658. *The Polarities of Molecules containing Iodine of Valency Higher than One.*

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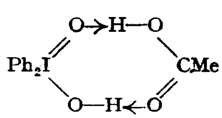
The following dipole moments are recorded : " diphenyliodyl acetate," 3·5—5D. ; iodosobenzene acetate, 4·9D. ; iodobenzene dichloride, 2·6D. ; *NN*-diacetaniline, 3·1D. ; benzylidene diacetate, 3·0D. ; and *p*-nitrobenzylidene diacetate, 4·2D. Indications are that iodoxybenzene has a polarity of 8 or more D. units.

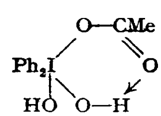
During 1936, at the request of Professor Irvine Masson, F.R.S., we measured the apparent dipole moments of " diphenyliodyl acetate " (I) and iodosobenzene acetate (II) ; for comparison, those of iodobenzene dichloride (III), diacetanilide (IV), benzylidene diacetate (V), and its *p*-nitro-derivative, were later determined. Results are shown beneath the formulae :

$Ph_2IO(OH),AcOH$	$PhI(OAc)_2$	$PhICl_2$	$PhNAc_2$	$PhCH(OAc)_2$
(I.) μ = 3·5—5D.	(II.) μ = 4·9D.	(III.) μ = 2·6D.	(IV.) μ = 3·1D.	(V.) μ = 3·0D.

Discussion.—The interest of (I) lies in its relation to iodoxybenzene, $PhIO_2$, the dipole moment of which cannot be directly measured. Chemically iodoxybenzene is not neutral as stated by Willgerodt (" Die Organischen Verbindungen mit Mehrwehrtigem Jod," Enke, Stuttgart, 1914, p. 35). With strong acids (*e.g.*, in H_2SO_4) it seems to behave as a cation, yet in cold dilute alkalis it gives an iodate and an unstable intermediate, " diphenyliodyl hydroxide," $Ph_2IO{\cdot}OH$ (formally analogous to the aryl-phosphonous and -arsonous acids) ; from this, *via* the carbonate, (I) is obtained by treatment with glacial acetic acid (Masson, Race, and Pounder, *J.*, 1935, 1669).

The Durham authors do not regard the derivatives from acetic and carbonic acids as ionic salts but rather as co-ordinated ring-compounds (*e.g.*, VI or less probably VII). Our measurements support this view, since the moment estimated in benzene or dioxan is several D. units below the values recorded for such compounds as silver perchlorate (μ = 11—12D.) (Kraus and Hooper, *Proc. Nat. Acad. Sci.*, 1933, **19**, 939 ; *J. Amer. Chem. Soc.*, 1935, **56**, 2265) or various alkylammonium halides, picrates, acetates, etc. (μ = 7—20D.) (Geddes and Kraus, *Trans. Faraday Soc.*, 1936, **32**, 585) in which ion-pair arrangements can be accepted.

(VI.) 

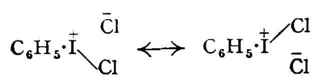
 (VII.)

The order of the moment of (VI) (3·5—5D.) suggests, further, that the Ar_2IO_2 fragment has considerable polarity, which, since μ_{O-I} is around 1·3D., must originate in the I–O links. In this connection the results for (II), (IV), and (V) are of interest. If these molecules have approximately similar Y-configurations, then it is clear from the fact that a *p*-nitro-group in (V) increases the molecular resultant by *ca.* 1D. that the net effect of the two acetoxy-groups in (V) is to produce a component acting *towards* the benzenoid ring. In (II) therefore either (*a*) the polarity of >I–O is in the sense $>\overset{\delta-}{\mathrm{I}}\!-\!\!-\overset{\delta+}{\mathrm{O}}$ and the resultant *ca.* 5D. is produced by the addition of 3 and 2, or (*b*) the IO bonds are polarised as $>\overset{\delta+}{\mathrm{I}}\!-\!\!-\overset{\delta-}{\mathrm{O}}$, and the resultant (4·9D.) represents the *difference*, 7·9 *minus* 3D. Of these alternatives (*b*) is more likely since the iodoxy-group is emphatically *meta*-orienting (Masson, Race, and Pounder, *loc. cit.*), a quality requiring a strong positive influence to be adjacent to the aryl nucleus (cf. *Annual Reports*, 1926, **23**, 130).

Recently Archer (*Acta Crystall.*, 1948, **1**, 64) has described an *X*-ray analysis of crystalline *p*-chloroiodoxybenzene. The angle O–I–O is 103°, with its plane at 90° to that of the C_6-ring; two I=O distances are given: 1·60 and 1·65A. Both of the latter figures are notably less than the arithmetical means (1·99, 1·88, and 1·78, respectively) of O–O and I–I (1·32 and 2·66A.), of O=O and I–I (1·11 and 2·66A.), and of O=O and I=I (1·11 and 2·46; cf. Table 21·2 of Pauling's "The Nature of the Chemical Bond," Cornell Univ. Press, 1945, p. 164). Instances of such disagreements are not unknown, however (cf. *op. cit.*, Chap. VI), and we infer therefore that in the iodoxy-group the IO bond is "double."

Because μ_{X-Y} is normally less than $\mu_{X=Y}$, our conclusion follows that $\mu_{C_6H_5IO_2}$ is usually large—most probably greater than 8D.

The moment now determined for iodobenzene dichloride is close to that (2·61D.) mentioned without observational data by Guryanova and Syrkin (*Acta Physicochim. U.R.S.S.*, 1939, **11**, 657). Their results for the *p*-methyl and *p*-chloro-derivatives (3·02 and 1·3D., respectively) make it obvious that the molecular resultant in iodobenzene dichloride vectorially resembles that in iodobenzene but with an augmentation of some 1·3D. To produce such an increase, if, as seems likely, the Cl–I–Cl angle is *ca.* 120°, each I–Cl link will itself need to exhibit a component of 1·3D. The moment of iodine monochloride (as a gas) being 0·5D. (Luft, *Z. Physik*, 1933, **84**, 767) resonance of the type suggested by the Russian authors (*loc. cit.*), *viz.*:



offers a credible explanation, although, since the iodo-dichlorides have all been examined as solutions, it should be recalled that iodine monochloride in the non-polar media carbon tetrachloride and *cyclo*hexane has shown apparent moments from 0·9 to 1·49D. (Malone and Ferguson, *J. Chem. Physics*, 1934, **2**, 99; Fairbrother, *J.*, 1936, 847).

Experimental.

Materials and Methods.—Compounds (I) and (II) were specimens given to us by Professor Masson (see *J.*, 1935, 1669; 1938, 1699), the others were obtained without difficulty by methods cited in Beilstein's "Handbuch" (V, p. 227; XII, p. 250). The experimental techniques used have been as described before ("Dipole Moments," Methuen, 1948, Chap. II) except that to avoid corrosion of the test condenser by iodobenzene dichloride solutions we found that a Sayce–Briscoe type of cell (*op. cit.*, p. 36) could be satisfactorily and easily coated with graphite instead of silver: the annular parts were first washed with sodium silicate solution and then left in contact with Acheson's "Aquadag" (diluted with an equal volume of distilled water) for a few minutes. Without movement of the cell, the liquid was withdrawn by suction and warm air passed until drying was apparently complete. The whole cell was then baked at 200° for an hour. Two repetitions gave tenacious films which were chemically quite inert and adequately electrically conducting (*vide* "Technical Bulletin No. 230·3," issued by Messrs. E. G. Achison, Ltd.). The cell bodies were of Pyrex glass.

Measurements.—These are tabulated below under the usual headings (cf. *Trans. Faraday Soc.*, 1950, **46**, 1, for definitions). With one exception all the sets refer to benzene as solvent. During earlier (1936) measurements concentrations were recorded as molar fractions, later (1937) weight fractions were adopted. In the former instances therefore extrapolation to infinite dilution requires Hedestrand's formula (*Z. physikal. Chem.*, 1929, *B*, **2**, 428) in place of the direct graphical method or that of Le Fèvre and Vine (*J.*, 1937, 1805). Results with "diphenyliodyl acetate" must be regarded as approximate only, because of uncertainties caused by its low solubility in benzene or dioxan. Dielectric constants and densities, respectively, are expressed on the basis of the following data for the pure liquids at 25°: benzene, 2·2725, 0·87378; dioxan, 2·2292, 1·03024.

"Diphenyliodyl acetate" in benzene.

$10^6 f_1$	90·6	143·1	144·6	174·7	307·8	335·8
ε^{25}	2·2751	2·2764	2·2771	2·2757	2·2820	2·2806
d_4^{25}	0·87396	0·87392	0·87047	0·87395	0·87437	0·87438

Whence average $\alpha\varepsilon_2$ = 26·8, average βd_2 = 1·49, and $_{\infty}P_1$ = 476 c.c.

The individual values of $\alpha\varepsilon_2$ and βd_2 range over 18—32 and 0·84—1·87, respectively; these correspond to maximum and minimum $_{\infty}P_1$ figures of 570 and 335 c.c. By using a divided cell on a Pulfrich refractometer and reading differences between solvent and solutions on the micrometer drum, estimates of $[R_L]_D$ of the order of 80 c.c. were obtained. These agreed roughly with the value expected from known atomic refractions. A moment between 3·5 and 4·9D. is accordingly indicated.

"Diphenyliodyl acetate" in dioxan.

$10^6 f_1$	190·8	608·9	695·5
ε^{25}	2·2378	2·2534	2·2560
d_4^{25}	1·03058	1·03130	1·03143

Whence average $\alpha\varepsilon_2$ = 41·1, average βd_2 = 1·74, and $_{\infty}P_1$ = 653 c.c.; if $_DP = [R_L]_D$ = 80 c.c., μ = 5·3D.

Iodosobenzene acetate in benzene.

$10^6 f_1$	663·6	1568·1	1907·7	5731·0
ε^{25}	2·2944	2·3212	2·3308	2·4471
d_4^{25}	0·87501	0·87657	0·87712	0·88370
P_1 (c.c.)	538	508	501	489
n_D^2 *	—	2·24314	—	2·24652
R_1 (c.c.)	—	65·8	—	67·7

Whence $_{\infty}P_1$ (graphically) = 563 c.c. If $_DP = [R_L]_D$ = 68 c.c., $\mu = 4{\cdot}9_2$D.

* $(n_D)_{C_6H_6}$ = 1·49733.

Iodobenzene dichloride in benzene.

$w_1 10^6$	1139	1216	2455	2961	3301
ε^{25}	2·3864	2·3894	2·5170	2·5578	2·5826
d_4^{25}	0·91786	0·92052	0·96507	0·98011	0·99472
P_1 (c.c.)	178	162	174	167	146

Whence $\Sigma(\varepsilon_{12} - \varepsilon_2)/\Sigma w_1$ = 9·67, $\Sigma(d_{12} - d_2)/\Sigma w_1$ = 3·70, and $_{\infty}P_1$ = 197 c.c. Taking $_DP = [R_L]_D$ as 55 c.c. (Sullivan, *Z. physikal. Chem.*, 1899, **28**, 531), $\mu = 2{\cdot}6_2$D.

NN-Diacetylaniline in benzene.

$w_1 10^6$	11,369	17,797	36,009	48,789
ε^{25}	2·3430	2·3870	2·4921	2·5748
d_4^{25}	0·87605	0·87734	0·88098	0·88312

Whence $\Sigma(\varepsilon_{12} - \varepsilon_2)/\Sigma w_1$ = 6·20, $\Sigma(d_{12} - d_2)/\Sigma w_1$ = 0·196, and $_{\infty}P_1$ = 253. Taking $_DP$ as $[R_L]_D$ (calc. from Vogel, *J.*, 1948, 1842) = 49 c.c., $\mu = 3{\cdot}1_5$D.

Benzylidene diacetate in benzene.

$10^6 f_1$	2935·7	5501·5	11024·9
ε^{25}	2·3083	2·3400	2·4066
d_4^{25}	0·87537	0·87676	0·87966
P_1	233·0	232·9	229·7

Whence $_{\infty}P_1$ (graphically) = 234·7 c.c. If $_DP = [R_L]_D$ (calc.) = 53 c.c., $\mu = 2{\cdot}9_8$D.

p-*Nitrobenzylidene diacetate in benzene.*

$10^6 f_1$	900·4	1965·5	1969·6	2506·7
ε^{25}	2·2949	2·3195	2·3205	2·3318
d_4^{25}	0·87461	0·87553	0·87555	0·87597
P_1	418	406	412	402

Whence $\Sigma(\varepsilon_{12} - \varepsilon_2)/\Sigma f_1$ = 24·1, $\Sigma(d_{12} - d_2)/\Sigma f_1$ = 0·891, and $_{\infty}P_1$ = 413 c.c. If $_DP = [R_L]_D$ (calc.) = 59, $\mu = 4{\cdot}1_6$D.

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[*Received, August 2nd,* 1950.]