The Relation between Configuration and Conjugation in Diphenyl Derivatives. Part IV. The Dipole Moments of the 2 : 2′-Dihalogeno- and 2 : 2′- and 3 : 3′-Dinitro-diphenyls.*

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The dipole moments of 2 : 2′-difluoro-, -dichloro-, -dibromo-, -di-iodo- and -dinitro-diphenyl and of 3 : 3′-dinitrodiphenyl have been determined in benzene solution at 25°. On the assumption that the primary moments of the substituent groups, and the induced moments which they produce in the rings in which they are present, are the same as in the monosubstituted benzenes, the moments induced by each substituent in the opposite ring and in the other substituent have been calculated for various angles of inclination of the planes of the rings. It is found that, so long as the rings are coaxial, the observed moments of the 2 : 2′-disubstituted diphenyls are in accord with the calculated values only if the substituent groups have a preferred slightly-*cis*-disposition. For 3 : 3′-dinitrodiphenyl the dipole moment value suggests preference for a slightly-*trans*-configuration. These conclusions hold over all reasonable ranges of the location of the dipole and are in qualitative accordance with electron-diffraction measurements.

INTEREST in the dipole moments of the 2 : 2′-disubstituted derivatives of diphenyl centres around the fact that the *cis*-coplanar configuration and a wide range of orientations of the planes of the rings around this relative position are precluded on steric grounds. Further, it has been found that compounds which depend for their enantiomorphism on interference between 2 : 2′-substituents and the 6- and the 6′-hydrogen atom can be resolved when the 2 : 2′-substituents are iodine or bromine atoms (2 : 2′-di-iodo- and 2 : 2′-dibromo-diphenyl-4 : 4′-dicarboxylic acids; Searle and Adams, *J. Amer. Chem. Soc.*, 1933, **55**, 1649; 1934, **56**, 2112), though the active forms are of relatively low optical stability. No optical activity has been observed, however, in analogous compounds containing 2 : 2′-dichloro- or difluoro-substituents. It may be inferred, therefore, that the *trans*-coplanar configuration also involves a much higher potential energy than the orthogonal configuration, a view which was supported by dipole-moment measurements on the 2-monosubstituted derivatives (Part II, *J.*, 1953, 2456). It would be expected, therefore, that the mean configuration of the rings in the 2 : 2′-disubstituted compounds would be not far removed from the orthogonal arrangement, but rather nearer to the *trans*- than to the *cis*-position.

It was shown by Hampson and Weissberger (*J. Amer. Chem. Soc.*, 1936, **58**, 2111), however, that the dipole moment of 2 : 2′-dichlorodiphenyl is greater than that of the 3 : 3′-isomeride. The difference between the moment observed for the latter (1·80 D) and the value calculated for free rotation on the assumption that the group moment is the same as in chlorobenzene (1·90 D) was attributed to induction effects, and these authors suggested that the higher value for 2 : 2′-dichlorodiphenyl (1·91 D) was due to London forces acting in such a manner as to maintain the mean configuration of the molecule as a *cis*-arrangement, with the rings in planes inclined at about 62°. Further, from electron-diffraction measurements on the vapours, Bastiansen (*Acta Chem. Scand.*, 1950, **4**, 926) has found that the mean angle between the planes of the rings is 74°, 75°, and 79° in 2 : 2′-dichloro-, 2 : 2′-dibromo-, and 2 : 2′-di-iodo-diphenyl, respectively, with halogen atoms *cis* to one another in each case. Again, *X*-ray crystal analysis has shown that in the solid state the inter-planar angles are 72° in 2 : 2′-dichlorobenzidine (Smare, *Acta Cryst.*, 1948, **1**, 150) and 71° in 2 : 2′-dimethylbenzidine dihydrochloride (Fowweather and Hargreaves, *Acta Cryst.*, 1950, **3**, 81), the 2 : 2′-groups having a *cis*-disposition in each case.

In view of this evidence it was of interest to study the dipole moments of a wider range of 2 : 2′-disubstituted diphenyls, in order to ascertain whether this preferential *cis*-disposition is general, irrespective of the size and nature of the substituent group. As

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* Part III, *J.*, 1954, 131.

they give rise to dipoles which are symmetrically disposed with respect to the ring in which they are substituted, thereby facilitating interpretation of the results, the halogen atoms and nitro-group were selected as substituents in this investigation. In view of Hampson and Weissberger's observations on the relative values of the moments for 2 : 2′- and 3 : 3′-dichlorodiphenyl, it was also of interest to compare the moment of 3 : 3′-dinitrodiphenyl with that of the 2 : 2′-isomer.

The results are summarised in Table 1, where α, β, and ν are the limiting values of $d\varepsilon/dw$, dv/dw, and dn^2/dw, respectively, and the other symbols have their usual significance.

TABLE 1. *Polarisation data for solutions in benzene at 25°.*

Diphenyl derivative	$10^3\alpha$	$-10^4\beta$	$10^3\nu$	$P_{2\infty}$ (c.c.)	$[R_D]$ (c.c.)	μ(D)	Previous values
2 : 2′-Difluoro-	2,120	3209	127	122·5	50·5	1·88	
2 : 2′-Dichloro-	2,095	3586	230	141·2	61·2	1·97	1·72,[a] 1·77,[b] 1·91[c]
2 : 2′-Dibromo-	1·460	5614	222	140·0	66·5	1·90	
2 : 2′-Di-iodo-	1,006	6633	232	135·0	74·9	1·71	
2 : 2′-Dinitro-	11,785	4304	244	593·3	62·5	5·10	5·12,[a] 5·19[d]
3 : 3′-Dinitro-	7,950	4387	226	416·5	61·1	4·17	

[a] Bretscher, *Helv. Phys. Acta*, 1929, **2**, 257. [b] Weissberger and Sängewald, *Z. physikal. Chem.*, 1933, **20**, *B*, 145. [c] Hampson and Weissberger, *J. Amer. Chem. Soc.*, 1936, **58**, 2111. [d] Le Fèvre and Vine, *J.*, 1938, 967.

Before these dipole-moment values can be applied in calculating the mean angle of inclination between the planes of the rings, correction must be made for inductive effects which need not be of the relatively secondary importance often ascribed to them. Their magnitudes vary with the angle between the planes of the rings, but, by applying the method used in Part II, they can be evaluated as functions of this angle ϕ.

These compounds differ from the monosubstituted derivatives studied previously in that they must be regarded as derived from the mono-derivative of benzene, not only by replacement of a hydrogen atom by a second benzene ring, but also by the introduction of a second substituent group. The inductive effects can therefore be regarded as comprising (i) the effects already present in the monosubstituted benzene, (ii) the effects of each dipole on the second ring, and (iii) the moment induced at each dipolar substituent by the presence of the other.

The inductive effect produced by each dipole in the opposite benzene ring is similar to that in the 2-monosubstituted diphenyl. From the geometry of the molecule, and the consideration that the polarisability of benzene at right angles to the plane of the ring is half of that in the plane of the ring, it follows that if effects (i) and (ii) only were present the moment should be given by

$$\mu = \left\{\sqrt{3}\,\mu_{\text{PhX}} + (\mu_y - \sqrt{3}\,\mu_x)\cos^2\frac{\phi}{2}\right\} . \cos\frac{\phi}{2} \quad . \quad . \quad . \quad . \quad (1)$$

where μ_{PhX} is the moment of the corresponding mono-derivative of benzene, and μ_x and μ_y are the induced moments produced at the centre of each ring, respectively parallel with and at right angles to the dipole in the other ring, when the rings are coplanar.

The method of evaluating μ_x and μ_y was discussed in Part II. There it was assumed that the point of action of the dipole was at the " point of contact " of the carbon and the halogen atom in the halogeno-derivatives and at the centre of the nitrogen atom in the nitro-compounds. Although the precise location of the dipole does not affect the arguments then advanced regarding the configurations of the mono-derivatives, these positions are probably rather too near to the centre of the benzene ring. On classical views the effective centre of the dipole must be located at some point between the position previously assumed and the polarisable centre of the substituent, whilst the present view that the moment in such halogeno-derivatives arises principally from the asymmetry of the non-bonding orbitals suggests that it cannot be far removed from the polarisable centre. Hence, in the present series of calculations the induced moments have been evaluated for these two extreme positions of the dipole and also for the dipole half-way between these positions. The following inter-nuclear distances have been used in calculating r (the distance between the dipole and the polarisable centre) and θ (the angle between r and the axis of the dipole) : C–C (aromatic) 1·40, C–C (centre bond) 1·50, C–N 1·45, C–F 1·495, C–Cl 1·765, C–Br 1·885, and C–I 2·105 Å.

The evaluation of the moment induced in one polar substituent by the presence of the other involves a knowledge of the polarisability of the substituent, its dielectric constant, the distance between each inducing dipole and the polarisable centre of the other substituent group, and the angle between the direction of the inducing dipole and the line from its point of action to the polarisable centre. The last two vary with ϕ, but the geometry of the problem does not permit the evaluation of the effect as a general function of this angle, so it is necessary to calculate the mutual polarisation effect for various values of ϕ, and to combine this result with the moment expected from consideration of the primary dipoles and ring induction only, as given by equation (1), so as to obtain " theoretical " dipole moment values for these different values of ϕ. The results so obtained can be compared with the observed moment and the angle between the planes corresponding with the latter deduced.

The following values, deduced from molecular refraction data, of the differences between the polarisabilities of the substituent groups and that of the hydrogen atom have been used in these calculations : F 0, Cl 1·91, Br 3·05, I 5·07, and NO_2 2·24, all $\times 10^{-25}$ c.c., respectively. The effective dielectric constant of the group is more difficult to decide, but, since this occurs in a term ($\varepsilon + 2$) only, no great error can be introduced by using the value for carbon tetrachloride (2·23).

The results of the introduction of these inductive effects are shown in Table 2. Column 4 gives the values of the angle between the planes of the rings if all induction effects are ignored; columns 5, 6, and 7 give the angles deduced for the three positions of the dipole if induction in the rings only is considered, and columns 8, 9, and 10 the corresponding angles when the mutual induction between the polar groups is also included.

TABLE 2. *Mean angles between planes of rings in disubstituted compounds.*

Diphenyl derivative	μ (D) observed	μ_{PhX} (D)	Mean angle between planes of rings						
			No allowance for induction	Corrected for induction in rings only			Corrected for induction in rings and polar groups		
				a	*b*	*c*	*a*	*b*	*c*
2 : 2′-Difluoro- ...	1·88	1·48	86°	71°	79°	74°	71°	79°	74°
2 : 2′-Dichloro- ...	1·97	1·58	88	75	84	80	69	82	75
2 : 2′-Dibromo- ...	1·90	1·56	90	79	88	84	68	85	77
2 : 2′-Di-iodo- ...	1·71	1·40	90	78	90	85	50	84	69
2 : 2′-Dinitro- ...	5·10	4·01	86	78	84	81	72	80	76
3 : 3′-Dinitro- ...	4·17	4·01	106	105	105	105	105	105	105
3 : 3′-Dichloro- ...	1·80 *	1·58	98	97	97	97	97	97	97

a, Dipole located at " point of contact " of carbon and halogen atom or centre of nitrogen atom. *b*, Dipole located at polarisable centre of substituent group. *c*, Dipole located mid-way between positions *a* and *b*.

* Hampson and Weissberger, *loc. cit.*

After all inductive effects have been taken into account the calculated angle ϕ varies most systematically with the size of the substituent group when the dipole is assumed to be located at the polarisable centre of the substituent group, although whatever assumption is made the mean angles found for the 2 : 2′-disubstituted compounds are less than 90°, *i.e.*, the groups have a slightly-*cis*-disposition. If, as is most probable, the dipole is effectively located near the polarisable centre of the substituent, the angle increases slightly from 2 : 2′-difluoro- to 2 : 2′-dibromo- and 2 : 2′-di-iodo-diphenyl. At an inclination of 79°, as is indicated for 2 : 2′-difluorodiphenyl, the overlap between the π-orbitals of the two rings would be expected to be small, but this overlap disappears completely only at 90°. Hence we would expect that, if the estimates of the inclinations between the ring planes are quantitatively reliable, there might be a very slight conjugation between the rings in the 2 : 2′-difluoro- and 2 : 2′-dinitro-compounds, but that this conjugation would be diminished in 2 : 2′-dichlorodiphenyl and become very small indeed in 2 : 2′-dibromo- and 2 : 2′-di-iodo-diphenyl. The ultra-violet absorption evidence for conjugation in the 2 : 2′-di-halogeno-compounds will be discussed in Part V.

The reason for the preferred *cis*-orientation is not obvious For a system of dipoles such as are present in these compounds it can be shown that the mutual dipolar potential energy is a minimum when the angle between the planes of the rings is between 70° and 80°, but the depth of this potential energy well is so small that it cannot affect the mean configuration of the molecules appreciably at 25°. The conjugation between the rings would also be expected to tend to diminish the angle between the rings, but, as they can obviously approach much nearer to coplanarity when the groups are *trans* to one another, conjugation would be expected to favour the latter disposition Again, the effect of London forces, such as was suggested by Hampson and Weissberger, might be expected to cause the groups to reside in the *cis*- rather longer than in the corresponding *trans*-configuration. On such a theory, however, the mean value of ϕ would be expected to increase much more than is observed on passing from the fluoro- to the iodo-compound.

Table 2 also includes similar interpretations of the dipole moment of 3 : 3′-dinitrodiphenyl now recorded and of the moment for 3 : 3′-dichlorodiphenyl reported by Hampson and Weissberger. The particular point of interest here is that the mean angle of inclination of the rings is slightly above 90°, *i.e.*, there is a slight tendency in each case for the groups to have a preferential *trans*-disposition, but the actual inter-planar angle is of the same order as in the 2 : 2′-derivatives, *viz.*, 75° and 83° for 3 : 3′-dinitro- and 3 : 3′-di-chloro-diphenyl, respectively. From electron-diffraction measurements, Bastiansen (*Acta Chem. Scand.*, 1949, **3**, 408) deduced that the angle between the planes of the rings was 54° ± 5° in 3 : 3′-dibromodiphenyl and 52° ± 10° in 3 : 3′-dichlorobenzidine, compared with 45° ± 10° for diphenyl itself. The halogen atoms appear to have a *trans*-disposition in each case. On the other hand X-ray crystal analysis of 3 : 3′-dichlorobenzidine indicates that in the solid state this molecule is probably planar or very nearly so, with the chlorine atoms *trans* to one another (Toussaint, *Acta Cryst.*, 1948, **1**, 43).

EXPERIMENTAL

Preparation and Purification of Materials.—2 : 2′-Dinitrodiphenyl, prepared by Shaw and Turner's method (*J.*, 1933, 135) and recrystallised from light petroleum (b. p. 100—120°), had m. p. 125·5° (lit., 123·5—124·5°).

TABLE 3.

$100w$	ε	v	n
	2 : 2′-Difluorodiphenyl		
0·0000	2·2725	1·14454	1·4981
0·8103	2·2898	1·14192	1·4984
1·4294	2·3030	1·13994	1·4987
2·3099	2·3217	1·13726	1·4990
2·7155	2·3344	1·13548	1·4993
4·1031	2·3610	1·13162	1·4999
	2 : 2′-Dichlorodiphenyl		
0·0000	2·2725	1·14462	1·4980
0·8710	2·2913	1·14150	1·4986
1·3960	2·3020	1·13955	1·4991
2·1093	2·3172	1·13708	1·4996
2·3441	2·3221	1·13622	1·4998
2·6680	2·3290	1·13507	1·5001
3·2365	2·3412	1·13302	1·5005
	2 : 2′-Dibromodiphenyl		
0·0000	2·2725	1·14462	1·4980
1·0275	2·2874	1·13884	1·4988
1·6191	2·2926	1·13554	1·4989
2·3093	2·3065	1·13164	1·4997
2·9714	2·3160	1·12794	1·5002
3·9714	2·3311	1·12233	1·5009
4·6202	2·3409	1·11867	1·5014
	2 : 2′-Di-iododiphenyl		
0·0000	2·2725	1·14462	1·4980
1·1007	2·2834	1·13732	—
1·7043	2·2897	1·13333	1·4993
2·2749	2·2952	1·12951	1·4997
2·6877	2·2998	1·12677	1·5001
3·3174	2·3061	1·12263	1·5006
3·7024	2·3096	1·12007	1·5009
	2 : 2′-Dinitrodiphenyl		
0·0000	2·2725	1·14459	1·4981
0·2506	2·3022	1·14349	1·4983
0·3720	2·3169	1·14294	1·4984
0·6009	2·3448	1·14201	1·4986
0·7729	2·3655	1·14129	1·4987
0·9357	2·3861	1·14054	1·4989
1·3687	2·4399	1·13876	1·4992
	3 : 3′-Dinitrodiphenyl		
0·0000	2·2725	1·14460	1·4979
0·1099	2·2809	1·14412	1·4980
0·4168	2·3058	1·14277	1·4982
0·8921	2·3435	1·14072	1·4985
1·3256	2·3783	1·13877	1·4989
1·4978	2·3925	1·13801	1·4991

2 : 2′-Diaminodiphenyl was prepared by reducing 2 : 2′-dinitrodiphenyl with iron filings and water in the presence of a little acetic acid, the product being made alkaline with ammonia and extracted with acetone. The acetone was distilled off, the residue extracted with hydrochloric acid, and the extract made alkaline with ammonia. The precipitated amine was separated and extracted with light petroleum (b. p. 40—60°) in a Soxhlet apparatus. The product separating from the extract had m. p. 81° (lit., 78—81°).

2 : 2′-Difluorodiphenyl, prepared from 2 : 2′-diaminodiphenyl by Schiemann and Roselius's method (*Ber.*, 1932, **65**, 737) and recrystallised from alcohol, had m. p. 118·5° (lit., 117—117·5°).

2 : 2′-Dichlorodiphenyl, prepared from 2 : 2′-dinitrodiphenyl by Mascarelli and Gatti's method (*Gazzetta*, 1932, **59**, 868) and recrystallised from methyl alcohol, had m. p. 61·5° (lit., 59—62°).

2 : 2′-Dibromodiphenyl, prepared from 2 : 2′-diaminodiphenyl by Schwechten's method (*Ber.*, 1932, **65**, 1605) and recrystallised from methyl alcohol, had m. p. 81·5° (lit., 80—81°).

2 : 2′-Di-iododiphenyl, prepared from 2 : 2′-diaminodiphenyl by Lothrop's method (*J. Amer. Chem. Soc.*, 1941, **63**, 1187) and recrystallised from ethyl alcohol, had m. p. 110° (lit., 108°).

3 : 3′-Dinitrodiphenyl, lent by Professor E. E. Turner and recrystallised from ethyl alcohol, had m. p. 199° (lit., 197—200°).

Apparatus and Measurements.—The dielectric constants, specific volumes, and refractive indices of the solutions at 25·0° are recorded in Table 3. These were determined by the methods used in Part II, and the parameters listed in Table 1 were derived from these figures by the same devices as previously.

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