498. *The Relation between Configuration and Conjugation in Diphenyl Derivatives. Part II.* The Dipole Moments of the Monohalogeno- and Mononitro-diphenyls.*

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The dipole moments of chloro-, bromo-, and iodo-benzene and of the mono-fluoro-, -chloro-, -bromo-, -iodo-, and -nitro-diphenyls have been determined in benzene solution at 25°. On the assumption that the difference between the moments of corresponding derivatives of benzene and diphenyl is due to classical induction effects only, " theoretical " values for the moments of the latter have been calculated from the measured values for the former. The observed moment for 4-fluorodiphenyl is slightly less, and that for 4-nitrodiphenyl appreciably greater, than the corresponding calculated moments, in accord with the existence of an increased mesomeric effect due to the introduction of the second aromatic ring. For the 3-halogenodiphenyls the observed moments are slightly greater than the calculated values, a result compatible with a suppression of the mesomeric effect of the halogens through conjugation between the rings. The moments of the 2-substituted diphenyls are in all cases greater than the values to be expected with the rings coplanar to one another, and, except for 2-bromodiphenyl, are approximately equal to the calculated values for a configuration with the rings in planes at right angles to one another. As an increased mesomeric effect would not be expected to alter these moments very much, it is inferred that the mean position of the rings is nearer to the perpendicular than to the coplanar arrangement.

THE dipole moments of a number of derivatives of diphenyl have been reported at various times, but the figures show a lack of agreement which renders their interpretation difficult. As an accurate knowledge of the effects on the polarity of the molecule of the introduction of substituents into various positions is of great importance in relation to the spatial arrangement within the molecules and to the character of the central bond, a systematic investigation of the apparent dipole moments of these compounds in benzene solution has been undertaken. In this paper the measurements on the mono-halogeno- and -nitro-diphenyls are reported. As different recorded data for chloro-, bromo-, and iodo-benzene are so much at variance that no satisfactory recalculation of their dipole moments can be carried out, measurements on these compounds have also been included.

Since this work was begun, Everard, Kumar, and Sutton (*J.*, 1951, 2807) have reported measurements on 4-bromo- and 4-nitro-diphenyl, and Everard and Sutton (*J.*, 1951, 2817) have tabulated and discussed the available data for the mono-chloro-, -nitro-, -amino-, and -cyano-diphenyls. Although the results included in this comparison were recalculated by Halverstadt and Kumler's method (*J. Amer. Chem. Soc.*, 1941, **64**, 2982), the original data were drawn from several sources, and in certain instances the figures derived differ appreciably from ours.

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* Part I, Beaven, Hall, Lesslie, and Turner, *J.*, 1952, 854.

The essential parameters and the values of $P_{2\infty}$, $[R_D]$, and μ derived from them are listed in Table 1, where α, β, and ν denote the limiting values of $\Delta\varepsilon/w$, $\Delta v/w$, and $\Delta n^2/w$, respectively, at zero concentration, and the other symbols have their usual significance. To facilitate comparison with previous measurements, and with the summary drawn up by Everard and Sutton, the dipole moments have been calculated on the assumption that P_{E+A} is represented sufficiently closely by $[R_D]$. This has some justification in the present instance since Le Fèvre and Le Fèvre (*J.*, 1936, 487) found that $P_{2\infty} \approx [R_D]$ for diphenyl and for 4 : 4′-dichlorodiphenyl. The previous values recorded all refer to measurements in benzene solution.

The moment now found for chlorobenzene supports the majority of the earlier measurements rather than the slightly higher value reported by Le Fèvre and used by Everard and Sutton in their comparisons. Of the other compounds which had been studied previously, the greatest deviation from earlier values occurs with 2-nitrodiphenyl. The reason is obscure, but the presence of isomers in the sample used would have been expected to cause the result to be higher than previous values, rather than lower, as is found.

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

Compound	$10^3\alpha$	$-10^4\beta$	$10^3\nu$	$P_{2\infty}$ (c.c.)	$[R_D]$ (c.c.)	μ (D.)	Previous values
Diphenyl derivatives.							
2-Fluoro ...	1,346	2514	196	89·4	51·6	1·36	
3-Fluoro ...	1,730	2490	195	102·0	51·6	1·57	
4-Fluoro ...	1,589	2484	210	97·4	52·1	1·49	1·50 [a]
2-Chloro ...	1,409	2808	256	98·5	57·2	1·42	1·30 [b], 1·44 [c], 1·45 [d]
3-Chloro ...	1,820	2847	283	112·9	57·6	1·65	1·79 [b], 1·64 [d]
4-Chloro ...	1,850	2846	286	114·0	57·8	1·66	1·58 [a], 1·53 [b], 1·63 [c], 1·63 [d], 1·64 [e]
2-Bromo ...	1,279	4159	248	106·7	60·8	1·50	
3-Bromo ...	1,506	4345	263	115·1	60·2	1·64	
4-Bromo ...	1,539	4343	267	116·8	60·3	1·66	1·64 [a], 1·65 [f]
2-Iodo ...	897	5119	284	100·0	67·1	1·27	
3-Iodo	1,110	5245	295	110·2	66·7	1·46	
4-Iodo ...	1,110	5313	312	109·7	67·0	1·45	
2-Nitro ...	7,720	3237	285	338·0	58·8	3·70	3·80 [a], 3·79 [c], 3·81 [e], 3·82 [g]
3-Nitro ...	9,523	3330	301	405·0	58·7	4·12	3·90 [c]
4-Nitro ...	10,670	3367	333	447·7	59·7	4·36	4·17 [a], 4·28 [c], 4·41 [f]
Benzene derivatives.							
Chloro ...	2,450	2328	68	82·4	31·5	1·58	1·53—1·64 [h], 1·60 [i]
Bromo	1,778	4711	129	84·0	34·1	1·56	1·48—1·58 [h], 1·55 [j], 1·57 [e]
Iodo	1,198	5949	175	79·4	39·5	1·40	1·25 [k], 1·295 [l], 1·38 [m], 1·42 [n]

[a] Le Fèvre and Le Fèvre, *J.*, 1936, 1130. [b] Weissberger and Sangewald, *Z. physikal. Chem.*, 1933, **20**, *B*, 145. [c] Naeshagen, *ibid.*, 1934, **25**, *B*, 157. [d] Hampson and Weissberger, *J. Amer. Chem. Soc.*, 1936, **58**, 2111. [e] Recalc. from previous data by Everard and Sutton, *J.*, 1951, 2817. [f] Everard, Kumar, and Sutton, *J.*, 1951, 2807. [g] Lumbroso, *Bull. Soc. chim.*, 1949, **16**, D387. [h] Various measurements prior to 1947, from Wesson, " Tables of Electric Dipole Moments," Technology Press, Cambridge, Mass., 1948. [i] Le Fèvre, *Trans. Faraday Soc.*, 1950, **46**, 1. [j] Brown and de Vries, *J. Amer. Chem. Soc.*, 1951, **73**, 1811. [k] Walden and Werner, *Z. physikal. Chem.*, 1929, **2**, *B*, 10. [l] Bergmann, Engel, and Sandor, *ibid.*, 1930, **10**, *B*, 106. [m] Tiganik, *ibid.*, 1931, **13**, *B*, 425. [n] Saxby, quoted by Everard and Sutton, *loc. cit.*

The molecular refractions deduced from the measurements on the solutions are generally close to those for the liquid state and to the values calculated by adding the difference between the molecular refraction of diphenyl (52·41 c.c.; von Auwers and Frühling, *Annalen*, 1921, **422**, 192) and benzene (26·21 c.c.) to the molecular refractions of the corresponding benzene derivatives (Vogel, Cresswell, Jeffrey, and Lester, *J.*, 1952, 514), *viz.*, fluoro- 52·18, chloro- 57·34, bromo- 60·19, iodo- 65·35, and nitro-diphenyl 58·92 c.c.

Everard and Sutton (*J.*, 1951, 2821) have discussed in detail the interactions between a substituent group and the aryl radical to which it is linked. These comprise: (*a*) the inductive effect, arising through polarisation of the radical by the electric field of the substituent, and now regarded as itself being the result of two components, namely, (i) the " classical " inductive effect (I_C), a purely electrostatic process influencing both σ- and π-electrons, and (ii) the " non-classical " inductive effect (I_N), leading to changes of π-bond order; and (*b*) the mesomeric effect arising through the tendency towards the formation of a π-bond between the substituent and the carbon atom to which it is linked, and causing modifications in the character of the other bonds present in the radical.

From electrostatic theory the I_C effect decreases as the inverse cube of the distance from a point dipole, and hence it is of relatively short range. The I_N effect, however, influences the whole of a conjugated system, and so becomes very closely associated with the mesomeric effect, although, like the I_C effect it may either reinforce or oppose the latter. As changes in π-electron distribution have a reciprocal effect in modifying the σ-bonds between the carbon atoms and the substituent group, and between one carbon atom and another, the whole problem is rather complex.

As the measurements on derivatives of diphenyl have been made in solution, the dipole moments deduced from them are modified by an unknown solvent effect. Hence no exact correlation between theory and observation can be expected, but as benzene was the solvent in all the determinations these solvent effects may be expected to be approximately proportional to the moments of the primary dipoles in these analogous series of compounds. Hence it is interesting to correlate these observations with those on the corresponding benzene derivatives in the same solvent.

Everard and Sutton (*J.*, 1951, 2818) have retained the original definition of the " mesomeric moment " of an aromatic compound as the vector difference between its dipole moment and that of its aliphatic analogue (Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 668). The mesomeric moments, in this sense, of the 4-substituted diphenyl compounds are compared with those of the benzene analogues in Table 2, where the convention adopted is that a positive sign indicates that the moment of the aromatic compound is less than that of its aliphatic analogue.

TABLE 2. *Mesomeric moments* (D) *of 4-substituted compounds.*

Substituent	F	Cl	Br	I	NO_2
Benzene compound	+0·41	+0·43	+0·44	+0·53	−0·76
Diphenyl compound	+0·40	+0·37	+0·34	+0·47	−1·11

As the moments of the C–X σ-bonds cannot differ appreciably between the two series, the differences between the mesomeric moments must be due to the combined action of the I_C and the I_N effect and of the true mesomeric effect. For nitro-compounds the effects all operate in the same sense and hence lead to an increase of 0·35 D in the mesomeric moment on addition of a second ring. For the halogeno-compounds, however, the inductive effects operate in the opposite sense to the mesomeric effect, with the result that when the second ring is added they appear to cancel one another in 4-fluorodiphenyl, whilst the inductive effects outweigh any increased mesomeric effect for the other halogeno-derivatives.

These results, however, do not permit any estimation of the relative magnitudes of the various effects, so it is of interest to calculate the extent to which the differences between the observed moments of the diphenyl and benzene compounds can be interpreted on the basis of the classical inductive effect.

According to the theory developed by Smallwood and Herzfeld (*J. Amer. Chem. Soc.*, 1930, **52**, 1919) and by Frank (*Proc. Roy. Soc.*, 1935, *A*, **152**, 171) the components of the induced moment μ_x and μ_y, respectively parallel to and at right angles to the inducing moment μ, are given by

$$\mu_x = \mu\alpha \, . \, \frac{\varepsilon_a + 2}{3\varepsilon_b r^3} (3 \cos^2\theta - 1) ; \quad \mu_y = \mu\alpha \, . \, \frac{\varepsilon_a + 2}{3\varepsilon_b r^3} \, . \, 3 \sin\theta \cos\theta ,$$

where α is the polarisability of the polarisable system, ε_a and ε_b are the dielectric constants of the polarisable system and of the medium between this and the primary dipole, respectively, r is the distance between the dipole and the polarisable centre, and θ is the angle between μ and r. According to the method by which this theory was applied by Hampson and Weissberger to naphthalene compounds (*J.*, 1936, 393) and to the chlorodiphenyls (*J. Amer. Chem. Soc.*, 1936, **58**, 2111), and by Le Fèvre and Le Fèvre to a few derivatives of diphenyl (*J.*, 1936, 1130), a mono-substituted diphenyl molecule may be regarded as the corresponding derivative of benzene to which an additional polarisable group, namely, a benzene ring, has been added. The polarisable centre of this additional group is at the middle of the unsubstituted ring, and α is the polarisability of benzene, *i.e.*, $12{\cdot}5 \times 10^{-24}$ in the plane of the ring and $6{\cdot}25 \times 10^{-24}$ at right angles to that plane (Debye, "Handbuch der Radiologie," Akademische Verlagsges., Leipzig, 1925, Vol. VI, 786). No great error can be introduced by taking both ε_a and ε_b as 2·27, the dielectric constant of benzene.

The inducing dipole has been assumed in each case to be equal to the dipole moment of the corresponding benzene derivative as measured in benzene solution. The error due to regarding this as a point dipole cannot be large so long as the dipole is at some distance from the polarisable centre.

As the moment of a halogeno-compound probably includes contributions in the sense $\overset{-}{\mathrm{C}}\ \overset{+}{\mathrm{X}}$ from both the σ- and the π-bonding orbitals, which are more than offset by the moment in the reverse sense due to the lone-pair electrons of the halogen atom, it follows that the "centre" of the electrical asymmetry will lie somewhere between the two nuclei. For the halogen compounds it has been taken as located at the "point of contact" of the carbon and the halogen atoms, *i.e.*, on the C–X bond and 0·77 Å from the carbon nucleus. For the nitrodiphenyls it has been taken as at the centre of the nitrogen atom. The internuclear distances used have been C–C (aromatic) 1·40, C–C (centre bond) 1·50, and C–N 1·45 Å.

When the rings are coplanar, and for all orientations when a symmetrical substituent is in the 4-position, the inducing field and induced moment are in the plane of the ring, and hence the value of α for the plane of the ring is applicable. On the other hand, when the rings are not coplanar and the substituent is in the 2- or the 3-position the field set up must be resolved in directions parallel to and at right angles to the plane of the unsubstituted ring, and the appropriate values of α used in each case. As the polarisability is less in the direction at right angles to the ring, the effect of the induced moment on the overall moment decreases progressively with increasing angle of inclination of the planes of the rings, and becomes a minimum for the right-angled position. The values of r and θ calculated for the various types of diphenyl compounds discussed are recorded in Table 3, together with the theoretical ratios of the moments of the corresponding diphenyl and benzene derivatives for the two extreme positions of the rings, *i.e.*, coplanar, and in planes at right angles.

TABLE 3.

			μ (calc.)/μ (benzene derivative)	
	r	θ	Rings coplanar	Rings at 90°
2-Halogenodiphenyl	3·73	89° 32′	0·849	0·906
3-Halogenodiphenyl	5·71	40° 41′	1·032	1·034
4-Halogenodiphenyl	6·47	0°	1·058	1·058
2-Nitrodiphenyl	3·79	79° 3′	0·876	0·908
3-Nitrodiphenyl	6·25	33° 34′	1·031	1·030
4-Nitrodiphenyl	7·17	0°	1·042	1·042

To derive calculated figures for comparison with the observed values the dipole moment of fluorobenzene has been taken as 1·48 D, the value used by Everard and Sutton. The moments of chloro-, bromo-, and iodo-benzene have been remeasured, whilst for nitrobenzene the value of $P_{2\infty}$ at 25° (362·0 c.c.) recalculated by Cleverdon and Smith (*Trans. Faraday Soc.*, 1949, **45**, 109) has been used in conjunction with $P_{E+A} = [R_D] = 32{\cdot}7$ c.c. to compute μ.

The observed and calculated values of the dipole moments of the diphenyl derivatives are compared in Table 4, in which the figure for 4-cyanodiphenyl reported by Everard, Kumar, and Sutton (*loc. cit.*) is also included.

The measured moments of 4-nitro- and 4-cyano-diphenyl are appreciably greater than the calculated values. For these compounds the I_N effect operates in the same sense as the mesomeric effect, each tending to increase the moment. The results, therefore, lead to the inference that the resultant of these two effects is increased considerably by introducing the second ring, indicating that the effects are transmitted through the central bond linking the two rings.

For the 4-halogenodiphenyls, however, the I_N effect operates in the reverse sense to the mesomeric effect, the former tending to increase the dipole moment and the latter to decrease it. For 4-fluorodiphenyl the mesomeric effect seems to be predominant, but in the other compounds of this class the two effects appear virtually to cancel one another. As the moment of the primary dipole in 4-fluorodiphenyl is about 0·1 D smaller than in 4-chloro- or in 4-bromo-diphenyl, the inductive effect will be slightly less than in either of the latter compounds, so the fact that the observed moment is 0·08 D less than the calculated value may be evidence of the greater mesomeric effect of fluorine compared with other halogen atoms. For the other 4-halogenodiphenyls the differences between the observed and the calculated values are within the possible errors of computation arising from the incidence of solvent effect and atom polarisation.

TABLE 4. *Comparison of observed with calculated dipole moments for diphenyl derivatives.*

	μ obs. (D)	μ calc. (D)	Difference (D)		μ obs. (D)	μ calc. (D)	Difference (D)
2-Fluorodiphenyl	1·36	1·26 (coplanar)	+0·10	3-Fluorodiphenyl...	1·57	1·53	+0·04
		1·34 (90°)	+0·02	3-Chlorodiphenyl...	1·65	1·63	+0·02
2-Chlorodiphenyl	1·42	1·34 (coplanar)	+0·08	3-Bromodiphenyl...	1·64	1·61	+0·03
		1·43 (90°)	−0·01	3-Iododiphenyl ...	1·46	1·45	+0·01
2-Bromodiphenyl	1·50	1·32 (coplanar)	+0·18	3-Nitrodiphenyl ...	4·12	4·13	−0·01
		1·41 (90°)	+0·09	4-Fluorodiphenyl...	1·49	1·57	−0·08
2-Iododiphenyl ...	1·27	1·19 (coplanar)	+0·08	4-Chlorodiphenyl...	1·66	1·67	−0·01
		1·27 (90°)	0·0	4-Bromodiphenyl...	1·66	1·65	+0·01
2-Nitrodiphenyl	3·70	3·51 (coplanar)	+0·19	4-Iododiphenyl ...	1·45	1·48	−0·03
		3·64 (90°)	+0·06	4-Nitrodiphenyl ...	4·36	4·18	+0·18
				4-Cyanodiphenyl ...	4·33	4·22	+0·11

If conjugation occurs across the bond between the two nuclei, the introduction of a phenyl group into the 3-position of a benzene derivative would be expected to decrease slightly the mesomeric effect of a halogen atom, and to increase slightly that of a nitro-group. The differences between the observed and the calculated moments for the 3-substituted diphenyl derivatives are small, and within the possible errors referred to above, but in each case they are in the sense expected from the modification in mesomeric effect, and hence are not incompatible with conjugation between the rings.

The evidence of the measurements on the 4- and 3-substituted derivatives of diphenyl is therefore in general confirmation of the conclusion reached from a number of different approaches to the problem, both chemical and physical, that in the diphenyl skeleton conjugation occurs through the central bond (cf. Part I, *loc. cit.*).

In 2-substituted diphenyl derivatives an increased mesomeric effect should lead to electron drifts along the axis of the dipole and in a direction at 120° to this axis. The resultant effect upon the dipole moment of the moment would therefore be expected to be small. As, with the possible exception of 2-fluorodiphenyl, it is impossible on steric grounds for any of these molecules to assume a fixed coplanar configuration, their dipole moments would be expected to lie between the values calculated for the coplanar and the right-angled positions of the rings. The observed moments are much greater than the values calculated for the coplanar position, and, except for 2-bromodiphenyl, the value for which is anomalously high, they all lie near the figures calculated for the perpendicular configuration. Although for the latter configuration the calculated inductive effect does not depend very critically upon the exact location assumed for the point dipole, the polarisable centres are much nearer to the dipole in these compounds than in the 3- and 4-substituted derivatives. I_C effects almost identical with those used are obtained if the unsubstituted ring is regarded as six polarisable centres located either at the carbon nuclei or at the mid-points of the C–C bonds, instead of as a polarisable whole, but the assumption of a point dipole may lead to some error in this case. Therefore, beyond the general inference that the mean position of the rings in these compounds is probably much nearer the right-angled than the coplanar position, it is not justifiable to draw further conclusions from the small differences between the observed and the calculated figures.

EXPERIMENTAL

Preparation and Purification of Materials.—" Crystallisable "-grade benzene was purified as described by Few and Smith (*J.*, 1949, 753). All batches were of constant b. p. within ±0·02°; d_4^{25} 0·87368 ± 0·00003; n_D^{25} 1·4980 ± 0·0001 (" Selected Values of the Properties of Hydrocarbons," American Petroleum Institute, 1948, gives d_4^{25} 0·87370, n_D^{25} 1·49791).

2- and 4-Nitrodiphenyl were prepared by Bell, Kenyon, and Robinson's method (*J.*, 1926, 1242), the former being purified by Gull and Turner's method (*J.*, 1929, 491). These and all other solid compounds were recrystallised to constant m. p. (38° and 114°, respectively; lit., 35—38° and 113—114°).

3-Nitrodiphenyl, prepared by Elks, Haworth, and Hey's method (*J.*, 1940, 1284) and recrystallised successively from light petroleum (b. p. 40—60°) and alcohol, had m. p. 60·5° (Gomberg and Bachmann, *J. Amer. Chem. Soc.*, 1924, **46**, 2339, and Elks, Haworth, and Hey, give 61°).

Aminodiphenyls were prepared by reducing the nitrodiphenyls with iron filings and water in the presence of a trace of acetic acid, the product being made alkaline with ammonia and extracted with acetone. These were converted into the fluorodiphenyls by Schiemann and Roselius's method (*Ber.*, 1929, **62**, 1805), the products being recrystallised from alcohol. 2-, 3-,

TABLE 5.

100w	ε	v	n
2-Fluorodiphenyl (sample i)			
0·0000	2·2725	1·14459	1·4980
1·0632	2·2868	1·14195	1·4987
1·8077	2·2969	1·14006	1·4991
2·3776	2·3047	1·13857	1·4994
2·8719	2·3113	1·13742	1·4999
3·7650	2·3234	1·13514	1·5006
4·6775	2·3356	1·13280	1·5012
2-Fluorodiphenyl (sample ii)			
0·0000	2·2725	1·14462	1·4980
1·0240	2·2860	1·14205	1·4987
1·5003	2·2927	1·14082	1·4989
1·8791	2·2975	1·13987	1·4992
3·0648	2·3137	1·13691	1·5000
2-Chlorodiphenyl			
0·0000	2·2725	1·14459	1·4980
1·0334	2·2874	1·14167	1·4988
1·5409	2·2940	1·14028	1·4991
2·1712	2·3034	1·13845	1·4996
2·4536	2·3075	1·13774	1·4999
3·1671	2·3167	1·13573	1·5004
3·5204	2·3216	1·13471	1·5009
4·3726	2·3342	1·13222	1·5017
4-Chlorodiphenyl			
0·0000	2·2725	1·14461	1·4980
0·9463	2·2903	1·14198	1·4989
1·6477	2·3028	1·13997	1·4996
2·1235	2·3117	1·13857	1·5001
2·6418	2·3211	1·13710	1·5006
3·0548	2·3292	1·13590	1·5010
3·5108	2·3378	1·13459	1·5013
4·9308	2·3634	1·13056	1·5025
3-Fluorodiphenyl			
0·0000	2·2725	1·14462	1·4980
1·1203	2·2917	1·14184	1·4988
1·6617	2·3014	1·14046	1·4991
2·2278	2·3111	1·13904	1·4994
2·4626	2·3156	1·13846	1·4996
3·2667	2·3291	1·13654	1·5001
3·3654	2·3314	1·13621	1·5002
4·4766	2·3503	1·13352	1·5009
4-Fluorodiphenyl			
0·0000	2·2725	1·14454	1·4981
0·5190	2·2806	1·14330	1·4984
1·1198	2·2903	1·14175	1·4989
1·6251	2·2984	1·14050	1·4992
2·2328	2·3079	1·13901	1·4996
2·6494	2·3142	1·13796	1·5000
2·9683	2·3192	1·13713	1·5002
3·4652	2·3269	1·13590	1·5006
3-Chlorodiphenyl			
0·0000	2·2725	1·14462	1·4980
0·8622	2·2885	1·14216	1·4988
1·3345	2·2968	1·14082	1·4993
1·4790	2·2994	1·14040	1·4994
2·2495	2·3136	1·13821	1·5001
2·9636	2·3267	1·13618	1·5008
3·9578	2·3450	1·13337	1·5019
2-Bromodiphenyl			
0·0000	2·2725	1·14462	1·4979
1·1689	2·2877	1·13977	1·4989
1·8598	2·2964	1·13680	1·4995
2·8137	2·3084	1·13297	1·5002
3·6557	2·3190	1·12948	1·5009
4·0959	2·3252	1·12742	1·5013
4·6656	2·3294	1·12532	1·5017
3-Bromodiphenyl			
0·0000	2·2725	1·14452	1·4980
1·3745	2·2932	1·13858	1·4992
2·1059	2·3044	1·13524	1·4998
2·9722	2·3174	1·13171	1·5006
3·2150	2·3220	1·13060	1·5008
4·1031	2·3347	1·12670	1·5015
4·7750	2·3452	1·12368	1·5023
5·2729	2·3539	1·12164	1·5027
2-Iododiphenyl			
0·0000	2·2725	1·14462	1·4980
0·8993	2·2808	1·14001	1·4988
1·4505	2·2858	1·13717	1·4994
2·0141	2·2919	1·13426	1·4999
2·6443	2·2978	1·13108	1·5004
3·0305	2·3024	1·12912	1·5009
3·2094	2·3030	1·12824	1·5011
3·9546	2·3119	1·12440	1·5018

TABLE 5.—*Continued.*

100w	ε	v	n
4-Iododiphenyl			
0·0000	2·2725	1·14462	1·4980
1·0507	2·2843	1·13902	1·4991
1·3481	2·2873	1·13754	1·4994
2·0467	2·2956	1·13378	1·5001
2·4159	2·2996	1·13176	1·5005
3·0618	2·3075	1·12833	1·5012
3·6434	2·3142	1·12527	1·5018
3-Nitrodiphenyl			
0·0000	2·2725	1·14459	1·4980
1·0458	2·3726	1·14108	1·4990
1·5716	2·4233	1·13935	1·4996
1·9760	2·4626	1·13800	1·5000
2·4938	2·5130	1·13633	1·5005
2·9697	2·5597	1·13471	1·5010
3·2971	2·5917	1·13364	1·5013
4·1664	2·6775	1·13068	1·5022
4-Bromodiphenyl			
0·0000	2·2725	1·14459	1·4980
0·5154	2·2806	1·14239	1·4984
1·2248	2·2914	1·13926	1·4991
1·7120	2·2989	1·13715	1·4995
1·9057	2·3018	1·13629	1·4997
2·4967	2·3107	1·13371	1·5002
3·0626	2·3196	1·13135	1·5008
3-Iododiphenyl			
0·0000	2·2725	1·14462	1·4980
1·0788	2·2849	1·13897	1·4990
1·4705	2·2893	1·13694	1·4995
2·0026	2·2952	1·13403	1·5000
2·8073	2·3043	1·12984	1·5008
3·4686	2·3119	1·12646	1·5014
3·7644	2·3146	1·12489	1·5017
4·9218	2·3273	1·11885	1·5028
2-Nitrodiphenyl			
0·0000	2·2725	1·14459	1·4980
0·9915	2·3477	1·14139	1·4990
1·2801	2·3716	1·14048	1·4992
2·1704	2·4409	1·13761	1·5001
2·5328	2·4684	1·13636	1·5004
3·0716	2·5111	1·13459	1·5009
3·4107	2·5378	1·13355	1·5012
4-Nitrodiphenyl			
0·0000	2·2725	1·14459	1·4980
1·1622	2·3968	1·14069	1·4993
1·5389	2·4381	1·13933	1·4997
2·1324	2·5031	1·13743	1·5003
2·4178	2·5343	1·13423	1·5007
3·0743	2·6059	1·13423	1·5013
3·5503	2·6582	1·13266	1·5020
4·3400	2·7470	1·13000	1·5029
Chlorobenzene			
0·0000	2·2725	1·14462	1·4977
0·9667	2·2960	1·14237	1·4979
1·4006	2·3071	1·14131	1·4980
2·1528	2·3254	1·13958	1·4982
3·0452	2·3478	1·13757	1·4984
4·0086	2·3723	1·13533	1·4986
5·3106	2·4050	1·13226	1·4989
Iodobenzene			
0·0000	2·2725	1·14462	1·4980
1·1250	2·2860	1·13792	1·4987
1·8641	2·2949	1·13357	1·4991
2·4291	2·3015	1·13015	1·4994
3·1596	2·3103	1·12587	1·4999
4·6528	2·3285	1·11691	1·5007
5·5135	2·3384	1·11181	1·5012
6·7262	2·3541	1·10459	1·5019
Bromobenzene			
0·0000	2·2725	1·14462	1·4980
0·6423	2·2838	1·14161	1·4982
0·1847	2·2867	1·14087	1·4984
1·2156	2·2942	1·13890	1·4985
1·7062	2·3029	1·13663	1·4987
1·8568	—	1·13577	1·4988
2·7268	2·3209	1·13175	—
3·3684	—	1·12834	1·4992
4·4817	2·3532	1·12327	—
5·2954	—	1·11954	1·4999
7·2217	—	1·11043	1·5005
8·6312	—	1·10371	1·5012

and 4-Fluorodiphenyl had m. p. 74·5°, 29·5°, and 75°, respectively (Schiemann and Roselius gave 72°, 26—26°, and 74—75°, respectively).

Chlorodiphenyls were prepared by Sandmeyer's method (Zaheer and Faseeh, *J. Indian Chem. Soc.*, 1944, **21**, 27), the 2- and 3-isomers being fractionally distilled at reduced pressure. 2- and 4-Chlorodiphenyl, recrystallised from alcohol, had m.p. 32·5° and 77°, respectively (lit., 31—34° and 75·5—77·7°). 3-Chlorodiphenyl had d_4^{25} 1·1579, n_D^{25} 1·6181, [R_D] 57·1 c.c.

2-Bromodiphenyl was prepared by Sandmeyer's method, the diazotisation being effected in hydrobromic acid, and the product was fractionally distilled at low pressure. It had d_4^{25} 1·3522, n_D^{25} 1·6248, [R_D] 60·9 c.c.

3-Bromodiphenyl, prepared by Huber, Renoll, Rossow, and Mowry's method (*J. Amer. Chem. Soc.*, 1946, **68**, 1109), had d_4^{25} 1·3976, n_D^{25} 1·6385, [R_D] 60·0 c.c. (Huber *et al.* give n_D^{25} 1·6390).

4-Bromodiphenyl, lent by Professor Turner and recrystallised from alcohol, had m. p. 90·5° (lit., 89—91·2°).

Iododiphenyls were prepared by diazotising the corresponding amines and adding the products to potassium iodide solution. 2-Iododiphenyl, isolated by extraction with ether, had d_4^{25} 1·5511, n_D^{25} 1·6548, [R_D] 66·2 c.c. 3-Iododiphenyl, isolated by Campaigne and Reid's method (*J. Amer. Chem. Soc.*, 1946, **68**, 1663), had d_4^{25} 1·5967, n_D^{25} 1·6730, [R_D] 65·8 c.c. 4-Iododiphenyl, recrystallised from acetic acid, had m.p. 114° (lit., 112—114°).

Apparatus and Measurements.—The dielectric constants were determined relative to benzene as standard, with a heterodyne beat apparatus (Few, Smith, and Witten, *Trans. Faraday Soc.*, 1952, **48**, 211). Specific volumes were measured with a pyknometer, and the refractive indices with a Hilger Abbé refractometer. All measurements were made at 25·0°.

The results from which the parameters listed in Table 1 were derived are summarised in Table 5, where the symbols have their usual significance. For many of the compounds the dielectric constants of the solutions were linear with w over the concentration range studied, and hence the slope of the best straight line through these values was taken as α. For the nitrodiphenyls, however, the variation of ε with w was not linear, and hence the limiting value of $\delta\varepsilon/\delta w$ at low concentration was used. In all cases both v and n^2 were linear with w, and the slopes of the best straight lines were taken for β and ν, respectively. The values of $P_{2\infty}$ deduced from these parameters were in each case checked with the result of plotting against w the values of P_2 calculated from the data for each concentration, and extrapolating to zero concentration. The values of $[R_D]$ were similarly checked against the values derived for the individual concentrations.

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