca.* 10°. Nevertheless, a single solute species is not reasonably to be expected: Leybold models display a freedom of rotation of the methyl groups over roughly ±120°, a range limited, of course, by repulsions between the methylene C–H bonds and the sulphur "lone-pair" orbitals. Probably, in fact, there is vibration about some equilibrium arrangement, to which a specific value of α_{equil} could be ascribed, so that the $_{m}K$ from experiment is dependent upon an appropriately weighted mean of angles greater and less than α_{equil} by unknown amounts. Accordingly we advance 2c as an "equivalent" conformation, meaning thereby nothing more than that it permits *a priori* calculation of an observed quantity (the $_{m}K$) in terms of one specific conformation even if, in reality, an infinitude are present. *Mutatis mutandis*, these remarks apply also to the case of di-n-propyl sulphide below.

TABLE 3.

Structure	α	b (calc.)	Direction cosines with			$10^{12}\,{}_{m}K$ (calc.)
			X	Y	Z	
2a	0°	$b_1 = 1{\cdot}084$	+1	0	0	$-3{\cdot}3$
		$b_2 = 1{\cdot}162$	0	+1	0	
		$b_3 = 1{\cdot}032$	0	0	+1	
2b	5	$b_1 = 1{\cdot}083$	+1	0	0	$-3{\cdot}6$
		$b_2 = 1{\cdot}162$	0	+0·996	+0·085	
		$b_3 = 1{\cdot}032$	0	−0·085	+0·996	
2c	10	$b_1 = 1{\cdot}082$	+1	0	0	$-4{\cdot}2$
		$b_2 = 1{\cdot}163$	0	+0·986	+0·166	
		$b_3 = 1{\cdot}033$	0	−0·166	+0·986	
2d	23	$b_1 = 1{\cdot}075$	+1	0	0	$-7{\cdot}2$
		$b_2 = 1{\cdot}167$	0	+0·928	+0·373	
		$b_3 = 1{\cdot}035$	0	−0·373	+0·928	

Di-n-propyl Sulphide.—Structure 3a for di-n-propyl sulphide is such that the group $C\overset{\beta}{-}C\overset{\gamma}{-}S\overset{\delta}{-}C\overset{\epsilon}{-}C$ is spatially arranged as for configuration 2c of diethyl sulphide, with $C\overset{\beta}{-}C$ above and $C\overset{\epsilon}{-}C$ below the XY-plane and with each terminal C–C bond parallel with its nearer C–S link (α with γ; ω with δ). If ϕ be the angle between a terminal C–C bond and its projection in the XY-plane, then for structure 3a, $\phi = 0$ since each of the links, α and ω, though they lie respectively above and below this plane, are parallel with it. If the C–C links, α and ω, are rotated away from their positions in 3a, α in the $+Z$ direction (*i.e.*, down into and subsequently below the plane of X and Y), and ω in the $-Z$ direction, they give rise to structures 3b—e (not illustrated), each corresponding to a particular

---

[19] Le Fèvre and Le Fèvre, *J.*, 1956, 3549.

[20] Aroney, Le Fèvre, and Saxby, *J.*, 1962, 2886.

value of ϕ. Polarisability semiaxes and molar Kerr constants have been calculated on the basis that the permanent dipole moment in each case acts along the $+X$ direction; these are listed in Table 4.

TABLE 4.

Structure	ϕ	b (calc.)	Direction cosines with X	Y	Z	$10^{12}{}_{m}K$ (calc.)
3a	0°	$b_1 = 1{\cdot}453$	$+1$	0	0	$+2{\cdot}7$
		$b_2 = 1{\cdot}555$	0	$+0{\cdot}995$	$+0{\cdot}102$	
		$b_3 = 1{\cdot}344$	0	$-0{\cdot}102$	$+0{\cdot}995$	
3b	32	$b_1 = 1{\cdot}444$	$+1$	0	0	$-1{\cdot}5$
		$b_2 = 1{\cdot}549$	0	$+0{\cdot}924$	$+0{\cdot}382$	
		$b_3 = 1{\cdot}359$	0	$-0{\cdot}382$	$+0{\cdot}924$	
3c	39	$b_1 = 1{\cdot}431$	$+1$	0	0	$-7{\cdot}2$
		$b_2 = 1{\cdot}554$	0	$+0{\cdot}898$	$+0{\cdot}440$	
		$b_3 = 1{\cdot}367$	0	$-0{\cdot}440$	$+0{\cdot}898$	
3d	45	$b_1 = 1{\cdot}422$	$+1$	0	0	$-11{\cdot}2$
		$b_2 = 1{\cdot}555$	0	$+0{\cdot}872$	$+0{\cdot}490$	
		$b_3 = 1{\cdot}375$	0	$-0{\cdot}490$	$+0{\cdot}872$	
3e	90	$b_1 = 1{\cdot}393$	$+1$	0	0	$-24{\cdot}3$
		$b_2 = 1{\cdot}429$	0	$+0{\cdot}752$	$-0{\cdot}659$	
		$b_3 = 1{\cdot}530$	0	$+0{\cdot}659$	$+0{\cdot}752$	

From Table 2, ${}_{\infty}({}_{m}K_2)$ for di-n-propyl sulphide is $-7{\cdot}3 \times 10^{-12}$, in agreement with the computed value for configuration 3c.

Di-n-butyl Sulphide.—Because of the large number of possible rotational isomers, calculations for individual isomers are of little significance. We note, however, that if the changes in semiaxes from form 2c of diethyl sulphide to form 3c of di-n-propyl sulphide be continued to di-n-butyl sulphide, then b_1, b_2, and b_3 for the last-named should be, respectively, $1{\cdot}78$, $1{\cdot}94_5$, and $1{\cdot}70$, whence ${}_{m}K$ would follow as $-10{\cdot}1 \times 10^{-12}$, which is near the ${}_{m}K$ ($-9{\cdot}5 \times 10^{-12}$) actually observed.

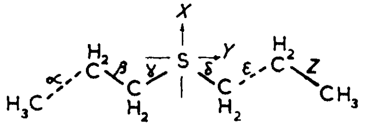
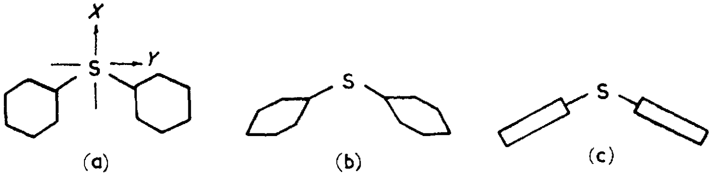


FIG. 3.



(a) (b) (c)

FIG. 4.

Diphenyl Sulphide.—Figs. 4a and 4c represent structures in which the benzene ring planes are respectively parallel with and perpendicular to the C–S–C plane; 4b is an intermediate configuration achieved by rotation of each phenyl group about its S–C$_1$ bond as axis, through χ°. The semiaxes of the phenyl group, derived by subtraction of one C–H bond contribution from the molecular polarisabilities of benzene, are: $b_{L}^{C_6H_5} = b_{T}^{C_6H_5} = 1{\cdot}056$, $b_{V}^{C_6H_5} = 0{\cdot}672$. In accord with Leonard and Sutton's work,[21] the bond angle CSC for diphenyl sulphide has been taken as $106 \pm 4°$. Comparison of $[R]_{D}^{exp}$($= 60{\cdot}0$ c.c.)

---

[21] Leonard and Sutton, *J. Amer. Chem. Soc.*, 1948, **70**, 1564.

with that calculated by summation of bond refractions [22] (= 60·2 c.c.) shows that inter-ring conjugation, if it exists, does not lead to a measurable exaltation of molecular polarisability. Table 5 summarises the calculations (the dipole moment is assumed to act along the $+X$ direction).

TABLE 5.

			Direction cosines with			
Structure	χ	b (calc.)	X	Y	Z	$10^{12}{}_{\mathrm{m}}K$ (calc.)
4a	0°	$b_1 = 2{\cdot}464$	+1	0	0	+127
		$b_2 = 2{\cdot}474$	0	+1	0	
		$b_3 = 1{\cdot}682$	0	0	+1	
4b	42	$b_1 = 2{\cdot}244$	+1	0	0	+25·9
		$b_2 = 2{\cdot}469$	0	+0·888	−0·460	
		$b_3 = 1{\cdot}907$	0	+0·460	+0·888	
,,	45	$b_1 = 2{\cdot}220$	+1	0	0	+15·6
		$b_2 = 2{\cdot}468$	0	+0·867	−0·498	
		$b_3 = 1{\cdot}933$	0	+0·498	+0·867	
4c	90	$b_1 = 1{\cdot}974$	+1	0	0	−78·3
		$b_2 = 2{\cdot}197$	0	+1	0	
		$b_3 = 2{\cdot}450$	0	0	+1	

The molar Kerr constant from experiment is $+24{\cdot}7 \times 10^{-12}$, in good agreement with that calculated for $\chi = 42°$ [cf. diphenyl ether in benzene solution, for which $\chi = 37°$ (ref. 23)].

1,3,5-*Trithian.*—Hassel *et al.*[24] have shown by electron diffraction that the cyclic molecules 1,3,5-trithian and tristhioacetaldehyde have chair configurations with presumably

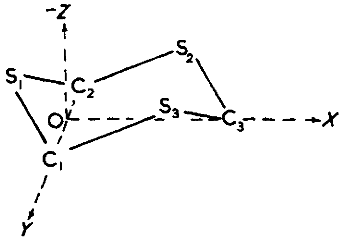


FIG. 5.

(see ref. 25, M 152, M 206) the following molecular parameters: ∠CSC = 106·5°; ∠SCS = 114·5°; S–C = 1·81 Å; S...S = 3·05 Å. These can be used to calculate (by Corey and Sneen's method [26]) position co-ordinates for each carbon and sulphur atom of 1,3,5-trithian with respect to a chosen set of Cartesian co-ordinate axes $OXYZ$ (in Fig. 5), and thence to locate, *via* direction cosines, all of the C–S bond semiaxes. As we treat each of the C–H bonds as isotropically polarisable, their directional properties are of no consequence in the following calculations. The origin O is taken as the mid-point of the line $C_1 \ldots C_2$ which is the Y axis; X coincides with a line joining O with C_3 and is thus perpendicular to Y; Z, which is normal to both X and Y, is parallel to the three-fold symmetry axis. Resolution of all the C–S and C–H bond polarisabilities (as previously listed) along the reference axes allows the elements of the molecular polarisability tensor to be evaluated as: $b_{\mathrm{XX}} = b_{\mathrm{YY}} = 1{\cdot}449$; $b_{\mathrm{ZZ}} = 1{\cdot}409$; $b_{\mathrm{XY}} = b_{\mathrm{XZ}} = b_{\mathrm{YZ}} = 0$. Thus $b_1 = b_2 = 1{\cdot}449$, and $b_3 = 1{\cdot}409$, where the computed molecular semiaxes b_1, b_2, b_3 are coincident with the directions X, Y, and Z, respectively.

---

[22] Vogel, *J.*, 1948, 607; 1952, 514.

[23] Le Fèvre, Sundaram, and Sundaram, *Bull. Chem. Soc. Japan*, 1962, **35**, 690.

[24] Hassel and Øre, *Tidsskr. Kjemi Bergv.*, 1946, **6**, 72; Hassel and Viervoll, *Acta Chem. Scand.*, 1947, **1**, 149.

[25] Sutton *et al.*, "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Spec. Publ.*, No. 11, 1958.

[26] Corey and Sneen, *J. Amer. Chem. Soc.*, 1955, 2505.

The permanent dipole moment, being the vector sum of three components of equal magnitude, each bisecting an angle CSC, will act along the $-Z$ direction. If then $b_1 = b_2$ and $\mu_3 = \mu_r$, the equations in b, obtained from the molar Kerr constant and the electronic polarisation (estimated by addition of the bond ${}_{\mathrm{E}}P$'s in ref. 18), may be solved; from these $b_1^{\mathrm{exp}} = b_2^{\mathrm{exp}} = 1{\cdot}446$, $b_3^{\mathrm{exp}} = 1{\cdot}416$, in satisfactory agreement with the calculated values.

The award of a University Research Scholarship to J. S. is gratefully acknowledged.

UNIVERSITY OF SYDNEY, N.S.W., AUSTRALIA. [*Received, May* 29*th*, 1962.]