**350.** *The Electric Dipole Moments of Diphenyl Ether and Some Derivatives in the Vapour Phase ; and a Revision of the Oxygen Valency Angle in these Compounds.*

By I. E. Coop and L. E. Sutton.

From the electric dipole moments of diphenyl ether and $p$-substituted or $pp'$-disubstituted derivatives it is in principle possible to calculate values of the angle between the C–O valencies. If no account is taken of the effect of interaction between the substituent groups and the ether group, the values obtained vary greatly and are obviously unreliable. In an earlier communication a method of making an allowance for this was described, which, when applied to measurements made in solution, gave a value of 128° ± 4°.

Owing to the fact that the solvent may have a considerable effect on the value observed for a dipole moment, it appeared possible that further error in the angle would arise from this cause, although according to current theories of the solvent effect this should not be serious. In order to verify the angle value, the moments of diphenyl ether and a number of suitable derivatives have now been determined in the vapour phase, and they give a corrected value of 124° ± 5°, which is in satisfactory agreement with the earlier one.

THE possibility of determining the oxygen valency angle in diphenyl ether from measurements of the moments of this and some derived ethers was suggested by Bergmann and his co-workers (*Z. physikal. Chem.*, 1930, *B*, **10**, 397; 1932, *B*, **17**, 107) and by Smyth and Walls (*J. Amer. Chem. Soc.*, 1932, **54**, 3230). The method was critically examined by various workers (Hampson and Sutton, *Proc. Roy. Soc.*, 1933, *A*, **140**, 562; Hampson, Farmer, and Sutton, *ibid.*, 1933, *A*, **143**, 147; Bennett and Glasstone, *ibid.*, 1934, *A*, **145**, 71; Bennett, *Trans. Faraday Soc.*, 1934, **30**, 853; Sutton and Hampson, *ibid.*, 1935, **31**, 945), and methods of eliminating the most important of the probable errors have been developed.

The measurements have hitherto all been made in solution, and although it was certain that the solvent effect would modify the individual moments of the compounds, it seemed probable that this would have little or no effect upon the angles calculated from them

(Sutton and Hampson, *loc. cit.*). Nevertheless, it was obviously very desirable that measurements of the moments in the vapour phase should be made, and this has accordingly been done for diphenyl ether and its *p*-bromo-, *pp'*-dibromo-, *pp'*-dimethyl, *p*-nitro-, and *p*-bromo-*p'*-methyl derivatives.

## EXPERIMENTAL.

*Preparation and Purification of Materials.*—The specimens were those used in solution measurements (Hampson, Farmer, and Sutton, *loc. cit.*). They were recrystallised as described therein and had the same m. p.'s, within experimental error. (The b. p. range 238—245° given for *pp'*-dibromodiphenyl ether in the above paper was a misprint for 338—345°/760 mm.)

*Measurement of Dipole Moments.*—The dipole moments were measured in the apparatus described by Coop and Sutton (this vol., p. 1269). All the compounds were solids, and the method of measurement was the same as that already described. The values of the total polarisation refer, as before, to the standard $\varepsilon = 1.000582$ for dry air, free from carbon dioxide, at 0° and 760 mm.

All the compounds were rather unstable under the conditions of measurement, gaseous decomposition products being formed which condensed in liquid air but not at room temperatures. As the pressures of vapour measured were very small, even a pressure of a few tenths of a mm. of decomposition products was sufficient to cause serious errors. To a certain extent these were overcome by measuring each time the pressure and polarisation of the products and thus allowing for them. As a result, not only of the decomposition but also of the small temperature ranges possible, the optical method was adopted for calculating the dipole moment, the electron polarisation values being taken from Hampson, Farmer, and Sutton (*loc. cit.*) or Sutton and Hampson (*loc. cit.*). For all the compounds we have adopted the convention of allowing 5% of $P_E$ for $P_A$ (Groves and Sugden, J., 1937, 1779). In view of the absence of highly polar bonds, this is probably as accurate an estimate as our present knowledge allows, and only in the case of *pp'*-dibromodiphenyl ether is this uncertainty likely to cause a greater error than that arising from decomposition. In determining the errors in the dipole moments given below, an uncertainty of $\pm 1$ c.c. in the total polarisation values has been assumed, this being a maximum estimate. For *p*-nitrodiphenyl ether, which was very unstable, we have allowed an error of $\pm 20$ c.c.

In the following tables, $T$ represents the absolute temperature, $N$ the number of complete measurements at that temperature, $p$ the pressure range to the nearest mm., $P$ the mean observed polarisation, and $\mu$ the dipole moment. The use of different samples is indicated by signs in the first column.

### TABLE I.

| $T$. | $N$. | $p$. | $P$. | $\mu$. |
|---|---|---|---|---|
| *Diphenyl ether.* | | | | |
| 444·5° | 5 | 27—50 | 73·4 | 1·14 |
| *482·9 | 7 | 18—78 | 71·9 | 1·13 |
| †482·9 | 4 | 39—70 | 72·0 | 1·13 |

$P_E = 52.8$ c.c.; $(P_A = 2.6$ c.c.$)$;
$\mu = 1.14 \pm 0.02$ D.

| $T$. | $N$. | $p$. | $P$. | $\mu$. |
|---|---|---|---|---|
| *p-Bromodiphenyl ether.* | | | | |
| 516·2 | 6 | 26—55 | 106·9 | 1·89 |
| *516·2 | 5 | 25—60 | 107·3 | 1·90 |

$P_E = 61.0$ c.c.; $(P_A = 3.05$ c.c.$)$;
$\mu = 1.90 \pm 0.02$ D.

| $T$. | $N$. | $p$. | $P$. | $\mu$. |
|---|---|---|---|---|
| *pp'-Dibromodiphenyl ether.* | | | | |
| 516·8 | 5 | 25—42 | 82·2 | 0·85 |
| *516·8 | 6 | 18—39 | 82·6 | 0·87 |

$P_E = 70.0$ c.c.; $(P_A = 3.5$ c.c.$)$;
$\mu = 0.86 \pm 0.05$ D.

| $T$. | $N$. | $p$. | $P$. | $\mu$. |
|---|---|---|---|---|
| *Di-p-tolyl ether.* | | | | |
| 501·5 | 5 | 26—72 | 91·0 | 1·43 |
| *501·5 | 5 | 29—74 | 91·8 | 1·45 |

$P_E = 62.7$ c.c.; $(P_A = 3.1$ c.c.$)$;
$\mu = 1.44 \pm 0.03$ D.

| $T$. | $N$. | $p$. | $P$. | $\mu$. |
|---|---|---|---|---|
| *p-Bromophenyl p-tolyl ether.* | | | | |
| 501·5 | 5 | 23—45 | 140·5 | 2·39 |
| *517·8 | 5 | 29—48 | 138·3 | 2·39 |

$P_E = 67.1$ c.c.; $(P_A = 3.35$ c.c.$)$;
$\mu = 2.39 \pm 0.02$ D.

| $T$. | $N$. | $p$. | $P$. | $\mu$. |
|---|---|---|---|---|
| *p-Nitrodiphenyl ether.* | | | | |
| 498·9 | 2 | 16—19 | 311 | 4·41 |
| *516·2 | 3 | 19—22 | 308 | 4·46 |

$P_E = 62.2$ c.c.; $(P_A = 3.1$ c.c.$)$;
$\mu = 4.44 \pm 0.18$ D.

In view of the considerable difference between the moments of diphenyl ether as now reported, 1·14 D., and as given by Groves and Sugden, 1·35 D. (J., 1937, 1782), three different samples were measured in the present determination. They were recrystallised several times without change of m. p., and several measurements were made on each sample as indicated.

Furthermore, the cell calibration was repeated and found to be unchanged. If, as Groves and Sugden's value would indicate, there is a considerable solvent effect for diphenyl ether, then this would also be expected in ditolyl ether; but our value for the latter substance shows none and is therefore consistent with our value for diphenyl ether (cf. p. 1872).

## DISCUSSION.

Just as with the solution data, so with the vapour data, widely differing values for the valency angle are obtained if no allowance is made for the effect of interaction between the ether group and the $p$-substituents in either or both benzene rings. They are given in Table II, where, under the headings $\mu_O$, $\mu_S$, and $\mu_T$, are the names of the substances whose moments were used as the original, substituent, and total moments respectively (see Hampson and Sutton, *loc. cit*) for the several calculations of $\theta$, the uncorrected angle between the ether valencies. For convenience, the angles calculated from solution measurements are here included.

### TABLE II.

| $\mu_O$. | $\mu_S$. | $\mu_T$. | $\theta_{vap.}$. | $\theta_{soln.}$. |
|---|---|---|---|---|
| Diphenyl ether | Bromobenzene | $p$-Bromodiphenyl ether | 162° | 142° 40' |
| ,,  ,, | ,, | $pp'$-Dibromodiphenyl ether * | 108·5° | 123° 30' |
| ,,  ,, | Toluene | Di-$p$-tolyl ether | 132° | 142° |
| ,,  ,, | Nitrobenzene | $p$-Nitrodiphenyl ether | >180° | >180° |
| Di-$p$-tolyl ether | $p$-Bromotoluene | $p$-Bromophenyl $p$-tolyl ether | 166° | 139° |

* The resultant dipole of this compound was assumed to have its *positive* pole towards the oxygen atom, *i.e.*, to be anti-parallel to that of the parent ether (Sutton and Hampson, *loc. cit.*).
The values of the moments (in D.) used are : Diphenyl ether, 1·14; $p$-bromodiphenyl ether, 1·90; $pp'$-dibromodiphenyl ether, 0·86; di-$p$-tolyl ether, 1·44; $p$-bromophenyl $p$-tolyl ether, 2·39; $p$-nitrodiphenyl ether, 4·44; bromobenzene, 1·71 (Groves and Sugden, J., 1935, 971); toluene, 0·37 (McAlpine and Smyth, *J. Amer. Chem. Soc.*, 1933, **55**, 453); $p$-bromotoluene (calc. as 1·71 + 0·37), 2·08; nitrobenzene, 4·23 (Groves and Sugden, J., 1934, 1094).

The variations in the values found from vapour and from solution data are parallel; thus the nitro-ether, the bromo-ether, the ditolyl ether, and the bromophenyl tolyl ether all give high values, while the dibromo-ether gives low ones : but the variations seem to be more extreme in the vapour series than in the solution series.

If allowance for interaction of the ether and the substituent groups be made by the method developed previously (Sutton and Hampson, *loc. cit.*), much more concordant values are obtained (see Table III). As before, two sets of corrected values have been calculated, one based on the assumption that the interaction in each substituted ring is the same in the mono- as it is in the di-substituted compound ($\delta_1\mu_S = \delta_2\mu_S$), and the other on the assumption that the interaction in the former is twice that in the latter ($\delta_1\mu_S = 2\delta_2\mu_S$); these being the extremes between which the true state of affairs probably lies.

### TABLE III.

| Parent ether and substituted groups. | $\delta_1\mu_S = \delta_2\mu_S$. | | | $\delta_1\mu_S = 2\delta_2\mu_S$. | | |
|---|---|---|---|---|---|---|
| | $\theta_{vap.}$. | ($\theta_{soln.}$). | $\delta_1\mu_S$. | $\theta_{vap.}$. | ($\theta_{soln.}$). | $\delta_1\mu_S$. |
| Diphenyl ether; bromo- ......... | 124° | (132°) | 0·43 | 118° | (128°) | 0·50 |
| Di-$p$-tolyl ether; bromo- ......... | 128 | (126) | 0·55 | 125·5 | (123) | 0·63 |

The most probable value for the angle therefore appears to be 124° ± 5°. The agreement of this with the best value obtained from solution measurements, 128° ± 4°, within the limits of error assigned, bears out very well the prediction made on the basis of the theory of solvent effects, and gives increased confidence in determinations of valency angle made by the method used above. The latest value also agrees quite well with one obtained by an electron-diffraction investigation of $pp'$-di-iododiphenyl ether (Maxwell, Hendricks, and Mosley, *J. Chem. Physics*, 1935, **3**, 699) of 118° ± 3°. It is therefore certain that the oxygen valency angle in diphenyl ether and its derivatives is considerably larger than that in dimethyl ether, a phenomenon which may be attributed to " resonance " (Sutton and Hampson, *loc. cit.*).

The fact that the uncorrected angles from vapour data show a larger scatter than those from solution data is reflected in Table III by the values of $\delta_1\mu_S$ or $\delta_2\mu_S$ being larger also (cf. Sutton and Hampson, *loc. cit.*, Table 3).

Attention may be directed to the fact that the moments of the several ethers are differently affected by solvent, as Table IV shows. For instance, those ethers, (1) and (4),

TABLE IV.

| | | $\mu_{soln.}$ | |
| Ether. | $\mu_{vap.}$ | *n*-Hexane ($\epsilon = 1.89$). | Benzene ($\epsilon = 2.27$). |
|---|---|---|---|
| (1) Diphenyl | 1·14 | 1·18 | 1·16 |
| (2) Monobromodiphenyl | 1·90 | 1·75 | 1·59 |
| (3) Dibromodiphenyl | 0·86 | 0·43 | 0·28 |
| (4) Ditolyl | 1·44 | — | 1·42 |
| (5) Bromophenyl tolyl | 2·39 | — | 1·98 |
| (6) Nitrodiphenyl | 4·44 | — | 4·29 |

in which the main moments are those of the C–O links, and in which therefore the polar unit consists of two dipoles close together and each at an angle of about 60° to the axis of symmetry, are but little affected. On the other hand, the ethers which have also a polar bond or group projecting from one or both of the benzene rings have their moments considerably reduced by the solvent. This difference of behaviour agrees with the predictions of the theory of solvent effect developed by Frank (*Proc. Roy. Soc.*, 1935, *A*, **152**, 171) and by Higasi (*Sci. Papers Inst. Phys. Chem. Res. Tokio*, 1936, **28**, 284).

THE DYSON PERRINS LABORATORY, OXFORD.