

421. *The Dipole Moments of Vapours. Part VI. Bond Moments and Mesomeric Moments.*

By L. G. GROVES and S. SUGDEN.

An approximate method has been worked out for calculating the induced dipoles produced in the non-polar parts of a molecule by induction from a primary dipole. This method, which is a development of that suggested by Frank (*Proc. Roy. Soc.*, 1935, *A*, 152, 171), allows for the rapid variation of electric field in the neighbourhood of the dipole.

When these induced moments are allowed for, fairly consistent bond moments for polar groups can be obtained from the data for aliphatic compounds. When these bond moments are used to compute the moments of aromatic compounds, it is found that in these substances additional moments are present which are identified as the mesomeric moments which correspond with the permanent electronic displacements postulated in the general electronic theories of organic reactions.

The directions of the mesomeric moments obtained from the dipole observations are in agreement with those deduced from organic reactions. In general, aromatic compounds containing ortho-para-directing groups exhibit large mesomeric moments whilst those containing meta-directing groups possess much smaller mesomeric moments.

IN Parts I—V of this series we have recorded measurements of the dipole moments of 53 substances in the vapour state. These, together with other observations in the literature,

provide a considerable mass of data which are not subject to error due to solvent effect. In the present paper an attempt is made to analyse the observed moments in terms of bond moments and, in the case of aromatic compounds, to obtain information concerning the magnitude and direction of the mesomeric moments.

The chief difficulties encountered in such an analysis are connected with (a) valency angles and (b) induction within the molecule. Many attempts have been made to determine valency angles by the combination of suitable measurements of dipole moments (usually in solution) but such computations are beset with many sources of error. Wherever possible we have used the values of valency angles given by the analysis of band spectra, or X-ray or electron diffraction, as these methods in our opinion give more accurate values.

Sutton (*Proc. Roy. Soc.*, 1931, A, 133, 668) has already discussed the dipole-moment evidence for the existence and direction of mesomeric moments. He used dipole moments determined in solution, and to allow for the induction, compared (when possible) *tert.*-butyl compounds with aromatic compounds. The following discussion deals only with dipole moments in the vapour state, and an attempt has been made to deal with induction quantitatively. Our general conclusions agree qualitatively with those of Sutton, but we believe that we have obtained a closer estimate of the magnitude of the mesomeric moments.

The calculation of induction within the molecule can only be carried out approximately, but by using a method of graphical integration suggested by Frank (*Proc. Roy. Soc.*, 1935, A, 152, 171), the magnitude and direction of the induced moments can be computed with sufficient accuracy. It is, of course, necessary to adopt some simplified model of a molecule in order to make the problem amenable to calculation. Two such models have been used elsewhere. Smyth and McAlpine (*J. Chem. Physics*, 1933, 1, 190) calculated the induction in each bond and obtained the bond polarisabilities in terms of bond refractions. Smallwood and Herzfeld (*J. Amer. Chem. Soc.*, 1930, 52, 1919) regard each atom or group as a sphere of uniform polarisability and calculate the induced moment by assuming that this sphere is subjected to a field which is that produced at the centre of the sphere by the primary dipole. This model is sufficiently accurate when the atom or group is several A. distant from the primary dipole, for the field is then nearly constant over the volume of the atom considered. When the atom is near the primary dipole, the field is no longer approximately uniform, and some allowance must be made for the change in the field over the volume of the atom. This can be done by means of the graphical integration suggested by Frank.

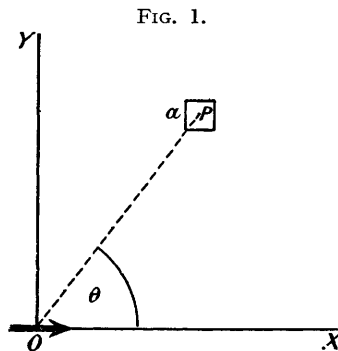


FIG. 1.

Let the primary dipole of moment μ be situated at the origin and directed along the X axis (Fig. 1). At a point P the fields in the X and the Y direction are given by

$$\begin{aligned} E_x &= \mu(3 \cos^2 \theta - 1)/\epsilon_0 r^3 \\ E_y &= \mu(3 \sin \theta \cos \theta)/\epsilon_0 r^3 \end{aligned} \quad \dots \dots \dots (1)$$

and

where $r = OP$ and ϵ_0 is the dielectric constant of the intervening medium.

The induced moment per unit volume, I , is equal to $E(\epsilon - 1)/4\pi$, where ϵ is the dielectric constant of the atom at P. Hence, if δV is the volume of the atom, the induced moment in the OX direction is

$$\mu_{ix} = [\delta V(\epsilon - 1)/4\pi][\mu(3 \cos^2 \theta - 1)/\epsilon_0 r^3]$$

Now if R is the refraction of the atom

$$\frac{R}{N} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{Nd} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \delta V = \frac{4\pi\alpha}{3}, \text{ whence } \delta V = \frac{4\pi\alpha}{3} \cdot \frac{\epsilon + 2}{\epsilon - 1}$$

and

Similarly,

$$\begin{aligned} \mu_{ix} &= \mu\alpha[(\epsilon + 2)/3\epsilon_0][(3 \cos^2 \theta - 1)/r^3] \\ \mu_{iy} &= \mu\alpha[(\epsilon + 2)/3\epsilon_0][3 \sin \theta \cos \theta/r^3] \end{aligned} \quad \dots \dots \dots (2)$$

If r is large, then equations (2) can be used to compute μ_{ix} and μ_{iy} in a manner similar to that of Smallwood and Herzfeld. If r is small, it is necessary to use the method of graphical integration. Consider, first, the X component. For a small square of side a at P , the volume of the ring produced by revolution of the square about the OX axis is $2\pi r a^2 \sin \theta$. If β is the polarisability per unit volume, the moment produced in this ring, in the OX direction, is

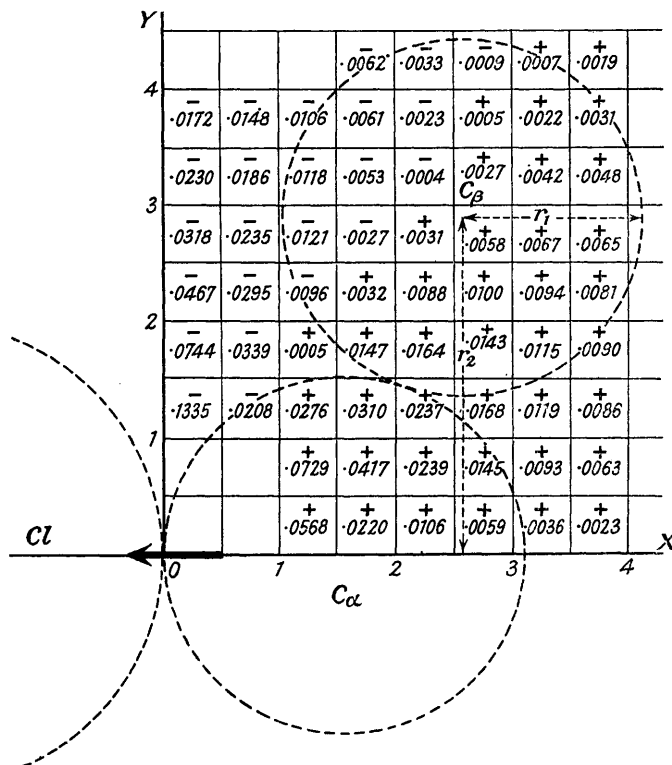
$$\mu_{ix} = [\mu(\epsilon + 2)/3\epsilon_0]\beta[a^2 2\pi r \sin \theta(3 \cos^2 \theta - 1)/r^3]$$

or

$$\mu_{ix}/\mu = \beta[(\epsilon + 2)/3\epsilon_0][2\pi \sin \theta(3 \cos^2 \theta - 1)a^2/r^2]$$

Now the quantity $A = \sin \theta(3 \cos^2 \theta - 1)a^2/r^2$ is dimensionless. Let it be computed for each of a number of small squares in the YOX quadrant, and the actual value of A

FIG. 2.



inserted in each such element of area. Now, choosing a suitable scale, draw on this diagram circles of diameter appropriate to the atoms concerned (Fig. 2 shows such a diagram with a scale sectional drawing for ethyl chloride superimposed). The primary dipole is assumed to be situated at the point of contact of the chlorine and the α -carbon atom, and the induced moment in the β -carbon is to be determined. Let ΣA_x be the sum of the values of A for the elementary squares and parts thereof included in the circle C_β . Then the induction in the anchor ring produced by revolution of this circle about the OX axis, $\mu_{ix}/\mu = [(\epsilon + 2)/3\epsilon_0]\beta \cdot 2\pi \cdot \Sigma A_x$. The volume of this ring is $\pi r_1^2 \cdot 2\pi r_2$, and that of the C_β atom is $\frac{4}{3} \cdot \pi r_1^3$. Hence, it being assumed that the induction in the sphere representing the C_β atom is to induction in the anchor ring in the ratio of their volumes, the induced moment in C_β in a direction parallel to the primary dipole is

$$\mu_{ix} = \mu\beta(4\pi r_1^3/3)[(\epsilon + 2)/3\epsilon_0]\Sigma A_x/\pi r_1^2 r_2$$

whence, since $\alpha = \beta \cdot \frac{4}{3} \cdot \pi r_1^3$,

$$\mu_{ix}/\mu = \alpha[(\epsilon + 2)/3\epsilon_0]\Sigma A_x/\pi r_1^2 r_2 \quad \dots \quad (3)$$

Similarly for the Y component we have (for the element of area a^2) a ring produced by revolution about the OY axis of volume $a^2 \cdot 2\pi r \cos \theta$ and

$$\mu_{iy} = \mu \cdot \beta \cdot a^2 \cdot 2\pi r \cos \theta \cdot 3 \sin \theta \cos \theta (\epsilon + 2) / 3\epsilon_0 r^3$$

or

$$\mu_{iy}/\mu = 2\pi\beta[(\epsilon + 2)/3\epsilon_0] 3 \sin \theta \cos^2 \theta / (r^2/a^2)$$

Writing A_y for the dimensionless quantity $3 \sin \theta \cos^2 \theta / (r^2/a^2)$, we can evaluate this for each unit of area on a second diagram, and following an identical procedure to that used in obtaining equation (3),

$$\mu_{iy}/\mu = \alpha[(\epsilon + 2)/3\epsilon_0] \Sigma A_y / \pi r_1^2 r_2 \dots \dots \dots (4)$$

In this equation r_2 refers to the distance of the centre of the atom from the Y axis. The values of the constants in equations (3) and (4) now require consideration. Values of α for aliphatic compounds are readily obtained from the refractions, and those for the aromatic compounds are derived from the work of Stuart and Volkmann (*Ann. Physik*, 1933, 18, 121):

Values of α , c.c. $\times 10^{-24}$.			
Aliphatic.		Aromatic.	
H	0.433	CH_2	1.82
C	0.961	CH_3	2.25
CH	1.39	CH (in plane of ring)	2.06
		C (atom 1 in phenyl radical)	1.63

Values for ϵ and ϵ_0 are less certain; little error is introduced, however, in assigning to these quantities 2.0 for aliphatic compounds and 2.4 for aromatic compounds.

Atomic radii, A.		Internuclear distances, A.	
C (al.)	0.77	N	0.70
C (ar.)	0.70	Cl	1.00
H	0.32	Br	1.14
O	0.66	I	1.33
		C—Cl (al.)	1.76
		C—Cl (ar.)	1.69
		C—Br (al.)	1.93
		C—Br (ar.)	1.88
		C—O (al.)	1.43
		C=O (al.)	1.28
		C \equiv N	1.16

In discussing induction within the molecule it is necessary to adopt some convention concerning the induction in the atoms which are joined by the bond in which the dipole is assumed to be situated. Thus, for example, in methyl chloride one might adopt the model of a primary dipole of negligible length situated between the carbon and the chlorine atom and then attempt to calculate the induction in the carbon and the chlorine atom. This induction would, however, be very large and would vary rapidly with changes in position of the dipole. It is indeed very doubtful whether the model of a dipole of negligible length is adequate to deal with this problem.

We have therefore adopted the convention of neglecting the induction in the atoms which are immediately adjacent to the dipole, and our "bond moments" therefore include the induction in these adjacent atoms. This convention is convenient since our main object was to determine such bond moments from aliphatic compounds and then, by comparison with appropriate aromatic compounds, to determine the sign and magnitude of the mesomeric moments.

Numerical Calculations.

Convention as to Sign of Moments.—Since we are mainly interested in determining whether the mesomeric moment is parallel or opposed to the primary moment, and since all the aromatic compounds considered have the negative end of the dipole remote from the ring, we have assigned positive values to such dipoles to avoid a multiplicity of minus signs in the calculations. This convention is, of course, the reverse of that used by Sutton (*loc. cit.*); to comply with his convention all the signs in Table II should be reversed.

(1) *Nitriles.*—*Acetonitrile.* The primary dipole $\text{C}\equiv\text{N}$ is assumed to be midway between the nuclei, *i.e.*, 0.58 A. from the carbon nucleus. For the methyl carbon atom $\Sigma A_x = 0.0661$. In this case, since the atom is on the dipole axis, revolution of the semicircle drawn on the diagram gives a sphere and hence the induction directly.

$$\mu_{ix}/\mu_{\text{C}\equiv\text{N}} = [(\epsilon + 2)/3\epsilon_0](\alpha/(\frac{4}{3}\pi r_1^3)) \cdot 2\pi \cdot \Sigma A_x = 0.138$$

For each hydrogen atom $\Sigma A_x = 0.0266$ and $r_2 = 1.04$, hence

$$\mu_{ix}/\mu_{\text{C}\equiv\text{N}} = 0.433 \times (4/6) \times 0.0266 / (6\pi \times 0.32^2 \times 1.04) = 0.023$$

The Y components vanish by symmetry, and we therefore have the total induction parallel to the primary dipole and $\mu_{ix}/\mu = 0.138 + (3 \times 0.023) = 0.207$. Hence

$$\mu_{\text{CH}_3\text{CN}} = \mu_{\text{CN}} + \mu_{ix} = 1.207\mu_{\text{CN}} = 3.94, * \text{ i.e., } \mu_{\text{CN}} = 3.94/1.207 = 3.26.$$

In this calculation the shared electrons which hold the hydrogen atoms are assumed to be spread over the hydrogen sphere, whereas in fact they are largely located between the hydrogen and the carbon nuclei. A closer approximation to the true induction will probably be given by assigning the whole polarisability of the methyl group to the sphere representing the carbon atom. On this hypothesis $\mu_{ix}/\mu_{\text{CN}} = 2.25 \times 0.0661/0.77^3 = 0.326$, whence $\mu_{\text{CN}} = 3.94/1.326 = 2.97$.

Propionitrile. For the CH_2 group, $\mu_{ix} = 0.264\mu_{\text{CN}}$ and $\mu_{iy} = 0$. For the CH_3 group, $\mu_{ix} = 0.067\mu_{\text{CN}}$ and $\mu_{iy} = 0.074\mu_{\text{CN}}$. Hence the total moment $= \mu_{\text{CN}}(1.331^2 + 0.074^2)^{1/2} = 1.333\mu_{\text{CN}}$; i.e., $\mu_{\text{CN}} = 4.04/1.333 = 3.03$. This is in good agreement with the value 2.97 calculated from acetonitrile. The moment of the $\text{C}\equiv\text{N}$ dipole may therefore be taken as 3.00 ± 0.03 . This differs little from the moment of hydrogen cyanide, viz., 2.88.

Benzonitrile. μ_{iy} vanishes by symmetry, and we are left with μ_{ix} alone:

Atom	C ₁	C ₂ (× 2)	C ₃ (× 2)	C ₄	Total = 0.441.
μ_{ix}/μ_{CN}	0.246	0.126	0.052	0.017	

Hence assuming $\mu_{\text{CN}} = 3.00$, $\mu_{\text{calc.}}$ for benzonitrile $= 1.441 \times 3.0 = 4.32$; since $\mu_{\text{obs.}} = 4.37$, the mesomeric moment is $+0.05$. This is small, but is in the direction predicted by theory.

(2) *Halides.*—The primary moment μ is of necessity identified with the observed moment of the methyl derivatives.

Ethyl halides. For the β -carbon atom, $\Sigma A_x = 0.076$ and $r_2 = 1.47$. If we take $\alpha = 1.82$ —the value for CH_2 —to allow for the hydrogen atom replaced in CH_2X , $\mu_{ix}/\mu = 0.034$. $\Sigma A_y = 0.4731$ and $r_2 = 1.30$, whence $\mu_{iy}/\mu = 0.237$ and the resultant moment $= (1.034^2 + 0.237^2)^{1/2}\mu = 1.061\mu$.

isopropyl halides. $\mu_{ix}/\mu = 2 \times 0.034$ and $\mu_{iy}/\mu = 0.237$, since this is the resultant of the Y components of the two methyl groups which are at 120° to one another. The resultant moment is given by $\mu_{\text{calc.}} = (1.068^2 + 0.237^2)^{1/2}\mu = 1.094\mu$. Values of $\mu_{\text{obs.}}$ and $\mu_{\text{calc.}}$ for methyl, ethyl, and isopropyl halides are set out in Table I.

TABLE I.

X =	Cl.			Br.			I.		
	$\mu_{\text{obs.}}$	$\mu_{\text{calc.}}$	δ .	$\mu_{\text{obs.}}$	$\mu_{\text{calc.}}$	δ .	$\mu_{\text{obs.}}$	$\mu_{\text{calc.}}$	δ .
CH_3X	1.87	—	—	1.80	—	—	1.64	—	—
$\text{C}_2\text{H}_5\text{X}$	2.05	1.98	0.07	2.01	1.91	0.10	1.87	1.74	0.13
Pr^βX	2.15	2.05	0.10	2.19	1.97	0.12	—	—	—

It will be seen that the observed moments are all greater than those calculated and that the value of δ increases in the order $\text{Cl} < \text{Br} < \text{I}$. This effect is probably due to the field redistribution discussed in Part III.

Halogenobenzenes. For the five CH groups of the phenyl nucleus $\Sigma\mu_{ix}/\mu = 0.433$, and the primary moments are taken as those of the methyl halides. Whence, we have:

Substance.	$\mu_{\text{prim.}}$	$\mu_{\text{calc.}}$	$\mu_{\text{obs.}}$	μ_{me}
Fluorobenzene	1.81 *	2.61	1.61 †	-1.00
Chlorobenzene	1.87	2.70	1.73	-0.97
Bromobenzene	1.80	2.60	1.71	-0.89
Iodobenzene	1.64	2.37	1.50 †	-0.87

* Values due to Smyth (*J. Chem. Physics*, 1933, 1, 190).

† Obtained from values in benzene solution by multiplication by the factor $\mu_{\text{vap.}}/\mu_{\text{sol.}}$ for chlorobenzene.

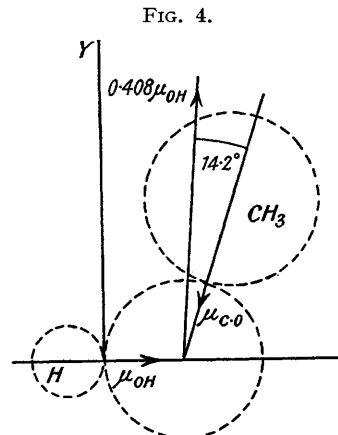
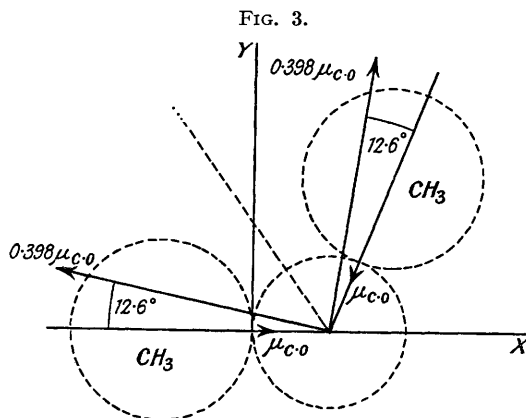
The values of μ_{me} —the mesomeric moment—are all negative, indicating opposition to the primary moment and hence drift of negative charge into the ring.

(3) *Ethers.*—*Dimethyl ether.* In this ether the oxygen bond angle is $111^\circ \pm 4^\circ$ (Ackermann and Mayer, *J. Chem. Physics*, 1936, 4, 377; Sutton and Brockway, *J. Amer.*

* All moments are given in Debye units, i.e., e.s.u. $\times 10^{-18}$.

Chem. Soc., 1935, 57, 473). In accordance with the convention adopted for methyl halides, the primary C–O moment is assumed to be that of either CH₃–O link. It remains to calculate the moment induced in each methyl group by the more distant C–O dipole. From the appropriate diagrams $\mu_{ix} = 0.058\mu_{CO}$ and $\mu_{iy} = 0.393\mu_{CO}$, giving a resultant of $0.398\mu_{CO}$ at an angle of 81.6° ($\tan^{-1} = 0.393/0.058$) to the OX axis or at an angle of 12.6° to the adjacent C–O bond. The moment of dimethyl ether is therefore obtained by compounding the moments shown in Fig. 3 :

$$\begin{aligned} \mu_{\text{obs.}} &= 1.28 = 2\mu_{CO} \cos 55.5^\circ - 2 \times 0.398\mu_{CO} \cos 42.9^\circ \\ \text{whence } \mu_{CO} &= 0.64 / (\cos 55.5^\circ - 0.398 \cos 42.9^\circ) = 2.33. \end{aligned}$$



Water. For water $\mu_{\text{obs.}} = 1.84$ and $\theta = 105^\circ$ from band spectra data; hence $\mu_{\text{OH}} = 1.51$.

Methyl alcohol. The oxygen angle being assumed to be 108° , intermediate between the values for water and dimethyl ether, we have only to consider the moment induced in the methyl group by the O–H dipole: $\mu_{ix} = 0.027\mu_{\text{OH}}$ and $\mu_{iy} = 0.408\mu_{\text{OH}}$, giving a resultant of $0.408\mu_{\text{OH}}$ at 14.2° to the OMe link. The observed moment of methyl alcohol is thus made up of (1) a component parallel to the OMe link $= \mu_{CO} - 1.51 \cos 72^\circ - 0.408 \times 1.51 \cos 14.2^\circ = \mu_{CO} - 1.065$, and (2) a component normal to the OMe link $= 1.51 \sin 72^\circ - 0.408 \times 1.51 \sin 14.2^\circ = 1.288$ (see Fig. 4). Therefore $\mu_{\text{obs.}}^2 = 1.69^2 = (\mu_{CO} - 1.065)^2 + 1.288^2$

$$\text{or } \mu_{CO} = 1.065 \pm 1.094 = 2.16 \text{ or } -0.03.$$

The latter value is inadmissible. Repeating the calculation with $\theta = 111^\circ$ for both dimethyl ether and methyl alcohol, we have :

Substance.	Oxygen angle.	μ_{C-O} .	Substance.	Oxygen angle.	μ_{C-O} .
Dimethyl ether	111°	} 2.33	Methyl alcohol	111°	2.24
" "	108		" "	108	2.16

For use in subsequent calculations we shall adopt a value of $\mu_{C-O} = 2.30$.

Diphenyl ether. From electron-diffraction measurements on 4:4'-di-iododiphenyl ether (Maxwell, Hendricks, and Mosley, *J. Chem. Physics*, 1935, 3, 699), the oxygen valency angle is $118^\circ \pm 3^\circ$, and we shall assume this value in diphenyl ether. From results for halogenobenzenes, the induction in each phenyl radical adjacent to each C–O link is 0.433, parallel to the primary moment, but the induction in each phenyl radical due to the more distant C–O link must be calculated as in the case of dimethyl ether. The assumption will be made that the phenyl radicals and the C–O–C bonds are coplanar. Calculation gives a resultant moment of 1.068 at an angle of 78.3° to the OX axis, derived as follows :

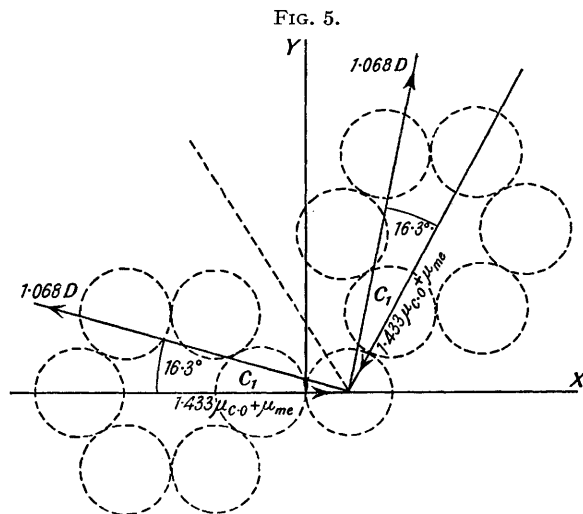
	C ₁ .	C ₂ .	C ₃ .	C ₄ .	C ₅ .	C ₆ .	$\Sigma\mu$.
μ_{ix}	0.208	-0.135	-0.032	negl.	0.033	0.142	0.216
μ_{iy}	0.606	0.184	0.048	0.043	0.052	0.112	1.045

Since the oxygen angle is 118° , the induced moment is at an angle of 16.3° to the OPh link (Fig. 5). The observed moment is obtained by suitable compounding of primary and induced moments, the mesomeric moment being assumed to act along the O-C-Ph axis. Hence

$$\mu_{\text{obs.}} = 1.35 = 2(2.30 \times 1.433 + \mu_{\text{me}}) \cos 59^\circ - 2 \times 1.068 \times \cos 42.7^\circ$$

i.e., $1.35/2 = 1.700 + 0.515\mu_{\text{me}} - 0.785$, or $\mu_{\text{me}} = -0.47$.

This is a fairly large moment and acts in opposition to the primary moment, as suggested by theory. It is observed that the assumption of coplanarity of rings and O-C-O bonds



is substantially correct, for though the phenyl radicals are capable of free rotation, inspection of the table above shows that most of the induction occurs in carbon atom C_1 . Little error will arise if free rotation be admitted but not allowed for.

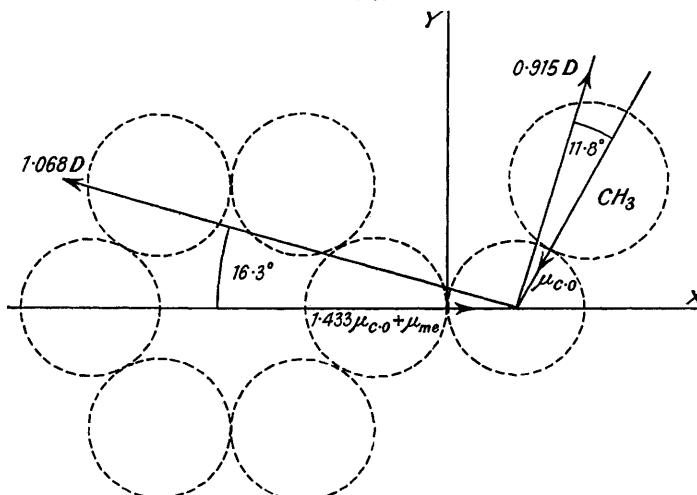
Anisole. The oxygen angle will be assumed equal to that in diphenyl ether, since the resonance which gives rise to the mesomeric moment will tend to increase the "double bond" character of the PhO link. The value of μ_{me} may be derived from constants obtained in the calculations for diphenyl ether, and from the moment induced in the methyl group by the OPh dipole. The latter is $0.398\mu_{\text{CO}} = 0.915$ at an angle of 73.8°

to the OX axis or 11.8° to the OMe link. Resolving parallel and perpendicular to the OPh link (Fig. 6), we have:

$$\mu = 3.30 + \mu_{\text{me}} - 2.30 \cos 62^\circ + 0.915 \cos 73.8^\circ - 1.068 \cos 16.3^\circ = \mu_{\text{me}} + 1.45 \text{ (parallel)}$$

$$\text{and } \mu = 2.30 \sin 62^\circ - 0.915 \sin 73.8^\circ - 1.068 \sin 16.3^\circ = 0.85 \text{ (perpendicular)}$$

FIG. 6.



Hence, $\mu_{\text{obs.}}^2 = 1.35^2 = (\mu_{\text{me}} + 1.45)^2 + 0.85^2$ and $\mu_{\text{me}} = -1.45 \pm 1.048 = -0.40$ or -2.50 .

The larger value is improbable, but the smaller is comparable in magnitude and direction to that of diphenyl ether.

Phenol. A bond angle of 118° being assumed, the mesomeric moment may again be calculated from accumulated results. The moment induced in the phenyl group due to the O-H dipole is $0.70 (= 1.068 \times 1.51/2.30)$ at 16.3° to the OPh link. The moments to be compounded are therefore $3.30 + \mu_{me} - 0.70 \times \cos 16.3^\circ - 1.51 \cos 62^\circ = \mu_{me} + 1.92$ (parallel) and $1.51 \sin 62^\circ - 0.70 \sin 16.3^\circ = 1.13$ (perpendicular). Hence, $\mu_{obs.}^2 = 1.40^2 = (\mu_{me} + 1.92)^2 + 1.13^2$ and $\mu_{me} = -1.12$ or -2.74 .

Again the larger value is improbable, but it is interesting to note the sudden increase in magnitude shown by -1.12 as compared with approximately -0.5 in anisole and diphenyl ether.

(4) *Carbonyl Compounds.—Acetone.* The dipole here is assumed to be midway between the carbon and the oxygen nucleus, *i.e.*, 0.64 A. from Me

the former, and the $O=C$ angle is taken as 125° ; $\mu_{ix} = 0.125\mu_{C:O}$, so $\mu_{obs.} = 2.85 = \mu_{C:O} + 2\mu_{ix} = 1.25\mu_{C:O}$ (Y components vanish by symmetry) and $\mu_{C:O} = 2.28$ (Fig. 7).

Acetaldehyde. In this compound the value of μ_{iy}/μ for the methyl group must be considered. This is 0.271 , so that, the hydrogen atom being neglected, the total moment is given by compounding $\mu_{C:O} + 0.125\mu_{C:O}$ parallel, and $0.271\mu_{C:O}$ perpendicular, to the $C=O$ link; *i.e.*,

$$\mu_{obs.} = 2.68 = \mu_{C:O}(1.125^2 + 0.271^2)^{\frac{1}{2}} = 1.158\mu_{C:O}, \text{ or } \mu_{C:O} = 2.32.$$

If the induction in the hydrogen atom be included, for which $\mu_{ix}/\mu = 0.070$ and $\mu_{iy}/\mu = 0.103$, then we must compound $\mu_{C:O} + (0.125 + 0.070)\mu_{C:O}$ parallel, and $(0.271 - 0.103)\mu_{C:O}$ perpendicular, to the $C=O$ link. Hence

$$2.68 = \mu_{C:O}(1.195^2 + 0.168^2)^{\frac{1}{2}} = 1.202\mu_{C:O} \text{ and } \mu_{C:O} = 2.23.$$

The mean of all three is 2.28 , which is remarkably close to the value for μ_{O-O} , *viz.*, 2.30 .

Acetophenone. The angle $O=C$ being assumed to be 125° , the induced moments in the phenyl radical are as follows:

	C ₁ .	C ₂ .	C ₃ .	C ₄ .	C ₅ .	C ₆ .	$\Sigma\mu_i/\mu$.
μ_{ix}/μ	0.098	-0.044	-0.009	0.003	0.018	0.067	0.133
μ_{iy}/μ	0.199	0.073	0.023	0.017	0.020	0.041	0.373

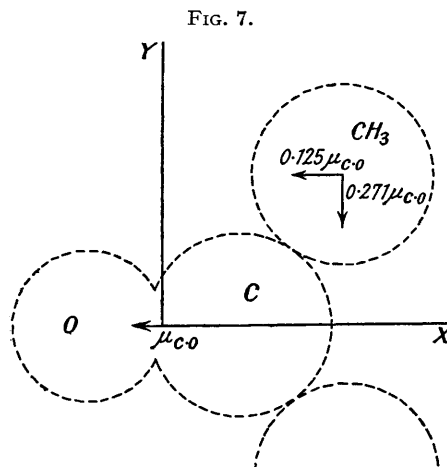
The argument respecting the plane of the phenyl radical is the same as for diphenyl ether, and the mesomeric moment is assumed to act along the $C_{al.}-C_{ar.}$ axis of the ring. If we take $\mu_{C:O} = 2.28$, $\mu_{ix} = 0.31$, and $\mu_{iy} = 0.85$, then by the usual calculation

$$\mu_{obs.}^2 = 3.00^2 = (2.88 + \mu_{me} \cos 55^\circ)^2 + (0.23 + \mu_{me} \sin 55^\circ)^2 \text{ and } \mu_{me} = 0.17 \text{ or } -3.87.$$

The small positive value is of comparable magnitude with other meta-directing groups and indicates a drift of negative charge out of the ring.

(5) *Nitro-compounds.*—The moment of the nitro-group may be regarded as due to two moments, the larger one being between the nitrogen and the oxygen atoms. Because of resonance, this moment is symmetrically directed along the line of the N-C bond. The latter itself may possess a small moment, which, owing to electron loss from the nitrogen atom, will have its negative end directed towards the carbon atom. As a first approximation the moment of the nitro-group will be considered as a dipole situated at the periphery of the nitrogen atom.

Nitromethane. $\mu_{ix}/\mu = 0.284$ and $\mu_{obs.} = 3.54$, whence $\mu_{NO_2} = 3.54/1.284 = 2.76$.



Nitroethane. For the CH₂ group, $\mu_{ix}/\mu = 0.230$, and for the CH₃ group, $\mu_{ix}/\mu = 0.064$ and $\mu_{iy}/\mu = 0.062$. We thus have

$$\mu_{\text{obs.}} = 3.58 = \mu_{\text{NO}_2}(1.294^2 + 0.062^2)^{\frac{1}{2}} \text{ or } \mu_{\text{NO}_2} = 2.76.$$

This value agrees well with that of nitromethane.

Nitrobenzene. The induction in the phenyl radical is

Atom	C ₁	C ₂ (× 2)	C ₃ (× 2)	C ₄	Total 0.431.
μ_{ix}/μ	0.223	0.130	0.052	0.026	

therefore $\mu_{\text{obs.}} = 4.24 = \mu_{\text{me}} + 1.431\mu_{\text{NO}_2}$, and $\mu_{\text{me}} = 0.29$. This has the same sign as the primary moment and indicates electron drift from the ring as required by theory.

TABLE II.

<i>Bond moments, D.</i>		<i>Mesomeric moments, D.</i>	
H ₃ C—F	1.81	Fluorobenzene	−1.00
H ₃ C—Cl	1.87	Chlorobenzene	−0.97
H ₃ C—Br	1.80	Bromobenzene	−0.89
H ₃ C—I	1.64	Iodobenzene	−0.87
C—O	2.30	Diphenyl ether	−0.47
		(in each Ph group)	
		Anisole	−0.40
		Phenol	−1.12
C=O	2.28	Acetophenone	0.17
C≡N	3.00	Benzonitrile	0.05
NO ₂	2.76	Nitrobenzene	0.29

The results of this investigation are summarised in Table II. It will be seen that all the *op*-directing groups give a large negative mesomeric moment whilst the three *m*-directing groups give a small value of opposite sign. The value for benzonitrile is indeed not larger than the uncertainties in the method of calculation. The general conception of mesomeric displacement is thus confirmed, but the interesting fact emerges that the permanent mesomeric displacement is much smaller for *m*- than for *op*-directing systems.

We are indebted to Dr. J. J. Fox, O.B.E., for giving us facilities for carrying out this work.

BIRKBECK COLLEGE, FETTER LANE, LONDON, E.C. 4.
GOVERNMENT LABORATORY, CLEMENT'S INN PASSAGE,
STRAND.

[Received, November 2nd, 1937.]