534. *Molecular Polarisability. The Molar Kerr Constants of Certain Derivatives of Diphenyl.*

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The molar Kerr constants of diphenyl and its 4-fluoro-, -chloro-, -bromo-, -iodo-, -nitro-, and 2 : 2′- and 3 : 3′-dinitro-derivatives are reported and discussed. They indicate a rough orthogonality of configuration for the last two molecules, and may be reconciled with flat configurations for the first six, among which conjugation is presumably causing a polarisability exaltation parallel to the 1 : 1′-bond.

The measurements now recorded were started in the hope that they would assist decisions on the configurations adopted by diphenyl and certain of its derivatives when present as solutes at room temperatures.

The last thirty years' literature shows that configuration in this series is strongly affected by substitution. The diphenyl skeleton was originally expected by Le Fèvre and Turner [1] to possess a tendency to planarity owing to conjugation, opposed by the volumes and electrical effects of substituents; the hydrocarbon itself is now known by *X*-ray analysis and electron diffraction to be planar [2] in the crystal but non-planar [3] in the vapour. Dipole moments [4] in solution have indicated that 2 : 2′-dinitrodiphenyls have their rings rotated out of the *cis*-position so that the angles between them range from 70° to 90° and that these (azimuthal) angles are exceeded in the corresponding 3 : 3′-isomers. In gaseous 2 : 2′-dihalogeno-diphenyls [5] the azimuthal angles are about 75°, as in crystalline [6] 2 : 2′-dichlorobenzidine (72°) and [7] *m*-tolidine dihydrochloride (71°); yet while 3 : 3′-dichlorobenzidine is [3] non-planar (*ca.* 52°) as a gas, it is stated [8] as a solid to have the chlorine atoms disposed *trans* in a model which is flat or nearly so. No information by the above methods appears to exist concerning the configurations of 4-monosubstituted diphenyls.

Present Measurements.—Standard techniques being used,[9,10] the dielectric constants, densities, electric double refractions, etc., have been observed for solutions of the solutes named in Tables 1 and 2. Symbols are defined in refs. 9 and 10.

The dipole moments of the five monosubstituted diphenyls in Table 2 have the slight novelty of being determined in carbon tetrachloride instead of benzene.[4,11] The values are qualitatively consistent with past studies of relationships between polarisation and medium (cf. ref. 9, Chap. III).

Discussion.—It is of interest to compare experimental molar Kerr constants with those calculable from known bond or group polarisabilities. Data by Le Fèvre and Purnachandra Rao [12] are relevant. For example, in computing ${}_{\mathrm{m}}K$ for 2 : 2′- or 3 : 3′-dinitrodiphenyl, use can be made of the molecular semi-axes reported for nitrobenzene,[12] *viz.*, $b_1 = 1{\cdot}617$, $b_2 = 1{\cdot}200$, and $b_3 = 0{\cdot}862 \times 10^{-23}$ c.c., where b_1 lies collinear with $\mu_{\text{resultant}}$, b_2 collinear with the 2 : 6 direction, and b_3 perpendicular to the molecular plane.

[1] Le Fèvre and Turner, *Chem. and Ind.*, 1926, **45**, 831.
[2] Dhar, *Proc. Nat. Inst. Sci. India*, 1949, **15**, 11.
[3] Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 408.
[4] Le Fèvre and Le Fèvre, *J.*, 1936, 1130; Le Fèvre and Vine, *J.*, 1938, 967; Weissberger, Sängewald, and Hampson, *Trans. Faraday Soc.*, 1934, **30**, 884; Littlejohn and Smith, *J.*, 1953, 2456, 1954, 2552.
[5] Bastiensen, *Acta Chem. Scand.*, 1950, **4**, 926.
[6] Smare, *Acta Cryst.*, 1948, **1**, 150.
[7] Fowweather and Hargreaves, *ibid.*, p. 81.
[8] Toussaint, *ibid.*, p. 43.
[9] Le Fèvre, " Dipole Moments," Methuen, London, 3rd Edn., 1953.
[10] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.*, 1955, **5**, 261.
[11] Wesson, " Tables of Electric Dipole Moments," Technology Press, Massachusetts Institute of Technology, 1948.
[12] Le Fèvre and Purnachandra Rao, *J.*, 1958, 1465.

TABLE 1. *Dielectric polarisations, Kerr effects, etc., at 25°.*

*Diphenyl in carbon tetrachloride.**

10^5w_2	778	969	1762	2712	3464	4196
ε_{12}	2·2315	2·2326	—	—	2·2470	2·2518
d_{12}	1·5784	1·5771	—	—	1·5568	1·5505
n_{12}	1·4594	1·4601	—	—	1·4658	1·4679
$10^7\Delta B$	0·018	0·023	0·041	0·064	$0{\cdot}080_5$	0·097

whence $\sum\Delta\varepsilon/\sum w_2 = 0{\cdot}585$, $\sum\Delta d/\sum w_2 = -0{\cdot}799_4$, $\sum\Delta n/\sum w_2 = 0{\cdot}246_6$, $10^7\Delta B = 2{\cdot}37_9 w_2 - 1{\cdot}41 w_2^2$.

*4-Fluorodiphenyl in carbon tetrachloride.**

10^5w_2	227	266	295	304	329	411
ε_{12}	2·2335	2·2345	2·2353	2·2363	2·2366	2·2384
d_{12}	1·5830	—	1·5825	1·5825	1·5823	—
10^5w_2	480	818	885			
n_{12}	1·4584	1·4589	1·4596			
10^5w_2	176	245	724	795	901	1465
$10^7\Delta B$	0·023	0·033	0·096	0·103	0·118	0·192

whence $\sum\Delta\varepsilon/\sum w_2 = 2{\cdot}87_1$, $\sum\Delta d/\sum w_2 = -0{\cdot}666_7$, $\sum\Delta n/\sum w_2 = 0{\cdot}183_2$, $\sum\Delta B/\sum w_2 = 13{\cdot}1_2$.

*4-Chlorodiphenyl in carbon tetrachloride.**

10^5w_2	384	412	561	725	734	1223	1232	1534
ε_{12}	2·2399	2·2403	2·2445	2·2506	2·2518	2·2671	2·2665	2·2778
d_{12}	1·5820	1·5818	1·5809	1·5806	1·5797	1·5773	1·5770	1·5700
10^5w_2	394	395	650					
n_{12}	1·4582	1·4583	1·4589					
10^5w_2	209	366	637	846	902	997		
$10^7\Delta B$	0·043	0·082	0·126	0·185	0·187	0·214		

whence $\sum\Delta\varepsilon/\sum w_2 = 3{\cdot}27_0$, $\sum\Delta d/\sum w_2 = -0{\cdot}686_3$, $\sum\Delta n/\sum w_2 = 0{\cdot}201_5$, $\sum\Delta B/\sum w_2 = 21{\cdot}1_5$.

*4-Bromodiphenyl in carbon tetrachloride.**

10_5w_2	375	392	554	767	813	1058	1249	1598
ε_{12}	2·2380	2·2385	2·2433	2·2500	2·2514	2·2576	2·2630	2·2710
d_{12}	1·5834	1·5832	1·5831	1·5826	1·5825	1·5820	1·5815	1·5807
10^5w_2	308	324	365					
n_{12}	1·4583	1·4584	1·4585					
10^5w_2	54	156	402	445	569	614		
$10^7\Delta B$	0·008	0·027	0·073	0·080	0·107	0·115		

whence $\sum\Delta\varepsilon/\sum w_2 = 2{\cdot}89_1$, $\sum\Delta d/\sum w_2 = -0{\cdot}249_8$, $\sum\Delta n/\sum w_2 = 0{\cdot}270_8$, $\sum\Delta B/\sum w_2 = 18{\cdot}3_0$.

*4-Iododiphenyl in carbon tetrachloride.**

10^5w_2	46	49	86	88	102	104
ε_{12}	2·2280	2·2280	2·2286	2·2287	2·2291	2·2291
d_{12}	1·5845	1·5845	1·5845	1·5844	1·5844	1·5844
n_{12}	1·4576	1·4576	—	—	—	1·4578
$10^7\Delta B$	0·010	0·011	0·020	0·020	0·021	0·021

whence $\sum\Delta\varepsilon/\sum w_2 = 2{\cdot}00$, $\sum\Delta d/\sum w_2 = -0{\cdot}063$, $\sum\Delta n/\sum w_2 = 0{\cdot}301_5$, $\sum\Delta B/\sum w_2 = 21{\cdot}7$.

*4-Nitrodiphenyl in carbon tetrachloride.**

10^5w_2	39	56	94	132	175	211
$10^7\Delta B$	0·062	0·084	0·144	0·205	0·266	0·326
10^5w_2	185	230	385			
n_{12}	1·4579	1·4580	1·4586			

whence $\sum\Delta B/\sum w_2 = 153{\cdot}7$, $\sum\Delta n/\sum w_2 = 0{\cdot}250_0$.

2 : 2′-Dinitrodiphenyl in benzene.†

10^5w_2	418	829	1112	1297	1301
$10^7\Delta B$	−0·083	−0·158	−0·205	−0·252	−0·255

whence $\sum\Delta B/\sum w_2 = -19{\cdot}22$.

3 : 3′-Dinitrodiphenyl in benzene.†

10^5w_2	171	172	174	212	214	268
ε_{12}	2·2856	2·2859	2·2859	2·2885	2·2889	2·2938
d_{12}	0·8744	0·8744	0·8744	0·8745	0·8746	0·8748
10^5w_2	249	268	373	398		
n_{12}	1·4978	1·4978	1·4979	1·4980		
10^5w_2	33	50	65	76	80	82
$10^7\Delta B$	−0·005	−0·009	−0·012	−0·014	−0·014	−0·015

whence $\sum\Delta\varepsilon/\sum w_2 = 7{\cdot}72_9$, $\sum\Delta d/\sum w_2 = 0{\cdot}355_0$, $\sum\Delta n/\sum w_2 = 0{\cdot}085_4$, $\sum\Delta B/\sum w_2 = -17{\cdot}8_6$.

* For $w_2 = 0$, $\varepsilon^{25} = 2{\cdot}2270$, $d_4^{25} = 1{\cdot}5845$, $n_D^{25} = 1{\cdot}4575$, $B_D^{25} = 0{\cdot}070 \times 10^{-7}$.
† For $w_2 = 0$, $\varepsilon^{25} = 2{\cdot}2725$, $d_4^{25} = 0{\cdot}8738$, $n_D^{25} = 1{\cdot}4976$, $B_D^{25} = 0{\cdot}410 \times 10^{-7}$.

TABLE 2. *Calculation of results.*

Solute	$\alpha\varepsilon_1$	β	γ	δ	$_\infty P_2$ (c.c.)	$_D P$ (c.c.)	μ (D)	$10^{-12}{}_\infty({}_mK_2)$
Diphenyl	0·585	$-0{\cdot}504_5$	0·169	$33{\cdot}9_9$	$52{\cdot}0_6$	(52·1)	*ca.* 0	40·5
4-Fluoro-	$2{\cdot}87_1$	$-0{\cdot}420_8$	0·126	187·4	$97{\cdot}2_0$	51·8 [a]	$1{\cdot}4_9$	242
4-Chloro- ,,	$3{\cdot}27_0$	$-0{\cdot}433_1$	0·138	302·1	114·8	57·0 [a]	$1{\cdot}6_8$	426
4-Bromo- ,,	$2{\cdot}89_1$	$-0{\cdot}157_7$	0·186	261·4	120·8	60·0 [a]	$1{\cdot}7_2$	456
4-Iodo- ,,	2·00	−0·063	0·207	310	112·7	65·6 [a]	$1{\cdot}5_2$	671
4-Nitro- ,,	18·92 [b]	$-0{\cdot}477_5$ [b]	0·172	2196	453·3	57·9 [a]	$4{\cdot}4_0$	3265
2 : 2′-Dinitro- [c]	12·43	$0{\cdot}367_0$ [d]	0·057 [d]	$-46{\cdot}8_8$	623·6	63·8 [a]	$5{\cdot}2_3$	−962
3 : 3′-Dinitro- ,, [c]	$7{\cdot}72_9$	$0{\cdot}406_3$	0·057	$-43{\cdot}5_6$	404·4	63·8 [a]	$4{\cdot}0_8$	−861

[a] Calc. from $_\infty P_2$ for diphenyl by use of the $R_{G'}$ group values listed by Vogel, *J.*, 1948, 1833. [b] From Chau and Le Fèvre, *J.*, 1957, 2300. [c] Determinations in benzene. [d] From Le Fèvre and Vine, *J.*, 1938, 967.

Accordingly, if for the 2 : 2′- or 3 : 3′-dinitrodiphenyl we assume an azimuthal angle of χ^0 (such that $\chi = 0$ or 180° for the fully *cis*- or *trans*-arrangements of the C–NO_2 links), and write b_1^{dndp} (dndp = dinitrodiphenyl) as the polarisability in the direction of action of $\mu_{\text{resultant}}$, *i.e.*, along the bisector of the angle χ, and b_2^{dndp} as the polarisability parallel to the 4 : 1 : 1′ : 4′-line, we have, by transposing the values b_1, b_2, and b_3 for nitrobenzene:

$$b_1^{\text{dndp}} = 2[b_1 \cos^2 30 + b_2 \sin^2 30 - b^{\text{CH}}] \cos^2 \chi/2 + 2(b_3 - b^{\text{CH}}) \sin^2 \chi/2 + b_{\text{T}}^{\text{CC}}$$

$$b_2^{\text{dndp}} = 2[b_1 \cos^2 60 + b_2 \sin^2 60 - b^{\text{CH}}] + b_{\text{L}}^{\text{CC}}$$

$$b_3^{\text{dndp}} = 2[b_1 \cos^2 30 + b_2 \sin^2 30 - b^{\text{CH}}]\sin^2 \chi/2 + 2(b_3 - b^{\text{CH}}) \cos^2 \chi/2 + b_{\text{T}}^{\text{CC}}$$

Using $10^{23}b^{\text{CH}} = 0{\cdot}063_5$, $10^{23}b_{\text{L}}^{\text{CH}} = 0{\cdot}098_6$, and $10^{23}b_{\text{T}}^{\text{CC}} = 0{\cdot}027_4$ (*i.e.*, taking the C–C internuclear bond, in the absence of better knowledge of the effects of conjugation, as though it were single), we can compute the quantity $(2b_1 - b_2 - b_3)^{\text{dndp}}$, which enters the " dipole terms " of the dinitrodiphenyls, for various values of χ; it becomes algebraically negative when χ exceeds *ca.* 73°. Calculation also shows that for all these values of χ, θ_1 lies between 3 and 4 × 10^{-35}.

If now from the information obtained experimentally and listed in Table 2 under $_\infty({}_mK_2)$ and μ, the term $(\theta_1 + \theta_2)$ is deducted, and an allowance of 4 × 10^{-35} made for θ_1, then from θ_2, $(2b_1 - b_2 - b_3)$ emerges for 2 : 2′- and 3 : 3′-dinitrodiphenyl as −0·64 × 10^{-23} and −0·94 × 10^{-23} respectively. These figures when compared with our computed values for $(2b_1 - b_2 - b_3)$ correspond to the following specific values for χ: 2 : 2′-dinitrodiphenyl 92—93°, 3 : 3′-dinitrodiphenyl 101—102°. Such results resemble those previously obtained [4] from straightforward polarity considerations: the configurations are nearly orthogonal, with the azimuthal angle some 10° greater in the 3 : 3′- than in the 2 : 2′-isomer. Further, they illustrate once more the practicability of the method whereby b_1, b_2, and b_3 for a given structure can be predicted from link and group polarisabilities and used in the interpretation of experimental results.

Diphenyl and its 4-derivatives. By similar arguments the molar Kerr constants of diphenyl and its five *para*-derivatives can also be " synthesised " from available data (cf. ref. 12). For each of the six molecules the $_\infty({}_mK_2)$ expected for the flat configuration is greater than that for the orthogonal. Thus with diphenyl we expect:

	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$	$10^{12}{}_mK_{\text{calc.}}$
Flat configuration	2·199	2·127	1·425	27·4
Orthogonal configuration	2·199	1·776	1·776	8·9

The value observed ($40{\cdot}5 \times 10^{-12}$) is larger than either of these ${}_{\rm m}K$'s. The remaining five compounds exhibit the same disagreement:

Substituent:	4-F	4-Cl	4-Br	4-I	4-NO_2
$10^{12}{}_{\rm m}K_{\rm calc.}$	152	269	337	320	1869
$10^{12}{}_{\infty}({}_{\rm m}K_2)_{\rm obs.}$	242	426	456	671	3265

(Only the calculated values for flat configurations are quoted, because those for $\chi = 90°$ are more distant still from those observed.) The ratios ${}_{\rm m}K_{\rm calc.}/{}_{\rm m}K_{\rm obs.}$ fall between 0·48 and 0·79.

The sum of the predicted semi-axes for diphenyl is $5{\cdot}751 \times 10^{-23}$, from which an electronic polarisation of 48·4 c.c. is calculable; the ${}_{\rm E}P$ reported by Le Fèvre and Narayana Rao[13] is 49·5 c.c., giving $b_1 + b_2 + b_3 = 5{\cdot}886 \times 10^{-23}$. Parallel calculations for the other five molecules indicate a general deficiency throughout of *ca.* 1 c.c. in the electronic polarisations (taken as ${}_{\rm D}P \times 0{\cdot}95$). When however the semi-axes are proportionately increased, the ${}_{\rm m}K$'s computed for flat configurations are only brought slightly nearer the experimental values (*e.g.*, multiplication of the $10^{23}b$'s for diphenyl by 5·886/5·751 gives 2·251, 2·177, and 1·458, whence ${}_{\rm m}K_{\rm calc.}$ is $28{\cdot}8 \times 10^{-12}$). The cause of the lowness of ${}_{\rm m}K_{\rm calc.}$ (or the highness of ${}_{\rm m}K_{\rm expt.}$) must lie elsewhere.

The situation is understandable if diphenyl and its 4-derivatives have effectively flat configurations in solution. Spectroscopic evidence (occurrence of an intense absorption around 2500 Å with diphenyls unhindered in the *ortho*-positions, or forced into planarity as in fluorene) supports this.[14] Only in flat forms can ring-ring conjugation be strongly developed. Unpublished measurements (Bramley and Le Fèvre) on diarylpolyenes, together with data in refs. 10 and 12, show that molecular polarisability is notably enhanced in directions along which conjugation takes place. In terms of the present diphenyls, therefore, all the *a priori* estimates of b_1 are likely to be too small, and those of b_2 and b_3 too large; the greatest errors will probably (cf. ref. 12) be with the b_1's. Suppose, for the hydrocarbon, $10^{23}b_1 = 2{\cdot}4$, $10^{23}b_2 = 2{\cdot}1$, $10^{23}b_3 = 1{\cdot}4$, the total would be $5{\cdot}9 \times 10^{-23}$ (which is correct), and the expected ${}_{\rm m}K$ would be 39—40×10^{-12}, in agreement with measurement. (With the same semi-axes an orthogonal configuration would give ${}_{\rm m}K$ *ca.* 21×10^{-12}.) Like " adjustments " in the cases of the 4-derivatives produce similar results.

Attempts (by Purnachandra Rao) to test these remarks by determinations of depolarisation factors for the light scattered by carbon tetrachloride solutions of the 4-halogeno- and -nitro-diphenyls, and thus to ascertain b_1, b_2, and b_3 separately, have been defeated by fluorescence, which induced an excessively large apparent Δ (cf. refs. 10 and 12). Until a range of strong monochromatic light sources are available the subject cannot usefully be carried further. Evidently polarisability in the diphenyl series can be treated additively only when conjugation is absent, *i.e.*, when the species are non-planar.

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[13] Le Fèvre and Narayana Rao, *Austral. J. Chem.*, 1955, **8**, 39.
[14] Beaven, Hall, Lesslie, and Turner, *J.*, 1952, 854; *idem* and Bird, *J.*, 1954, 131; Everitt, Hall, and Turner, *J.*, 1956, 2286; Beaven and Hall, *J.*, 1956, 4637; Brawde and Forbes, *J.*, 1955, 3776.