626. *Molecular Polarisability. Carbon–Halogen Bond Polarisabilities in Some* p-*Disubstituted Benzenes*

By (MISS) M. L. KEMP and R. J. W. LE FÈVRE

Molar Kerr constants and apparent dipole moments in carbon tetrachloride at 25° are recorded for *p*-disubstituted benzenes, *p*-X·C$_6$H$_4$·Y, where X and Y are, respectively: F, F; Cl, F; Br, F; Cl, Cl; Br, Cl; Cl, I; Br, Br; I, I. The observed $_mK$ values lie between those calculated using carbon–halogen bond semi-axes derived from methyl and phenyl halides. The polarisability semi-axes of the carbon–halogen bonds in the symmetrically substituted benzenes are estimated and found to be satisfactorily applicable to the non-symmetric molecules.

THE measurements here reported have been made to examine the apparent anisotropic polarisabilities of carbon–halogen bonds when two of these are *para*-situated in a benzene ring.

EXPERIMENTAL

Materials, Apparatus, Etc.—Commercial samples of the following were recrystallised from ethanol: *p*-dichlorobenzene (m. p. 53°); *p*-bromochlorobenzene (m. p. 66·5°); *p*-dibromobenzene (m. p. 87°); *p*-di-iodobenzene (m. p. 129·5°); *p*-chlorofluorobenzene (b. p. 130°/760 mm.), and *p*-bromofluorobenzene (b. p. 152°/760 mm.) were prepared by the method of Kukui, *et al.*;[1] *p*-chloroiodobenzene (m. p. 54°) was obtained by the general procedure described by Vogel.[2] A commercial sample of *p*-difluorobenzene ($n_D^{19\cdot1}$ 1·4418) was used without further purification.

Apparatus, techniques, symbols used, and methods of calculation have been described before.[3,4] The quantities $\Delta\varepsilon$, Δd, Δn, and ΔB are the differences found between the dielectric constants, densities, refractive indices, and Kerr constants, respectively, of carbon tetrachloride as solvent, and of solutions containing weight fractions w_2 of solute. Observations and results are summarised in Tables 1 and 2. When $w_2 = 0$, the following apply at 25°: $\varepsilon_1 = 2\cdot2270$, $d_1 = 1\cdot58454$, $(n_1)_D = 1\cdot4575$, and $(B_1)_D = 0\cdot070 \times 10^{-7}$.

Previous Measurements.—McClellan[5] lists small apparent moments, ranging up to *ca.* 0·5 D, for some of the compounds under consideration when dissolved in non-polar media (usually benzene). No entry occurs for *p*-F·C$_6$H$_4$·F, and in no case is carbon tetrachloride shown as the solvent involved. A moment of 0·53 D is attributed to *p*-Br·C$_6$H$_4$·F as a gas or as a molten liquid (in which state the polarity of *p*-Cl·C$_6$H$_4$·F is given as 0·95—0·99 D). Differing methods of estimating distortion polarisations *may* account for such results. Hurdis and Smyth[6] record the total polarisations of *p*-Br·C$_6$H$_4$·F at seven temperatures between 436 and 524°K; $_TP$ values from 37·1 to 37·8 c.c. are scattered irregularly, and moments calculated at each point by taking $_DP = R_D = 33\cdot7$ c.c. The correct $_DP$ should undoubtedly be greater than this, and the moment correspondingly lower; moreover, Hurdis and Smyth raise the possibility that their substance had a small content of the *o*-isomer. In Table 2, the R_D values are those deduced from solution, and if the common convention be followed that $_DP = 1\cdot05R_D$ we must conclude that, within the limits of experimental accuracy, the moments in carbon tetrachloride are all indistinguishable from zero.

The $_\infty(_mK_2) \times 10^{12}$ published by Le Fèvre and Le Fèvre[7] for *p*-Cl·C$_6$H$_4$·Cl (38·6) is inexplicably higher than our now redetermined value (25·8), which is more in harmony with earlier data by Otterbein[8] and Briegleb;[9] the 40·3 ± 2 quoted in ref. 7 for *p*-Br·C$_6$H$_4$·Br is in satisfactory agreement with the 38·1 in Table 2.

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[1] Kukui *et al.*, *J. Chem. Soc. Japan*, 1958, **79**, 1120.

[2] Vogel, " Practical Organic Chemistry," Longmans, London, 3rd edn., 1956, p. 598.

[3] Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953.

[4] Le Fèvre and Le Fèvre (*a*) *Rev. Pure Appl. Chem.* (*Australia*), 1955, **2**, 261; (*b*) Ch. XXXVI in " Physical Methods of Organic Chemistry," ed. Weissberger, Interscience, New York, London, 3rd edn., vol. 1, p. 2459.

[5] McClellan, " Tables of Experimental Dipole Moments," Freeman, San Francisco, 1963.

[6] Hurdis and Smyth, *J. Amer. Chem. Soc.*, 1942, **64**, 2212.

[7] Le Fèvre and Le Fèvre, *J.*, 1954, 1577.

[8] Otterbein, *Physik. Z.*, 1933, **34**, 645; 1934, **35**, 249.

[9] Briegleb, *Z. physikal. Chem.*, 1932, *B***16**, 249.

TABLE 1

Incremental dielectric constants, densities, refractive indices, and Kerr constants of solutions in carbon tetrachloride at 25°

p-*Difluorobenzene*

10^5w_2	559	856	1131	3002
$10^4\Delta\varepsilon$	*ca.* 0 throughout			
$-10^5\Delta d$	301	498	658	1794
$10^4\Delta n$	*ca.* 0 throughout			
$10^{11}\Delta B$	45	55	90	202

whence $\Sigma\Delta\varepsilon/\Sigma w_2 =$ *ca.* 0; $\Sigma\Delta d/\Sigma w_2 = -0\cdot58_5$; $\Sigma\Delta n/\Sigma w_2 =$ *ca.* 0; $\Sigma\Delta B/\Sigma w_2 = 0\cdot71 \times 10^{-7}$

p-*Bromofluorobenzene*

10^5w_2	1901	2538	4825	6367	8750
$10^4\Delta\varepsilon$	42	58	110	148	206
$10^5\Delta d$	—	—	—	31	55
$10^4\Delta n$	15	—	—	48	65
$10^{10}\Delta B$	17	22	45	60	81

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 0\cdot231$; $\Sigma\Delta d/\Sigma w_2 = 0\cdot00_6$; $\Sigma\Delta n/\Sigma w_2 = 0\cdot075$; $\Sigma\Delta B/\Sigma w_2 = 0\cdot92_0 \times 10^{-7}$

p-*Chlorofluorobenzene*

10^5w_2	1298	1854	2556	2616	2676	3270	3817	3920	4023	5585	9796
$10^4\Delta\varepsilon$	18	27	41	—	40	47	54	—	55	90	150
$-10^5\Delta d$	—	—	—	—	1212	—	—	—	—	2551	4453
$10^4\Delta n$	—	—	—	—	12	—	—	—	—	25	43
$10^{10}\Delta B$	—	24	—	27	—	32	—	43	—	66	104

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 0\cdot150$; $\Sigma\Delta d/\Sigma w_2 = -0\cdot455$; $\Sigma\Delta n/\Sigma w_2 = 0\cdot044$; $\Sigma\Delta B/\Sigma w_2 = 1\cdot09 \times 10^{-7}$

p-*Dichlorobenzene*

10^5w_2	3476	5547	5686	6424	7385	7689	8056	9771	17,431
$10^4\Delta\varepsilon$	—	—	170	180	204	211	—	265	469
$-10^5\Delta d$	1248	1980	—	2285	—	—	2866	3471	—
$10^4\Delta n$	—	—	69	75	85	88	—	112	212

whence $\Delta\varepsilon = 0\cdot284w_2 - 0\cdot089w_2^2$; $\Sigma\Delta d/\Sigma w_2 = -0\cdot356$; $\Sigma\Delta n/\Sigma w_2 = 0\cdot117$

10^5w_2	548	821	1573	1839	3356	3374	4416	5554	6389	6397	10,270	11,416
$10^{11}\Delta B$	97	158	237	300	615	49_6	67_0	82_3	95_8	1073	159_5	179_6

whence $\Sigma\Delta B/\Sigma w_2 = 1\cdot57_0 \times 10^{-7}$

p-*Bromochlorobenzene*

10^5w_2	1231	2408	3632	4347	4503	5846	7857	9148	9302	9729
$10^4\Delta\varepsilon$	—	72	114	—	145	186	253	288	296	308
$10^5\Delta d$	—	—	—	—	219	289	385	451	452	—
$10^4\Delta n$	—	31	45	—	57	75	100	—	—	—
$10^{10}\Delta B$	20	—	—	58	68	82	106	—	—	—

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 0\cdot317$; $\Sigma\Delta d/\Sigma w_2 = 0\cdot049$; $\Sigma\Delta n/\Sigma w_2 = 0\cdot127$; $\Sigma\Delta B/\Sigma w_2 = 1\cdot40_4 \times 10^{-7}$

p-*Chloroiodobenzene*

10^5w_2	930	1011	1376	1382	1628	1698	2064	3056	3332
$10^4\Delta\varepsilon$	43	41	60	67	75	75	96	133	151
10^5w_2	2077	2373	3330	3912					
$10^5\Delta d$	700	731	1027	1233					
10^5w_2	1376	1698	2490	3093					
$10^4\Delta n$	20	27	38	45					
10^5w_2	812	1287	1576	2373	2425	3330	3912		
$10^{10}\Delta B$	15	22	26	47	50	66	77		

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 0\cdot45_0$; $\Sigma\Delta d/\Sigma w_2 = 0\cdot31_6$; $\Sigma\Delta n/\Sigma w_2 = 0\cdot150$; $\Sigma\Delta B/\Sigma w_2 = 1\cdot9_3 \times 10^{-7}$

p-*Dibromobenzene*

10^5w_2	1077	1860	2655	4283	5264	5905	7489
$10^4\Delta\varepsilon$	—	59	86	140	182	196	255
$10^5\Delta d$	—	580	820	1329	1625	—	2324
$10^4\Delta n$	14	25	35	55	67	76	97

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 0\cdot334$; $\Sigma\Delta d/\Sigma w_2 = 0\cdot310$; $\Sigma\Delta n/\Sigma w_2 = 0\cdot129$

10^5w_2	1633	2576	2751	3855	4315	4753	6874
$10^{10}\Delta B$	22	41	43	56	56	66	109

whence $\Sigma\Delta B/\Sigma w_2 = 1\cdot47 \times 10^{-7}$

p-*Di-iodobenzene*

10^5w_2	746	806	1217	1576	1767	2384	2758
$10^4\Delta\varepsilon$	33	34	—	67	—	—	—
$10^5\Delta d$	—	—	—	916	1012	—	1601
$10^4\Delta n$	13	13	20	26	—	40	—
$10^{10}\Delta B$	14	14	24	28	—	46	—

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 0\cdot428$; $\Sigma\Delta d/\Sigma w_2 = 0\cdot578$; $\Sigma\Delta n/\Sigma w_2 = 0\cdot166$; $\Sigma\Delta B/\Sigma w_2 = 1\cdot87 \times 10^{-7}$

TABLE 2

Polarisations, refractions, and molar Kerr constants in carbon tetrachloride at 25°

Solute	$\alpha\varepsilon_1$	β	γ	δ	$_\infty P_2$ (c.c.)	R_D (c.c.)	$10^{12}{}_\infty({}_mK_2)$
p-F·C_6H_4·F ...	0	−0·369	0	10·1	28·6	26·9	9·8
p-Cl·C_6H_4·F ...	0·150	−0·287	0·030	15·6	32·9	30·8	16·4
p-Br·C_6H_4·F ...	0·231	0·004	0·051	13·1	36·2	34·3	18·3
p-Cl·C_6H_4·Cl ...	0·284	−0·225	0·080	22·4	37·4	36·4	25·8
p-Br·C_6H_4·Cl...	0·317	0·031	0·087	20·1	40·4	39·9	29·9
p-Cl·C_6H_4·I ...	0·450	0·199	0·103	27·6	46·4	44·5	50·1
p-Br·C_6H_4·Br	0·334	0·196	0·089	21·0	43·1	42·6	38·1
p-I·C_6H_4·I	0·428	0·365	0·114	26·7	53·3	53·9	66·7

DISCUSSION

Applicability of Existing Carbon–Halogen Polarisabilities.—Molar Kerr constants were calculated from polarisability semi-axes for the C_6H_4 group ($b_1 = b_2 = 9{\cdot}86$; $b_3 = 6{\cdot}05$ *) and those previously found for C–X bonds in various types of molecular environment.

Exaltations of refraction (the differences between the R_D values in Table 2 and those computed from the Tables of Vogel *et al.*[10]) are generally very small and within the experimental errors in the observed R_D values; accordingly, in our calculations consideration of the directional properties of exaltation has not been attempted.

Results are shown in Table 3, where values in columns A, B, C, and D refer, respectively, to the $_MK$ values predicted using C–X bond parameters drawn from CH_3X, $(CH_3)_2CHX$, $(CH_3)_3CX$, and C_6H_5X (refs. 11 and 12). Comparison of the observed and calculated $_mK$ values suggests that C–X in p-X·C_6H_4·X is less anisotropically polarisable than in C_6H_5X; some quantitative estimates of the modifications involved are made in the following section.

TABLE 3

Solute	Calculated molar Kerr constants * ($\times 10^{-12}$) A	B	C	D	Observed $_\infty({}_mK_2) \times 10^{12}$
p-F·C_6H_4·F	11·9	—	—	10·6	9·8
p-Cl·C_6H_4·F	12·4	—	—	18·6	16·4
p-Br·C_6H_4·F	14·7	—	—	25·3	18·3
p-Cl·C_6H_4·Cl	12·9	22·2	27·2	33·2	25·8
p-Br·C_6H_4·Cl	15·3	27·7	34·7	43·2	29·9
p-Cl·C_6H_4·I	17·9	31·1	44·6	56·8	50·1
p-Br·C_6H_4·Br	18·0	34·0	43·3	53·7	38·1
p-I·C_6H_4·I	24·1	41·9	67·1	89·0	66·7

* Assuming $\mu = 0$.

Estimation of Carbon–Halogen Polarisabilities.—In the case of the four symmetrically substituted benzenes, it is possible to calculate polarisability semi-axes for the C–X bonds by the use of various assumptions. Since these compounds are non-polar, and since there appear to be no measurements in the literature of refractive indices along specific crystal axes, b_1, b_2, and b_3 cannot be calculated directly from experiment; this would be so even if reliable light scattering data were available. If, however, we assume that b_T and b_V for the C–X bonds in these molecules are equal, in turn, to those in $(CH_3)_2CHX$, $(CH_3)_3CX$, and C_6H_5X (noting that columns B, C, and D of Table 3 are in closest accord with observation), then the usual equations (ref. 4) can be solved to yield, in each case, the apparent b_L(C–X). A further assumption can be made, *viz.*, that $b_T = v_V$ for the C–X bond in p-X·C_6H_4·X. Calculation of the two unknowns, b_L and b_T, then requires both the experimental $_mK$ and $_EP$. For p-dichloro-, p-dibromo-, and p-di-iodo-benzene, the $_EP$ values were calculated from bond values given by Le Fèvre and Steel,[13] yielding 34·57,

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* Molecular and group polarisabilities are quoted throughout in 10^{-24} c.c. units.

[10] Vogel, Cresswell, Jeffery, and Leicester, *J.*, 1952, 514.

[11] Le Fèvre, *J. Proc. Roy. Soc. New South Wales*, 1961, **95**, 1.

[12] Chen and Le Fèvre, unpublished data.

[13] Le Fèvre and Steel, *Chem. and Ind.*, 1961, 670.

TABLE 4

Estimated polarisability semi-axes for C–X bond in p-X·C_6H_4·X

Bond	A	B	C	D	E
	b_L	b_L	b_L	b_L	b_T (= b_V)
C–F	—	—	$0{\cdot}5_1$	$0{\cdot}9_7$	$0{\cdot}4_5$
C–Cl	3·9	3·8	3·7	4·1	1·8
C–Br	5·9	5·7	5·3	5·7	2·6
C–I	9·3	8·8	8·0	8·6	4·0

39·98, and 49·69 c.c., respectively. For p-difluorobenzene, Timmerman's refractivity dispersion data[14] were extrapolated to infinite wavelength by means of the formula quoted by Le Fèvre (p. 18 ref. 3), giving $_EP = 24{\cdot}80$ c.c. Table 4 lists the b_L values, obtained by the procedures described above, under the headings A [using b_T(C–X) and b_V(C–X) from $(CH_3)_2CHX$], B [from $(CH_3)_3CX$], C [from C_6H_5X], and D [b_T(C–X) = b_V(C–X)]. Column E lists $b_T(=b_V)$ for the C–X bonds derived in the calculation of column D.

Some test of the validity of these values is obtained by using them, together with the corresponding b_T and b_V in each case, to calculate $_mK$ values for the p-X·C_6H_4·Y molecules, and by comparing these values with the observed $_mK$ values, as shown in Table 5.

TABLE 5

Solute	Calculated $_MK$ * (× 10^{12})				Observed
	A	B	C	D and E	$_\infty(_mK_2) \times 10^{12}$
p-Cl·C_6H_4·F	—	—	15·7	16·6	16·4
p-Br·C_6H_4·F	—	—	19·4	20·7	18·3
p-Br·C_6H_4·Cl	31·1	31·2	31·1	32·1	29·9
p-Cl·C_6H_4·I	43·3	43·2	43·6	44·2	50·1

* Assuming zero dipole moment.

It is to be noted that the observed $_mK$ values are quite small and may be subject to errors as high as 10%, and that a moment of 0·25 D for p-chloroiodobenzene would make the $_mK$ predicted, *e.g.*, by the fourth procedure (44·2), equal to the observed value. From Table 5, it can be seen that the calculated $_mK$ values are relatively insensitive to small changes in the semi-axes of the C–X bonds. Thus, it seems more reasonable, particularly in view of the approximations in estimating $_EP$ [and hence in the evaluation of absolute values of b_i(C–X)], to compare the effect of different environments on the anisotropy of the C–X bond. The anisotropy, defined by Smith and Mortensen[15] as $(2b_L - b_T - b_V)/2$ is accordingly computed for the C–X bond in CH_3X, C_6H_5X, and p-X·C_6H_4·X (in the latter case, using the semi-axes of columns D and E of Table 4). The results are summarised in Table 6.

TABLE 6

Anisotropy of C–X bonds * (in 10^{-24} c.c.)

Environment	C–F	C–Cl	C–Br	C–I
CH_3X	$0{\cdot}8_5$	$0{\cdot}9_3$	1·6	1·9
C_6H_5X	$0{\cdot}2_0$	2·5	3·9	4·8
p-X·C_6H_4·X	$0{\cdot}5_2$	2·3	3·1	4·6

* b_i for C–X in CH_3X and C_6H_5X from ref. 10, except CH_3I in which b_L^{CI} and b_T^{CI} have recently[16] been redetermined as 6·7 and 1·9, respectively.

Conclusions.—Table 6 shows (as would a comparison of Table 4 of this Paper with Table 1 of ref. 10) that carbon–halogen bonds in p-disubstituted benzenes are less anisotropically polarisable than in the related mono-derivatives of benzene. Such a result seems reasonable since the electropolar characters represented (in Ingold's symbolism) by $+M$, $+E$,

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[14] Timmerman, " Physico-chemical Constants of Organic Compounds," Elsevier, Amsterdam, 1950.

[15] Smith and Mortensen, *J. Chem. Phys.*, 1960, **32**, 502.

[16] Le Fèvre and Orr, unpublished data.

and $-I$ run as F > Cl > Br > I, and a 1,4-orientation is therefore one in which these " effects " of the substituents are in opposition; mesomeric displacements in particular are thought [17] to affect strongly the longitudinal polarisabilities of bonds attached to conjugated systems.

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UNIVERSITY OF SYDNEY, SYDNEY, N.S.W., AUSTRALIA. [*Received, September 14th*, 1964.]

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[17] Ingold, " Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, 1953, p. 137.