47. *The Intervalency Angles of Oxygen and Sulphur in Dioxan, Dithian, Trioxymethylene, and Trithioformaldehyde.*

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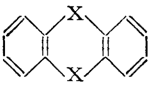
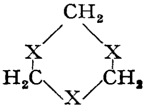
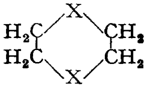
The dipole moments of trioxymethylene and trithioformaldehyde, determined in benzene solution, suggest that in molecules of type (II) the valency angles of sulphur and oxygen are approximately equal. This is in contrast to earlier conclusions drawn from measurements on molecules of type (I). Dioxan and dithian (type III) both have very small or zero moments.

BENNETT, EARP, and GLASSTONE (*J.*, 1934, 1179) showed the dipole moment of diphenylene dioxide (I, X = O) to be experimentally indistinguishable from zero, in contrast with that of thianthren (I, X = S) for which values of 1·7 D. (Bergmann and Tschudnowsky, *Ber.*, 1932, **65**, 458), 1·41 D. (Smyth and Walls, *J. Chem. Physics*, 1933, **1**, 337), 1·54 D. (Bennett and Glasstone, *J.*, 1934, 128), and 1·57 D. (Campbell, Le Fèvre, Le Fèvre, and Turner, *J.*, 1938, 404) have been recorded. The last two groups of authors concluded, therefore, that the intervalency angles of X in the structure (I) are *ca.* 120° for oxygen, and less than this, perhaps 110°, for sulphur. In view of the fairly high polarity of paraldehyde (2·03 D., Le Fèvre and Russell, *J.*, 1936, 496) and the low polarity of dioxan (for references, see below), it seemed of interest to make analogous comparisons for the oxygen and sulphur compounds corresponding to (II) and (III).


(I.)


(II.)


(III.)

Measurements of trioxymethylene, dithian, and trithioformaldehyde are therefore now reported ($\mu = 2{\cdot}1_6$, *ca.* 0, $2{\cdot}3_8$ D. respectively). Those on trioxymethylene were completed in 1939 at University College, London. During the war, Maryott and Acree (*J. Res. Nat. Bur. Stand.*, 1944, **33**, 71) also examined this molecule, finding $\mu = 2{\cdot}18$ D., with which our value is in excellent agreement.

Theoretically the structures represented by (II) may adopt strainless configurations of the Sachse type (*Ber.*, 1890, **23**, 1363), in which the three X atoms are either all above the plane containing the centres of the three carbon atoms (" chair " forms), or two above this plane and one below it (" boat " forms). In fact, however, such isomeric pairs do not seem to be isolable. An allegedly second form of trithioformaldehyde of m. p. 247° (Hinsberg, *Ber.*, 1923, **56**, 1850; 1924, **57**, 836; *J., pr. Chem.*, 1933, ii, **138**, 214) has been shown by Bell and Bennett (*J.*, 1929, 15) to disagree analytically with the formula $(CH_2S)_3$ although on recrystallisation the ordinary form, m. p. 216°, can be obtained from it. The *single* known substances therefore may each be either (*a*) wholly " boat " or " chair " individuals, or (*b*) equilibrium mixtures of the two configurations (resembling the equilibria commonly supposed for simple *cyclo*hexane rings).

Geometrical isomers of paraldehyde are likewise unknown, but electron diffraction studies on its vapour (Ackerman and Mayer, *J. Chem. Physics.*, 1936, **4**, 377; Carpenter and Brockway, *J. Amer. Chem. Soc.*, 1936, **58**, 1270) are compatible with a puckered ring of carbon and oxygen atoms, *i.e.*, a " chair " model. Trimethylene trioxide and trisulphide (II), whose crystal structures are found by *X*-ray investigation to be alike (Moerman, *Rec. Trav. chim.*, 1937, **56**, 161; Moerman and Wiebenga, *Z. Krist.*, 1937, **97**, 323), resemble gaseous paraldehyde in being also " chair " forms. Accordingly it seems *a priori* probable that these compounds will dissolve in benzene with retention of this molecular configuration.

Our results may be analysed as follows :

If μ_x is the appropriate C–X–C moment, the expected moments for the " boat " and " chair " varieties of (II) are calculable as $\mu_x \sin \theta$ and $3\mu_x \sin \theta$ respectively, where θ is the angle between the plane of the C–X–C bonds and that through the three methylene carbon atoms. The angle θ is readily given by

$$\cos \theta = \frac{(2 \sin \beta/2 - \sin \alpha/2)}{3^{1/2} \cos \alpha/2},$$

α being the valency angle of the atom X and β that of carbon.

A selection of our calculations, relating to α and β values around 110°, and utilising for μ_x the moments recorded for dimethyl ether and dimethyl sulphide (*Trans. Faraday Soc.*, 1934, **30**, Appendix), namely 1·3 and 1·4 D., is given in Table I.

TABLE I.

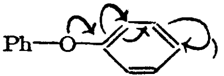
Estimated moments for $(CH_2X)_3$ (*chair form*).

Intervalency angle of X	95°	100°	105°	110°	115°	120°	125°
Intervalency angle of carbon = 105°.							
θ	43° 27′	42° 31′	41° 12′	39° 24′	37° 0′	33° 44′	28° 58′
X = O	2·7	2·6	2·6	2·5	2·3	2·1	1·9
X = S	2·9	2·8	2·8	2·7	2·5	2·3	2·0
Intervalency angle of carbon = 110°.							
θ	39° 39′	38° 37′	36° 43′	34° 28′	31° 21′	26° 55′	20° 2′
X = O	2·5	2·4	2·3	2·2	2·0	1·8	1·3
X = S	2·7	2·6	2·5	2·4	2·2	1·9	1·4
Intervalency angle of carbon = 115°							
θ	35° 46′	34° 12′	32° 5′	29° 9′	25° 0′	18° 36′	0°
X = O	2·3	2·2	2·0	1·9	1·7	1·2	0
X = S	2·5	2·4	2·2	2·0	1·8	1·3	0

The moments of the " boat " forms are of course ⅓ of the figures shown above. Comparison of the results now obtained (2·2, 2·4 D.) with the calculated values suggests that both compounds exist in a " chair " configuration, or as a mobile equilibrium in which this form considerably predominates. If the compounds are single rigid individuals then our present experiments provide immediate estimates of the valency angles, thus :

If the carbon angle = 105°, the oxygen and sulphur angles cannot be less than *ca.* 117°.
If the carbon angle = 110°, the oxygen and sulphur angles cannot be less than 110°.
If the carbon angle = 115°, the oxygen and sulphur angles cannot be less than 100°.

It is easily seen from Table I that if, instead of μ_{Me_2X}, larger values (*e.g.*, the moments reported for tetrahydrofuran and tetrahydrothiophen, Robles, *Rec. Trav. chim.*, 1939, **68**, 111) are adopted, these minimum angles would be enlarged. However, *X*-ray investigations on crystalline trioxymethylene and trithioformaldehyde (Moerman; Moerman and Wiebenga, *locc. cit.*) are in agreement with intervalency angles for oxygen and sulphur which are tetrahedral within rather wide limits of error. It is noteworthy that an assumption of 110° throughout for C, O, and S gives good accord with our measurements.

The valency angles of these elements in other compounds have been given values by various workers extending over a range of some 70°. (For references see below; Bennett and Glasstone, *loc. cit.*; Bennett, Earp, and Glasstone, *loc. cit.*) Perhaps aromatic and aliphatic compounds should be considered separately. Hampson and Sutton (*Trans. Faraday Soc.*, 1935, **31**, 945), having concluded that the O and S angles in diphenyl ether and sulphide respectively are 128° ± 4° and 113° ± 3°, point out that mesomeric shifts (such as ) could have the effect of increasing the central valency angle from the tetrahedral value up to as much as 145°, and—provided oxygen forms a double bond with an Ar-nucleus more readily than does sulphur —the planarity of diphenylene dioxide and the non-planarity of thianthren should be understandable. Yet, despite the fact that μ_{C-S} seems generally to be greater than μ_{C-O} (Hunter and Partington, *J.*, 1933, 87) the moments of 4 : 4′-dibromodiphenyl ether and sulphide are less than 0·2 D. from identical (Hampson, Farmer, and Sutton, *Proc. Roy. Soc.*, 1933, **143**, 147)—a difference of the order reported for aliphatic pairs (Hunter and Partington, *J.*, 1931, 2062; 1932, 2819) or for tetrahydrofuran and tetrahydrothiophen (Robles, *loc. cit.*). It therefore seems impracticable to take the view that either oxygen or sulphur has a "natural" intervalency angle. The possibility that the conclusions based on the dipole moments of the two structures of type (I) are not general was mentioned by Bennett and Glasstone (*loc. cit.*). The present measurements illustrate this, since by analogy with thianthren and diphenylene dioxide a much higher moment for trithioformaldehyde than for trioxymethylene should be expected; instead, the observed moments are not far from equal.

Again, with the recorded facts of the comparison (II) in mind, and applying arguments similar to those used for (? the flexible) 1 : 4-*cyclo*hexadione (Le Fèvre and Le Fèvre, *J.*, 1935, 1696), we expected the moment of 1 : 4-dithian to be greater than that of 1 : 4-dioxan. Instead we find no notable difference, dithian being non-polar within the limits of our experimental accuracy, while dioxan *may* have a small moment (as a liquid) of the order 0·4 D. Either, therefore, these two molecules (*a*) are not in mobile boat and chair equilibria at ordinary temperatures, but are flat, or (*b*) exist as rigid chair (*trans*) structures. The latter explanation requires a S angle of less than 120°, and/or a higher degree of resistance to valency deflection by S than by O. In all instances where related oxygen and sulphur compounds have been studied by the same method, the S angle has been reported as the smaller (Glasstone, *Ann. Reports*, 1935, 133; 1936, 84; Sutherland, *ibid.*, 1938, 51; Balfe and Kenyon, *ibid.*, 1942, 116); this is true even in the cases of furan and thiophen (∠COC = 107°, ∠CSC = 91°; Pauling and Schomaker, *J. Amer. Chem. Soc.*, 1939, **61**, 1769).

EXPERIMENTAL.

Materials.—The three solutes were prepared by the methods noted by Beilstein ("Handbuch", XIX, 3, 382; XIX*, 609, 804). The melting points conformed to the literature values.

Measurements.—These were made in the manner and on the apparatus described previously (*J.*, 1948, 1949). The symbols are those customarily used by us (cf. *J.*, 1937, 1805).

TABLE II.

$100w_1$.	$\epsilon^{25°}$.	$d_{4°}^{25°}$.	$\alpha\epsilon_2$.	βd_2.
0	2·2725	0·87378	—	—
Trioxymethylene in benzene.				
0·4106	2·2950	0·87475	5·48	0·236
0·4975	2·2992	0·87500	5·37	0·245
0·7751	2·3151	0·87569	5·50	0·246
0·9901	2·3285	0·87621	5·66	0·245

Dithian in benzene.

$100w_1$.	$\epsilon^{30°}$.	$d_{4°}^{30°}$.	$\alpha\epsilon_2$.	βd_2.
0	2·2626	0·86844	—	—
0·3252	—	0·86930	—	0·264
0·5074	2·2640	0·86951	0·276	0·211
0·8502	—	0·87044	—	0·235
1·2025	2·2652	0·87124	0·216	0·233
1·5560	2·2655	0·87230	0·186	0·235
2·7358	2·2685	0·87524	0·216	0·249

Trithioformaldehyde in benzene.

$100w_1$.	$\epsilon^{25°}$.	$d_{4°}^{25°}$.	$\alpha\epsilon_2$.	βd_2.
0·0851	2·2762	0·87414	4·35	0·423
0·1369	2·2775	0·87440	3·87	0·453
0·1633	—	0·87448	—	0·429
0·2008	2·2797	0·87464	3·59	0·428

$100w_1$.	$\epsilon^{25°}$.	$d_{4°}^{25°}$.	$\alpha\epsilon_2$.	βd_2.
0·2308	2·2808	0·87474	3·60	0·416
0·2433	2·2811	0·87478	3·53	0·411
0·3087	2·2822	0·87514	3·14	0·441

The extrapolated values of ${}_{T}P_1$ at infinite dilution have been calculated from the above data by the equation ${}_{T}P\infty = M_1[p_2(1 - \beta) + c\alpha\epsilon_2]$ (cf. *J.*, 1937, 1805). Temperatures of 30° were unfortunately necessitated by climatic conditions when the measurements on dithian were made. Appropriate values of p_2 and c are, for 25°, 0·3408 c.c. and 0·1881 c.c., and for 30°, 0·3411 c.c. and 0·1901 c.c. respectively. Since the drift in $\alpha\epsilon_2$ for trithioformaldehyde plotted fairly smoothly against ω_1, the value for $\omega_1 = 0$ was therefore used in the following Table. In the other two cases, and with β throughout, the figures are averages.

TABLE III.

Compound.	$\alpha\epsilon_2$.	β.	∞P_1 (c.c.).	$[R_L]_D$ (c.c.).	μ, D.
Trioxymethylene	5·50	0·278	115·3	19·3 *	$2{\cdot}1_6$
Trithioformaldehyde	4·50	0·491	155·0	37·8 †	$2{\cdot}3_8$
Dithian	$0{\cdot}22_4$	0·274	34·8	34·4 †	*ca.* 0

* Calculated as $[R]_{\text{paraldehyde}} - [R]_{C_3H_6}$.

† Calculated from atomic refractivities.

Maryott and Acree (*loc. cit.*) found $_{\infty}P_1$ for trioxymethylene in benzene at 25° to be 114·4 c.c.; this figure together with 18·8 c.c. for the distortion polarisation gives 2·18 D. for the moment.

Dipole Moment of Dioxan.—Greene and Schwingel (*J. Amer. Chem. Soc.*, 1934, **56**, 653) have shown that *as a gas* between 337° and 487° K. dioxan is non-polar. Recorded data for the liquid display variations—possibly due to the difficulties of obtaining an anhydrous pure specimen. Table IV lists the figures given by workers who have used dioxan as a solvent in dielectric-constant work.

TABLE IV.

Ref.	$\epsilon^{25°}$.	$d_{4°}^{25°}$.	$n_D^{25°}$.	$(P_1)_{25°}$, c.c.	$[R_L]_D$ c.c.
1	2·306	1·0311	1·42032	25·90	21·63
2	2·233	—	—	—	—
3	2·3060	1·02798	—	25·96	—
4	2·3051	1·0268	1·42025	26·00	21·71
5	2·2106	1·0277	—	24·64	—
6	2·2093	1·02920	—	24·58	—
7	2·2159	1·02750	—	24·72	—
8	2·2198	—	—	—	—
9	2·2178	1·02785	1·41990	25·62	21·68
	2·2075	1·02785	1·41990	24·59	
10	2·218	1·0281	—	24·73	—
	2·213	1·0278	—	24·67	—
	2·210	1·0277	—	24·63	—
	$\epsilon^{20°}$.	$d_{4°}^{20°}$.		$(P_1)_{20°}$.	
11	2·316	1·0330	—	26·00	21·7 *
	2·320	1·0340	—	26·01	
12	2·237	1·0325	—	24·90	
	2·243	1·0324	—	24·99	
	2·244	1·0326	—	25·00	

* From unquoted experimental observations in reference 11.

[1] Smyth and Walls (*J. Amer. Chem. Soc.*, 1931, **53**, 2117; 1932, **54**, 3230).

[2] Ulich and Nespital (*Z. physikal. Chem.*, 1932, *B*, **16**, 229).

[3] Le Fèvre and Le Fèvre (*J.*, 1935, 957).

[4] Frey and Gilbert (*J. Amer. Chem. Soc.*, 1937, **59**, 1344).

[5] Dostrovsky and Le Fèvre (*J.*, 1939, 535).

[6] Caldwell and Le Fèvre (*ibid.*, p. 1621).

[7] Bloom and Sutton (*J.*, 1941, 727).

[8] Berg and Jensen (*Annalen*, 1941, **548**, 116).

[9] Friediger and Jensen (*Kgl. Danske Videnskab. Selskab*, 1943, **20**, Nr. 20).

[10] Curran and Chaput (*J. Amer. Chem. Soc.*, 1947, **69**, 1134).

[11] Hunter and Partington (*J.*, 1935, 87).

[12] Cowley and Partington (*J.*, 1936, 47).

The total polarisations are seen to fall between 26·00 and 24·58 at 25° and 26·01 and 24·90 at 20°. Our own samples were *stored* over sodium in addition to having passed through the normal purification procedure (*e.g.*, that of Cowley and Partington, *loc. cit.*). Taking 24·6 c.c. as $_TP_{25°}$ and $[R_L]_D = 21·7$ c.c., the apparent moment is 0·38 D. at 20°; Cowley and Partington's lowest $_TP$, namely, 24·9 c.c., corresponds to $\mu = 0·40$ D. Greene and Schwingel (*loc. cit.*) give 24·5 c.c. as the mean polarisation over the temperature interval quoted above.

Note added May 24th, 1948.—When the above was written the paper by Hassel and Viervoll (*Acta Chem. Scand.*, 1947, **1**, 149) had not arrived in Australia. These authors report results of electron-diffraction studies on, *inter alia*, dioxan, dithian, and trithian. For all three, "staggered" or "chair" structures are indicated as the most probable. The angles recorded are: in dioxan, C–C–O = 106° and C–O–C = 108° (cf. Brockway and Sutton, *J. Amer. Chem. Soc.*, 1935, **57**, 473); in dithian, C–C–S = 111° and C–S–C = 100°; in trithian, S–C–S = 106·5° and C–S–C = 114·5°. In general, therefore, our results are reconcilable with those of Hassel and Viervoll notwithstanding the differences of method and state.

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