256. *The Valency Angle of Oxygen.*

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It has been shown (this vol., p. 128) that the large dipole moment (1·5 *D*) of thianthrene implies that the valency bonds of sulphur in this compound make an angle of less than 120° with one another, and consequently the natural valency angle of sulphur is also less than 120°. It seemed of interest, therefore, to study the polarisation of the corresponding oxygen compound, diphenylene dioxide, in order to obtain information on the valency angle of oxygen. Measurements have now been made in carbon tetrachloride, *cyclo*hexane, and benzene solutions, and the results show that the substance has no appreciable dipole moment. A small consistent difference between the total and the electron polarisation appears from the observations in carbon tetrachloride solutions, but this is probably due to a compound with the solvent rather than to the diphenylene dioxide itself.

The zero dipole moment of the dioxide indicates that the molecule is planar with an angle of about 120° between the oxygen bonds; the minimum value for the natural valency angle of oxygen in compounds of the same type must thus be 120°. Although there is evidence that in water (Barnes, *Proc. Roy. Soc.*, 1929, **125**, *A*, 670; Mecke, Baumann, and Freudenberg, *Z. Physik*, 1933, **81**, 313, 445, 465; van Vleck and Cross, *J. Chem. Physics*, 1933, **1**, 357), dimethyl ether (Pai, *Curr. Sci.*, 1934, **2**, 386), and arsenious and antimonous oxides (Bozorth, *J. Amer. Chem. Soc.*, 1923, **45**, 1621) the oxygen bond angle is 110° or less, yet an analysis of the dipole moments of some diphenyl ethers (Bennett and Glasstone, *Proc. Roy. Soc.*, 1934, **145**, *A*, 71) indicates that in these substances the angle is probably larger than the tetrahedral value. Recently, Hampson (Faraday Soc. Discussion, April, 1934), using another method, has calculated from similar data values of 124—132° for the oxygen-bond angle in these ethers. Since diphenylene dioxide may be regarded as a substituted diphenyl ether, the result of the present work is consistent with these conclusions. It is important to emphasise, however, that there is no justification for supposing that the valency angle of oxygen in other compounds is necessarily the same as in the diphenyl ethers.

Preparation of Diphenylene Dioxide.—The procedure described in D.R.P. 223,367 (1910) (Friedländer, Vol. X, 155) suggested a more convenient method than that used by Ullmann and Stein (*Ber.*, 1906, **39**, 623); the claim there made, however, appears to be exaggerated. The substance was obtained readily, although in poor immediate yield, by mixing *o*-bromophenol (28 g.), powdered potassium hydroxide (7 g.), and copper powder (1 g.) in a retort, and heating the mixture at atmospheric pressure so long as any distillate came over. Water and bromophenol distilled, and the diphenylene dioxide (1 g.) was obtained by collecting the whole distillate, making it alkaline, and filtering. The product after crystallisation from light petroleum was pure (m. p. 121°). The use of reduced pressure did not appear to be of any advantage. In the absence of copper powder the yield was extremely small.

Measurement of Dipole Moment.—The experimental details were the same as in the previous work (*loc. cit.*), and all measurements were made at 20·0°. The results obtained are given below, w_1 and w_2 being the weights of solvent and solute, respectively, and the other symbols having their usual significance; the method of calculating the polarisations was the simplified one which does not involve the use of molar fractions (cf. de Bruyne, Davis, and Gross, *J. Amer. Chem. Soc.*, **1933**, **55**, **3936**; Sugden, Faraday Soc. Discussion, April **1934**).

w_1.	w_2.	n_D.	ϵ.	d.	P_E.	P_2.
Carbon tetrachloride solutions.						
105·55	4·0094	1·46819	2·271	1·5782	53·1	58·7
106·24	3·0822	1·46681	2·269	1·5819	54·2	60·9
106·58	2·0467	1·46423	2·255	1·5860	52·9	56·5
102·95	1·0912	1·46304	2·252	1·5896	55·7	61·4
Pure CCl_4		1·46025	2·243	1·5943	26·47	28·28
*cyclo*Hexane solutions.						
49·305	2·0064	1·43117	2·045	0·7895	54·1	53·7
47·862	1·5152	1·43006	2·042	0·7870	54·0	53·2
47·959	1·0806	1·42906	2·039	0·7847	54·5	52·4
Pure C_6H_{12}		1·42634	2·032	0·7784	27·71	27·65
Benzene solutions.						
54·672	3·0246	1·50395	2·304	0·8897	53·6	59·1
54·411	2·0725	1·50237	2·295	0·8858	53·4	57·1
53·985	1·0177	1·50088	2·287	0·8809	54·3	55·3
Pure C_6H_6		1·49929	2·281	0·8763	26·15	26·65

It is evident from these results that the dipole moment of diphenylene dioxide is either very small or zero.

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