34. *The Valency Angle of Sulphur.*

By G. M. Bennett and S. Glasstone.

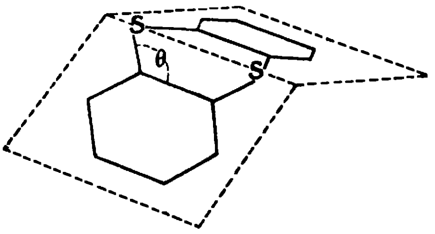
The values which have recently been ascribed to the valency angles of sulphur and oxygen are remarkably divergent. The simplest stereochemical assumption would be that the tetrahedral angle (109·5°) is normal, but figures have been put forward such as 62° and 66° (Hund, *Physikal. Z.*, 1925, **31**, 81) and 90° (Pauling, *J. Amer. Chem. Soc.*, 1931, **53**, 1367); and studies of the dipole moments of aromatic sulphur compounds and their substituted derivatives have led to values in the thiocyanates (Hunter and Partington, J., 1932, 2812) of 120° and in the sulphides of 142° (Bergmann, Engel, and Sándor, *Z. physikal. Chem.*, 1930, *B*, **10**, 397), 146° (Smyth and Walls, *J. Amer. Chem. Soc.*, 1932, **54**, 3230), and 118° ± 8° (Hampson, Sutton, and Farmer, *Proc. Roy. Soc.*, 1933, *A*, **143**, 147). The derivation of valency angles from dipole moment data has recently been critically examined by Hampson and Sutton (*Proc. Roy. Soc.*, 1933, *B*, **140**, 562), who regard the method as generally trustworthy. We are unable to accept this view and propose to discuss this question in detail in the near future.

In view of the consequent uncertainty, we wish to direct attention to a piece of available evidence the significance of which appears to have been overlooked. This is derived from the observation that thianthrene has a dipole moment of $1{\cdot}7 \times 10^{-18}$ unit in benzene solution (Bergmann and Tschudnowsky, *Ber.*, 1932, **65**, 457). As this result was unexpected and of considerable importance, we thought it desirable to confirm it experimentally and to eliminate the possibility that the observed polarisation might have been due to some influence of the solvent or to atom polarisation. The value $1{\cdot}50 \times 10^{-18}$ e.s.u. has now been found for solutions of the substance in both carbon disulphide and carbon tetrachloride (compare Smyth and Walls, *J. Chem. Phys.*, 1933, **1**, 337, who give the value $1{\cdot}41 \times 10^{-18}$ e.s.u.); and measurements at two temperatures indicate that the atom polarisation is negligible.

There can therefore be no doubt that thianthrene has a real dipole moment and must have a non-planar configuration. This was suggested by Bergmann and Tschudnowsky, but a more precise definition of the spatial arrangement is necessary. In view of the results of precise X-ray investigations of aromatic compounds (Lonsdale, *Trans. Faraday Soc.*, 1929, **25**, 356; *Proc. Roy. Soc.*, 1931, *A*, **133**, 536; Robertson, *Proc. Roy. Soc.*, 1933, *A*, **141**, 79, 594; Pickett, *ibid.*, **142**, 333), it is reasonable to assume that each aromatic nucleus and its directly attached atoms have a strong tendency to remain in a single plane. The non-planar configuration of the whole thianthrene molecule should consequently be one in which the molecule is bent across the middle of the central (heterocyclic) ring as shown in the adjacent figure. The two halves of the molecule lie in two inclined planes, the line of their intersection being that joining the two sulphur atoms in space. At the same time the molecule must be flexible about the middle line to some extent, for an entirely rigid configuration of the type depicted should lead to a number of additional stereoisomerides among the derivatives of thianthrene, whereas a careful study of the sulphoxides of several thianthrenes in this laboratory (shortly to be described) has given no evidence of this.

Consideration of this arrangement shows that it cannot arise in consequence of any tendency for the valency angle of the sulphur atoms to exceed 120°. A large angle of 140° or more would inevitably favour a completely planar structure of the molecule. The non-planar configuration appears to be a definite indication of a tendency for the valency bonds of sulphur to adopt an angle of *less than* 120°. This conclusion has been found, on further examination, to be in no way weakened by any possible influence of the different diameters of the sulphur and the carbon atom, nor by the deviation from exactly radial directions of the outer valencies of a benzene nucleus demonstrated by Mills and Nixon (J., 1930, 2510).

In the latter connexion the capacity of the benzene nucleus to adjust itself in such a way as to cause the angle θ to be either larger or smaller than 120° may be regarded as a buffer mechanism which should render any particular sulphur valency-angle less likely to cause a departure from the planar configuration than would be the case in its absence. That an attached six-membered ring may impose the larger nuclear angle θ was shown by Mills and Nixon for tetrahydronaphthalene. Apart from the stereochemical factors there is also the " chemical " or polar effect of the sulphur atoms to be considered. Of this we have no certain knowledge, but it seems probable that the well-known divergence of the dipole moments of *o*-disubstituted derivatives of benzene from the values calculated by vectorial addition is due, at least in part, to an actual angular outward deflexion of these two atoms or groups. Any such effect should tend to cause a separation of the sulphur atoms of thianthrene and would again lead to an angle θ larger than 120°. Such a conclusion serves to strengthen our deduction as to the valency angle of sulphur.



EXPERIMENTAL.

Measurements of the dielectric constants of solutions of thianthrene in carbon tetrachloride and carbon disulphide were made by the heterodyne beat method in an apparatus which will be described in a subsequent paper. Observations of the refractive index of the solutions were made with a Pulfrich refractometer using sodium light. The data and the calculated polarisations are given in the table below, where the symbols have their usual significance.

f_2.	ε.	*d*.	*n*.	P_2.	P_E.	P_{A+O}.
(In carbon tetrachloride at 24·92°.)						
—	2·230	1·5880	1·45457	—	—	—
0·004690	2·251	1·5851	1·45706	122·9	73·9	49·0
0·008644	2·268	1·5828	1·45916	121·1	73·4	47·7
whence $P^{\infty}_{A+O} = 51$; $\mu = 1·54 \times 10^{-18}$ e.s.u.						
(In carbon disulphide at 24·20°.)						
—	2·633	1·2580	1·62527	—	—	—
0·006858	2·652	1·2588	1·62736	113·9	71·5	42·4
0·017099	2·730	1·2595	1·63031	107·0	68·1	38·9
whence $P^{\infty}_{A+O} = 46$; $\mu = 1·47 \times 10^{-18}$ e.s.u.						
(In carbon disulphide at 0·0°.)						
—	2·703	1·2951	—	—	—	—
0·007612	2·762	1·2958	—	120·2	—	—

The data for P_2 at 0° (120) and at 24·2° (114) lead to a value of μ of the order $1·8 \times 10^{-18}$ e.s.u. Although this cannot be regarded as an accurate determination of dipole moment, yet it serves to show that atom polarisation is not an important factor.

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