Molecular Polarisability. Its Anisotropy in Aliphatic and Aromatic Structures.

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The use of depolarisation factors in the analysis of molecular polarisability is criticised on practical grounds, and an alternative information source is proposed. New determinations of the molar Kerr constants at infinite dilution are recorded for 26 substances, and the semi-axes of their optical polarisability ellipsoids calculated. Comparisons of data for structures related as alphyl–X and aryl–X suggest that exaltation of polarisability occurs preferentially in those directions for which electromeric shifts are, from organo-chemical theory, expected to be easiest. Anisotropic polarisabilities of bonds are considered incidentally, and signs detected of inductomeric polarisability effects in the *tert.*-butyl group. Results are generally in harmony with conclusions reached by Ingold in a recent monograph.

THE work described in this paper was started with the intention of comparing the anisotropic polarisabilities of structures related as alphyl–X and aryl–X. We have previously dealt with the determination of " molar Kerr constants " ($_mK_2$) of solutes and their extrapolation to infinite dilution (*J.*, 1953, 4041); by the same methods, new measurements have now been completed on 26 compounds, thus making available knowledge of $_\infty(_mK_2)$ for each of the molecules listed in Table 1. All except nitromethane and 1 : 3 : 5-trinitrobenzene have been examined in carbon tetrachloride.

TABLE 1. *Molar Kerr constants * at infinite dilution.*

Temp.	Solute	$_\infty(_mK_2) \times 10^{12}$	Temp.	Solute	$_\infty(_mK_2) \times 10^{12}$
20°	CH_3F	28·3 ± 3	25°	C_6H_5Br	171 ± 3
25	CH_3Cl	32·3 ± 2	20	C_6H_5I	186 ± 1·5
25	CH_3Br	51·6 ± 0·7	20	$C_6H_5{\cdot}NO_2$ ‡	1073 ± 14
25	CH_3I	54·2 ± 2	20	$C_6H_5{\cdot}CN$	1147 ± 35
25	$CH_3{\cdot}NO_2$ †	89·0 ± 3	20	1 : 2-$C_6H_4Me_2$	$25{\cdot}1_5$ ± 0·3
25	$CH_3{\cdot}CN$	219·5 ± 6	20	1 : 3-$C_6H_4Me_2$	13·0 ± 0·2
25	$(CH_3)_3CCl$	85·6 ± 3	25	1 : 4-$C_6H_4Me_2$	10·6 ± 0·5
25	$(CH_3)_3CBr$	146 ± 4	20	1 : 4-$C_6H_4Cl_2$	38·6 ± 2
25	$(CH_3)_3CI$	203 ± 6	20	1 : 4-$C_6H_4Br_2$	40·3 ± 2
25	C_2Cl_6	4·60 ± 0·8	20	1 : 3 : 5-$C_6H_3Me_3$	10·1 ± 0·3
20	C_6H_6	7·24 ± 0·4	20	1 : 3 : 5-$C_6H_3Cl_3$	37·6 ± 1
25	C_6H_5Me	12·8 ± $0{\cdot}2_5$	20	1 : 3 : 5-$C_6H_3Br_3$	24·3 ± 2
20	C_6H_5F	56·8 ± 0·8	25	1 : 3 : 5-$C_6H_3(NO_3)_3$ †	168 ± 12
20	C_6H_5Cl ‡	145 ± 1·5	25	C_6Me_6	16·0 ± 1
			20°	C_6Cl_6	103·6 ± 0·3

* With estimated standard errors.
‡ Data recalculated from *J.*, 1953, 4041.
† Examined in benzene.

Before proceeding to our primary objective we need to consider two matters : (*a*) the deduction from $_\infty(_mK_2)$ and other experimental quantities of estimates of molecular polarisability ellipsoids, and (*b*) the calculation of bond polarisabilities.

(a) *Calculation of Molecular Polarisability Ellipsoids.*—The problem, in the general case, is to find the principal half-axes, b_1, b_2, and b_3, of the ellipsoid of polarisability for a given molecule. Three equations are therefore necessary. The first of these involves ${}_{m}K_2$:

$$ {}_{m}K_2 = 2\pi N(\theta_1 + \theta_2)/9 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The second is derived from the electronic polarisation:

$$ {}_{\mathrm{E}}P = 4\pi N(b_1 + b_2 + b_3)/9 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The third expresses the depolarisation factor Δ of scattered light in terms of the required half-axes:

$$10\Delta/(6 - 7\Delta) = [(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2]/(b_1 + b_2 + b_3)^2 \quad . \quad (3)$$

In (1), θ_1 and θ_2 may be expanded as shown by the relations Nos. (13) and (14) in our previous paper. In particular, θ_1 becomes

$$\theta_1 = ({}_{\mathrm{D}}P/45kT \, . \, {}_{\mathrm{E}}P)[(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2] \quad . \quad . \quad (4)$$

If therefore ${}_{m}K_2$, ${}_{\mathrm{E}}P$, the distortion polarisation ${}_{\mathrm{D}}P$, $\mu_{\text{resultant}}$ (and its direction of action with respect to the polarisability ellipsoid), and Δ are known for a substance, b_1, b_2, and b_3 can be computed.

Unfortunately, however, depolarisation factors are available only for a few dozen molecules (Cabannes, " La Diffusion Moléculaire de la Lumière," Les Presses Universitaires de France, 1929, lists 61) of fairly simple type. Moreover, Δ is markedly affected by state, so that for the purposes of equation (3) one requires " la dépolarisation limite " (Cabannes, *op. cit.*, pp. 38, 105), *i.e.*, Δ for the scattering from a gas " assez voisin de l'état parfait." Recorded values for the same substance are not always in agreement with one another.

In a limited number of cases Δ can be checked, since for structures having, by symmetry, $b_1 = b_2$ or $b_2 = b_3$, half-axes may be computed without recourse to Δ. Table 4 contains 15 instances where this has been done. The b's so obtained can be used to estimate the numerator of the right-hand side of (3), and the result compared with the figure deduced *via* $2\delta_0^2 = 10\Delta/(6 - 7\Delta)$. An analysis of the five cases for which the requisite depolarisation factors have been reported is shown as Table 2. For brevity, A is written for $(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2$. Table 2 includes also the magnitudes of θ_1, for two unsymmetrical molecules, obtained from $2\delta_0^2$ and ${}_{\mathrm{E}}P$, set against the related $(\theta_1 + \theta_2)$ given by our experiments. Corresponding quantities derived from Stuart and Volkmann's observations (S. and V.) on gases (*Ann. Physik*, 1933, **18**, 121) are inserted throughout.

TABLE 2.

		$10^{46}A$ from		
Molecule	$2\delta_0^2 \times 10^3$	δ_0^2 and ${}_{\mathrm{E}}P$	S. and V.	${}_{\infty}({}_{m}K_2)$ and ${}_{\mathrm{E}}P$
CH_3Cl	28·4 [a]	0·050	0·033	0·019 [c]
$CHCl_3$	31·5 [b]	0·191	0·109	0·241 [d]
C_6H_6	77·3 [a]	0·677	0·710	0·290 [c]
	78·2 [b]	0·685		
		$10^{35}\theta_1$ from δ_0^2 and ${}_{\mathrm{E}}P$	$10^{35}\theta_1$ from S. and V.	$10^{35}(\theta_1 + \theta_2)$ from expt.
C_6H_5Me	74·7 [a]	5·42 at 25°	6·32 at 25°	3·02 [c] at 25°
	87·4 [b]	6·34 ,,		
1 : 3-$C_6H_4Me_2$	89·4 [b]	8·51 at 20°	8·39 at 20°	3·09 [c] at 20°

[a] Ref. 2 below Table 4. [b] Ref. 16 below Table 4. [c] From present measurements. [d] ${}_{\infty}({}_{m}K_2) = -28·5 \times 10^{-12}$ (cf. *J.*, 1953, 4041).

We note a general lack of concordance between the values of A from δ_0^2 and those from ${}_{\infty}({}_{m}K_2)$. Where the work of Stuart and Volkmann is concerned, disagreement is restricted to methyl chloride and chloroform; A for benzene, toluene, and *m*-xylene is of the order to be expected from δ_0^2, and—where two estimates of δ_0^2 exist in the literature—from that (higher) δ_0^2 quoted by Cabannes (*op. cit.*).

We have previously (*J.*, 1953, 4041) commented on the fact that, after conversion to

20°, Stuart and Volkmann's K_1 for benzene leads to a molar Kerr constant of *ca.* 17×10^{-12}, whereas for the pure liquid or at infinite dilution in carbon tetrachloride the ${}_mK$ is *ca.* 7×10^{-12}. A similar situation is now revealed for toluene and *m*-xylene, the ${}_\infty({}_mK_2)$ figure for each of which could only be reconciled with its $\delta_0{}^2$ if θ_2 were negative—a condition which is *a priori* unlikely. We are certain of our measured ${}_\infty({}_mK_2)$ values: the system C_6H_6–CCl_4 has been re-examined *de novo* for 8 concentrations, and C_6H_5Me–CCl_4 is here reported for 13. Either, therefore, θ_1 is unexpectedly solvent-dependent, or Stuart and Volkmann's observations are erroneously large. As to the former possibility, it is relevant that the molar Kerr constants of pure liquid benzene, toluene, or xylene are close to the ${}_\infty({}_mK_2)$ values now found in carbon tetrachloride—no *marked* solvent action is apparent. As to the latter possibility, we have considered the experimental details published by the German authors (*Z. physikal. Chem.*, 1932, **17**, *B*, 429) when recording *B* for benzene vapour as $1{\cdot}8 \times 10^{-10}$. We calculate that, in the apparatus described by them, this corresponds to a phase difference between 0·00005 and 0·00015λ; the threshold of detectability, however, for such optical determinations must be taken to be that (*viz.*, 5×10^{-5} λ) stated by Szivessy (*Z. Physik*, 1921, **6**, 311), who devised the technique used. It is our intention later to reinvestigate benzene and other gases; in the meantime, since our (repeatedly confirmed) measurements involve phase differences of 0·00025—0·02 λ, we feel justified in suspecting both the observations of Stuart and Volkmann *and* the depolarisation factors tabulated by Cabannes, at least when they relate to molecules of low—or no—polarity. Accordingly, procedures whereby b_1, b_2, and b_3 may be deduced without the use of equation (3) become highly desirable, and will be discussed next.

A priori *estimation of* b₃. Table 4 contains data for six derivatives of benzene for which $b_1 = b_2$. (For clarity we mention here our nomenclature for the mutually perpendicular half-axes of the molecular optical polarisability ellipsoids quoted: for a polar molecule, b_1 applies along the direction of action of the resultant dipole moment, and the lesser of the remaining two b's is written as b_3; for a non-polar molecule, the largest polarisability is denoted by b_1 and the smallest by b_3.) In particular, the cases of the tri- and hexa-methyl- and -chloro-benzenes are valuable in providing some support for the assumption that b_3 can be treated additively. In Table 3 we show the differences, Δb_3, between the b_3's observed for a given molecule and the b_3 found for benzene.

TABLE 3. *Values of* $\Delta b_3 \times 10^{23}$ *per molecule and per substituent.*

Molecule	Δb_3 per molecule	Δb_3 per substituent
1 : 3 : 5-$C_6H_3Me_3$	+0·514	+0·171
C_6Me_6	+0·948	+0·158
1 : 3 : 5-$C_6H_3Cl_3$	+0·255	+0·085
C_6Cl_6	+0·455	+0·076
1 : 3 : 5-$C_6H_3Br_3$	+0·669	+0·223
1 : 3 : 5-$C_6H_3(NO_2)_3$	−0·214	−0·071

It is seen that the changes in b_3 caused by three further substituents are somewhat less than those caused by the first three. Such an effect is to be expected on elementary electrostatic theory; it might, however, be connected with non-planarity of the hexa-substituted molecules—a condition which has been suggested for hexachlorobenzene (Bastiansen and Hassel, *Acta Chem. Scand.*, 1947, **1**, 489) and for octamethylnaphthalene but not for hexamethylbenzene (cf. Donaldson and Robertson, *J.*, 1953, 17). By addition to the "found" Δb_3's for benzene of the appropriate "Δb_3 per substituent" (obtained from the 1 : 3 : 5-trisubstituted derivatives) estimates of b_3 for toluene, chlorobenzene, bromobenzene, and nitrobenzene can be produced, and with their help the calculation of b_1 and b_2 for each of these molecules becomes possible. Results are shown in Table 4; they may be compared with the following, deduced from the same ${}_\infty({}_mK_2)$ figures in conjunction with the depolarisation factors also quoted in Table 4.

	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$
C_6H_5Me	(Solution unreasonable, see above)		
C_6H_5Cl	$1{\cdot}44_5$	1·40	0·685
C_6H_5Br	1·66	1·47	0·736
$C_6H_5{\cdot}NO_2$	1·60	1·36	0·690
1 : 3-$C_6H_4Me_2$	(Solution unreasonable, see above)		

It is seen that the values of b_1 obtained for chloro- or bromo-benzene by either method are similar, whereas for nitrobenzene they are substantially identical. For the last named—as for many molecules of high polarity—this is not surprising because $_\infty({}_mK_2)^{C_6H_5\cdot NO_2}$ is large, so that $\theta_2^{C_6H_5\cdot NO_2}$ greatly exceeds $\theta_1^{C_6H_5\cdot NO_2}$. Indeed, if θ_1 is neglected and θ_2 solved for the two unknowns b_1 and $(b_2 + b_3)$, these emerge as $1{\cdot}61 \times 10^{-23}$ and $2{\cdot}04 \times 10^{-23}$, respectively; obviously, incorrectness of δ_0^2 is relatively less significant here than it is when θ_1 and θ_2 are not so unequal, or at the extreme—as with toluene or *m*-xylene—of the same order of magnitude. Since in our judgment molar Kerr constants of solutes can be measured with more certainty than depolarisation factors of vapours, we prefer, for these five substances, the entries in Table 4 to the polarisabilities shown a few lines above.

The analyses of the $_\infty({}_mK_2)$'s for fluoro-, iodo-, and cyano-benzene remain to be discussed. No depolarisation factors for these compounds are on record, and the method described above cannot be used because the 1 : 3 : 5-trisubstituted benzenes required are either unknown or too insoluble. We therefore propose, *faute de mieux*, to compute b_3 with the help of measurments on the axially symmetric aliphatic analogues.

If we represent the polarisability of a link between two atoms as an ellipsoid having semi-axes, b_L, b_T, and b_V, where subscript L marks the longitudinal polarisability, and T and V mark the two transverse polarisabilities, then for single bonds $b_V = b_T$. Differences shown in Table 3—provided the polarisability of the basic benzenoid skeleton is unaffected by replacement of hydrogen—are clearly estimates of $b_T^{C_{Ar}-X} - b_T^{C_{Ar}-H}$; for the present we shall assume that this quantity is close to $b_3^{CH_3-X} - b_3^{CH_4}$.

Watson and Ramaswamy (*Proc. Roy. Soc.*, 1936, *A*, **156**, 144) have made careful measurements of, *inter alia*, the dispersion of the refractive index of methane, whence $_EP^{CH_4} = 6{\cdot}45$ c.c. and by symmetry $b_1^{CH_4} = b_2^{CH_4} = 0{\cdot}254 \times 10^{-23}$. The values of $\Delta b_3 = b_3^{\text{molecule}} - b_3^{CH_4}$ are, from Table 4, as follows :

Molecule	CH_3F	CH_3I	$CH_3\cdot CN$
$10^{23} \times \Delta b_3$	$-0{\cdot}022$	$0{\cdot}403$	$0{\cdot}116$

The sums of these with $b_3^{C_6H_6}$ have been taken as the b_3's of the monosubstituted benzenes concerned. Figures so obtained are indicated in Table 4, and in the text below, by braces.

As a check we may apply a parallel procedure to C_6H_5Cl and C_6H_5Br, and compare the b_1 and b_2 so found with those derived from 1 : 3 : 5-trichloro- or -tribromo-benzenes:

	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$		$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$
C_6H_5Cl	1·48	1·16	{0·890}	C_6H_5Br	1·69	$1{\cdot}18_5$	{0·978}
,, ...	1·47	1·24	(0·818)	,, ...	1·68	1·21	(0·956)

It is seen that variations in b_3 affect b_2 rather than b_1, and that b_1 and b_2 by either method are the same to two significant figures.

Table 4 summarises calculations, made in each case by one of the above three methods, for the 29 molecules considered in this paper. Comment on these results can be made more appropriately after the discussion in the next section.

(b) *Calculation of Bond Polarisability Ellipsoids.*—The suggestion referred to above that individual bonds may be described by polarisability ellipsoids was first advanced qualitatively by Meyer and Otterbein (*Physikal. Z.*, 1931, **32**, 290; 1934, **35**, 249). Sachsse (*ibid.*, 1935, **36**, 357), Wang (*J. Chem. Physics*, 1939, **7**, 1012), and Denbigh (*Trans. Faraday Soc.*, 1940, **36**, 936) later attempted to evaluate the half-axes of such ellipsoids from Kerr constant and refractivity data.

In order to simplify the following discussion we shall write $b_L^{C-H} = A$; $b_V^{C-H} = b_T^{C-H} = B$; $b_L^{C-Cl} = C$; $b_V^{C-Cl} = b_T^{C-Cl} = D$; $b_L^{C-C} = E$; and $b_V^{C-C} = b_T^{C-C} = F$.

Both Wang and Denbigh, in evaluating A, B, E, and F, started by adopting tetrahedral angles and using the following expressions :

$$4A/3 + 8B/3 = b_1^{CH_4} \text{ (ex molar refraction)} \quad . \quad . \quad . \quad . \quad (5)$$

$$E + 2F + 6A + 12B = (b_1 + b_2)^{C_2H_6} \text{ (ex molar refraction)} \quad . \quad . \quad (6)$$

$$E + 2A/3 + 16B/3 = b_1^{C_2H_6} \text{ (ex Kerr effect)} \quad . \quad . \quad . \quad . \quad (7)$$

The only other possible equation for a system having A, B, E, and F alone, would have been the following:

$$F + 8A/3 + 10B/3 = b_2^{C_6H_6} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

thus yielding at first sight four equations and four unknowns; yet on inspection, it is seen that (6) = (7) + twice (8); accordingly there remain three equations and four unknowns. Denbigh did not explicitly quote a fourth equation, but said "similar equations can be set up for other molecules, and, by elimination . . . the longitudinal and transverse polarisabilities of the bonds can be obtained."

TABLE 4. *Calculation of molecular polarisability ellipsoids.*

Solute	Temp.	$10^{35} \times (\theta_1 + \theta_2)$	$_{\mathrm{D}}P$ (c.c.)	$_{\mathrm{E}}P$ (c.c.)	$2\delta_0^2 \times 10^3$	μ, D	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$ *
CH_3F	20°	6·73	9 [1]	6·6 [1]	—	1·71	0·316	0·232	0·232
CH_3Cl	25	7·68	13·6 [3]	$11{\cdot}2_6$ [4]	28·4 [2]	1·72	0·509	0·411	0·411
CH_3Br	25	12·27	14·7 [5]	14·0 [4]	—	1·70	0·656	0·499	0·499
CH_3I	25	12·90	21·9 [6]	18·5 [6]	—	1·48	0·872	0·657	0·657
$CH_3{\cdot}NO_2$	25	21·2	18·3 [7]	12·0 [8]	—	3·14	0·518	0·717	0·183 †
$CH_3{\cdot}CN$	25	52·2	11·7 [9]	$10{\cdot}8_5$ [10]	—	$3{\cdot}37_5$	0·543	0·370	0·370
$(CH_3)_3CCl$	25	$20{\cdot}3_6$	29·3 [6]	24·9 [6]	—	2·14	$1{\cdot}09_2$	0·926	0·926
$(CH_3)_3CBr$	25	34·7	33·3 [6]	28·3 [6]	—	2·19	$1{\cdot}29_4$	$1{\cdot}02_6$	$1{\cdot}02_6$
$(CH_3)_3CI$	25	48·3	36·9 [6]	33·5 [6]	—	2·14	$1{\cdot}57_8$	$1{\cdot}19_1$	$1{\cdot}19_1$
C_2Cl_6	25	1·09	45·1 [11]	39·6 [12]	—	0	$1{\cdot}65_7$	$1{\cdot}65_7$	$1{\cdot}36_1$
C_6H_6	20	1·72	$26{\cdot}9_5$ [11]	$25{\cdot}0_5$ [13]	77·3 [2]	0	$1{\cdot}11_4$	$1{\cdot}11_4$	$0{\cdot}73_3$
C_6H_5Me	25	3·04	32·7 [9]	29·9 [14]	74·7 [2]	0·34	$1{\cdot}37_7$	$1{\cdot}25_3$	(0·904)
C_6H_5F	20	13·5	31·3 [6]	24·9 [6]	—	1·38	$1{\cdot}12_6$	$1{\cdot}10_6$	{0·711}
C_6H_5Cl	20	34·5	34·9 [15]	29·9 [13]	87·8 [16]	1·59	$1{\cdot}47_2$	$1{\cdot}24_4$	(0·818)
C_6H_5Br	25	40·7	35·6 [17]	32·6 [18]	93·8 [16]	1·51	$1{\cdot}68_4$	$1{\cdot}21_3$	(0·956)
C_6H_5I	20	44·2	41·4 [6]	38·3 [6]	—	1·39	$1{\cdot}98_4$	$1{\cdot}40_7$	{1·136}
$C_6H_5{\cdot}NO_2$	20	255·2	36·2 [15]	30·9 [13]	100 [16]	3·95	$1{\cdot}60_4$	$1{\cdot}38_6$	(0·662)
$C_6H_5{\cdot}CN$	20	272·8	33·1 [9]	30·2 [13]	—	4·02	$1{\cdot}63_8$	$1{\cdot}21_1$	{0·849}
1 : 2-$C_6H_4Me_2$	20	5·98	35·9 [6]	34·4 [13]	—	0·53	$1{\cdot}63_9$	$1{\cdot}35_2$	$(1{\cdot}07_5)$
1 : 3-$C_6H_4Me_2$	20	3·09	35·9 [6]	34·5 [13]	89·4 [16]	0·26	$1{\cdot}32_7$	$1{\cdot}68_2$	$(1{\cdot}07_5)$
1 : 4-$C_6H_4Me_2$	25	2·52	36·6 [11]	34·6 [13]	—	0	$1{\cdot}61_3$	$1{\cdot}40_2$	$(1{\cdot}07_5)$
1 : 4-$C_6H_4Cl_2$	25	9·18	36·9 [11]	34·7 [13]	—	0	$1{\cdot}92_3$	$1{\cdot}27_6$	(0·903)
1 : 4-$C_6H_4Br_2$	20	9·58	40·7 [11]	40·1 [4]	—	0	$2{\cdot}18_8$	$1{\cdot}37_3$	$(1{\cdot}17_9)$
1 : 3 : 5-$C_6H_3Me_3$...	20	2·40	41·9 [11]	39·2 [13]	—	0	$1{\cdot}69_6$	$1{\cdot}69_6$	$1{\cdot}24_7$
1 : 3 : 5-$C_6H_3Cl_3$ ...	20	8·94	45·0 [11]	$39{\cdot}3_5$ [4]	—	0	$1{\cdot}83_2$	$1{\cdot}83_2$	0·988
1 : 3 : 5-$C_6H_3Br_3$ ...	20	5·78	50·1 [11]	$47{\cdot}5_5$ [4]	—	0	$2{\cdot}10_9$	$2{\cdot}10_9$	$1{\cdot}40_2$
1 : 3 : 5-$C_6H_3(NO_2)_3$	25	39·9	54·2 [11]	41·7 [4]	—	0	$2{\cdot}20_5$	$2{\cdot}20_5$	$0{\cdot}51_9$
C_6Me_6	25	3·80	54·6 [11]	52·5 [4]	—	0	$2{\cdot}26_3$	$2{\cdot}26_3$	$1{\cdot}68_1$
C_6Cl_6	20	24·6	63·5 [11]	53·4 [4]	—	0	$2{\cdot}56_2$	$2{\cdot}56_2$	$1{\cdot}18_8$

References. [1] Smyth and McAlpine, *J. Chem. Physics*, 1934, **2**, 499. [2] Cabannes and Granier, *Compt. rend.*, 1926, **182**, 885. [3] Barclay and Le Fèvre, *J.*, 1950, 556. [4] Calc. from atomic refractivities listed by Vogel, *J.*, 1948, 1833. [5] Buckingham and Le Fèvre, *J.*, 1953, 3432. [6] Audsley and Goss, *J.*, 1941, 864; 1942, 358, 497. [7] Smyth and McAlpine, *J. Amer. Chem. Soc.*, 1934, **56**, 1697. [8] Extrapolated from molecular refractions by Vogel, *J.*, 1948, 1852. [9] Taken as $1{\cdot}05R_{\mathrm{D}}$. [10] Extrapolated from Jeffery and Vogel, *J.*, 1948, 674. [11] *I.e.*, $_{\infty}P_2$. [12] From $R_{C_2HCl_5}$ listed in Landolt–Börnstein's "Tabellen," 1912 Edn., plus constants given in ref. 4. [13] Calc. from molecular refractions listed in ref. 12. [14] Calc. from Vogel, *J.*, 1948, 607. [15] Sugden and Groves, *J.*, 1934, 1094. [16] Cabannes, *op. cit.*, Chap. XIII. [17] Groves and Sugden, *J.*, 1935, 971. [18] Extrapolated from Vogel, *J.*, 1948, 657.

* Values in parentheses in this column are calculated from $b_3^{C_6H_6}$ and data in Table 3; those in braces are explained in the text. Except for nitromethane, all others are derived by direct computation from $_{\infty}(_{m}K_2)$ and other observations now recorded.

† $b_3^{CH_3{\cdot}NO_2}$ calc. as $b_3^{CH_4} - 0{\cdot}07$ (from Table 3). If the assumption be made for nitromethane that $b_2 = b_3$, then $b_1 = 0{\cdot}527$, and $b_2 = b_3 = 0{\cdot}446 \times 10^{-23}$.

Wang introduced b_1, b_2, and b_3 for acetone, and thus provided three new relations containing—as he supposed—two further unknowns only, *viz.*, $b_L^{C=O}$ and $b_T^{C=O}$; however, Wang's underlying assumption, that $b_T^{C=O} = b_V^{C=O}$, is one with which we cannot agree. In general, attempts to solve for A, B, etc., by adding to an A, B, E, F system a double linkage (which would give rise to three extra and different expressions for b_1, b_2, and b_3 of the derivative) must fail. Inevitably with the three new equations there will be produced as many new unknowns. If, instead, we add C–R or C≡R, where $b_L^{C-R} \neq b_T^{C-R} = b_V^{C-R}$ or $b_L^{C\equiv R} \neq b_T^{C\equiv R} = b_V^{C\equiv R}$, then admittedly we add only two unknowns, but the molecule under consideration will have an axis of symmetry and accordingly one equation is lost.

In conclusion, we submit that, if the tetrahedral arrangement of methane and its derivatives is to be assumed, it is not possible to evaluate A, B, C, and D by the additivity methods discussed so far. We instance the following example to substantiate our point :

$$A + 2B = 0{\cdot}75\alpha^{CH_4} \quad (9)$$

$$C + 2D = 0{\cdot}75\alpha^{CCl_4} \quad (10)$$

$$A/3 + 8B/3 + C = b_1^{CH_3Cl} \quad (11)$$

$$4A/3 + 5B/3 + D = b_2^{CH_3Cl} \quad (12)$$

$$C/3 + 8D/3 + A = b_1^{CHCl_3} \quad (13)$$

$$4C/3 + 5D/3 + B = b_2^{CHCl_3} \quad (14)$$

One might reasonably expect solution of A, B, C, and D from the above expressions (9)—(14), but $\alpha^{CH_4} + \alpha^{CCl_4} = \alpha^{CH_3Cl} + \alpha^{CHCl_3}$, *i.e.*,

$$4/3(9) + 4/3(10) = 1/3\{(11) + 2(12)\} + 1/3\{(13) + 2(14)\}$$

or, (11), (12), (13), (14) are together transformable into (9) and (10), and accordingly we are reduced to two equations only, *viz.*, (9) and (10), with the four unknowns A, B, C, and D. The same argument applies to any attempted handling on similar lines of A, B, C, and D from polarisability data drawn from all (tetrahedral) structures containing the links to which A, B, etc., relate.

Sachsse differed from Denbigh and Wang in taking account, where possible, of deviations from regular tetrahedral configurations; *via* appropriate equations for, *e.g.*, CH_3Cl, CH_2Cl_2, and $CHCl_3$, he obtained numerical values for A, B, C, D, etc. In particular, he found A and B to be $0{\cdot}081 \times 10^{-23}$ and $0{\cdot}057 \times 10^{-23}$, respectively. These figures are not dissimilar from those of Wang ($0{\cdot}072 \times 10^{-23}$ and $0{\cdot}062 \times 10^{-23}$) or Denbigh ($0{\cdot}079 \times 10^{-23}$ and $0{\cdot}058 \times 10^{-23}$), despite the criticisms indicated above. This, we suggest, is because A and B are both small and nearly equal; indeed if, following Ingold ("Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, New York, 1953), we take $A = B$, then from (9) and ${}_{E}P^{CH_4}$ (Watson and Ramaswamy, *loc. cit.*), $A = B = 0{\cdot}064 \times 10^{-23}$. Since the slight inconsistencies in A and B scarely affect the main objective of this paper, and because Sachsse's derivation seems the most firmly based, we propose to accept his values, rounding them off to $A = 0{\cdot}08 \times 10^{-23}$ and $B = 0{\cdot}06 \times 10^{-23}$.

From the $b_1^{CH_4}$ previously quoted (Watson and Ramaswamy, *loc. cit.*) the polarisabilities of the methyl radical follow as $b_1^{CH_3} = 0{\cdot}17 \times 10^{-23}$ and $b_2^{CH_3} = b_3^{CH_3} = 0{\cdot}19 \times 10^{-23}$. At once, by appropriate subtractions from the b's of Table 4, estimates can be made of b_L^{C-X}, b_T^{C-X}, and b_V^{C-X}. (The directions indicated by the subscripts L, V, and T are related to b_1, b_2, and b_3 respectively in a molecule R–X.) Examples are included in Table 5. The C–C bond ellipsoid can be similarly deduced from ethane : Breazeale (*loc. cit.*) gives $B^{C_2H_6}$ as $10{\cdot}4 \times 10^{-12}$ at N.T.P.; $({}_{m}K_{gas})^{N.T.P.}$ is therefore $1{\cdot}122 \times 10^{-12}$, and—since ${}_{D}P = 11{\cdot}16$ c.c. (Watson and Ramaswamy, *loc. cit.*)—$b_1^{C_2H_6} = 0{\cdot}536 \times 10^{-23}$ and $b_2^{C_2H_6} = b_3^{C_2H_6} = 0{\cdot}386 \times 10^{-23}$; after allowance for two methyl groups, b_L^{C-C} is seen to be $0{\cdot}20 \times 10^{-23}$ and b_T^{C-C} to be $0{\cdot}01 \times 10^{-23}$.

Polarisabilities of Molecules related as Alphyl–X and Aryl–X.—The comparison may be made by the procedure explained by Ingold (*op. cit.*) : from the molecular b's listed in Table 4 we subtract the appropriate b_1, b_2, or b_3 of the radicals methyl or phenyl. (The former have been already given; the latter, from the results for C_6H_6 and the C–H bond, are : $b_1 = 1{\cdot}03 \times 10^{-23}$, $b_2 = 1{\cdot}05 \times 10^{-23}$, and $b_3 = 0{\cdot}67 \times 10^{-23}$). The upper part of Table 5 is thus obtained; the lower part shows the differences between the corresponding b_L's, b_V's, etc., for aryl–X and alphyl–X links in the phenyl and methyl compounds.

We note at once that, except with the C–CH_3 link, the algebraic sign of the largest Δb in each case is the same as that of the exaltation of refraction revealed by a parallel treatment of refractivity data and listed by Ingold (*op. cit.*, p. 127). The Δb_i's of Table 4 thus seem, in part, harmonious with a conclusion already reached by this author, namely that the " . . . exaltation of polarisability produced by substituents . . . in aromatic combination, is concentrated along the dipole axis : indeed this exaltation is augmented at the expense of polarisability in other directions. The whole effect is not very great for CH_3, but is larger for Cl . . . " (*op. cit.*, pp. 136, 137).

TABLE 5.* *Principal axes for* C–X *in various methyl and phenyl compounds.*

Compound	b_L	b_V	b_T	Compound	b_L	b_V	b_T
CH_3F	0·15	0·04	0·04	C_6H_5F	0·10	0·06	0·04
CH_3Cl	0·34	0·22	0·22	C_6H_5Cl	0·44	0·19	0·15
CH_3Br	0·49	0·31	0·31	C_6H_5Br	0·65	0·16	0·29
CH_3I	0·70	0·47	0·47	C_6H_5I	0·95	0·36	0·47
$CH_3{\cdot}CN$	0·37	0·18	0·18	$C_6H_5{\cdot}CN$	0·61	0·16	0·18
$CH_3{\cdot}NO_2$	0·35	0·53	−0·01	$C_6H_5{\cdot}NO_2$	0·57	0·34	−0·01
$CH_3{\cdot}CH_3$	0·37	0·20	0·20	C_6H_5Me	0·35	0·20	0·23

$$\Delta b_i = b_i^{\text{Aryl-X}} - b_i^{\text{Alphyl-X}}$$

	Δb_L	Δb_V	Δb_T		Δb_L	Δb_V	Δb_T
C–F	−0·05	+0·02	0	C–CN	+0·24	−0·02	0
C–Cl	+0·10	−0·03	−0·07	$C{-}NO_2$	+0·22	−0·19	0
C–Br	+0·16	−0·15	−0·03	$C{-}CH_3$	−0·02	0	+0·03
C–I	+0·25	−0·11	0				

* Units = 10^{-23} c.c.

Similar directed exaltations may be inferred for the disubstituted benzenes, both polar and non-polar, included in Table 4. When the bond values in Table 5, together with those for C–H and C–C already noted, are used in conjunction with b_1, b_2, and b_3 of benzene, the ellipsoid of a given structure $C_6H_4X_2$ can be computed and compared with that deduced from experiment; Table 6 summarises such calculations.

TABLE 6.* *Directed exaltations in molecules of type* $C_6H_4X_2$.

	Calculated			Found			Exaltations		
	b_1	b_2	b_3	b_1	b_2	b_3	Δb_1	Δb_2	Δb_3
1 : 2-$C_6H_4Me_2$ ...	1·61$_5$	1·46$_5$	1·01	1·64	1·35	1·07$_5$	+0·02$_5$	−0·11$_5$	+0·06$_5$
1 : 3-$C_6H_4Me_2$ ...	1·46$_5$	1·61$_5$	1·01	1·32	1·68	1·07$_5$	−0·14$_5$	+0·06$_5$	+0·06$_5$
1 : 4-$C_6H_4Me_2$ ...	1·69	1·39	1·01	1·61	1·40	1·07$_5$	−0·08	+0·01	+0·06$_5$
1 : 4-$C_6H_4Cl_2$ ...	1·63	1·43	1·05	1·92	1·28	0·90	+0·29	−0·15	−0·15
1 : 4-$C_6H_4Br_2$ ...	1·93	1·61	1·23	2·19	1·37	1·18	+0·26	−0·24	−0·05

* Units = 10^{-23} c.c.

With the two dihalogenobenzenes the positive exaltations along the 1 : 4-axes are notable, and compatible with the quoted statement by Ingold. Our results for the xylenes, however, resemble those for toluene in showing effects which, although slight, do not seem reconcilable either with the small positive exaltations of molecular refraction recognisable in these molecules or with the idea that such exaltations occur mainly along the CH_3–C bond directions. Unavoidable errors could produce this situation: for example, if the longitudinal polarisability of the $CH_3{-}C_{\text{Alphyl}}$ link were lower than that shown in Table 5 by only 0·02—0·04 unit, the difficulty would vanish; the figure in question is derived from the sole available measurements of the Kerr constant of ethane, those by Breazeale, on the gas, using light of λ 6500 Å; and $b_1^{C_2H_6}$ derived therefrom may be a little too high. Incidentally, the last point directly affects the magnitudes of b_L^{C-C} and b_T^{C-C}: taking these as $0{\cdot}20 \times 10^{-23}$ and $0{\cdot}01 \times 10^{-23}$ leads to a calculated average refractivity for the C–C bond of 1·8—1·9 c.c., whereas from a recent analysis (Vogel, Cresswell, Jeffery, and Leicester, *J.*, 1952, 514) *ca.* 1·3 c.c. seems most probable. A similar check on the other bond data of this paper is made in Table 7.

TABLE 7. *Calculated and found bond refractions.*

	Mean R_{Bond} calc. ex Table 5 (c.c.)		Mean R_{Bond} given by Vogel *et al.* for *D* line (c.c.)	
Bond	Aliphatic	Aromatic	Aliphatic	Aromatic
C–F	1·9	1·7	1·4 *	1·5
C–Cl	6·6	6·6	6·5	6·6
C–Br	9·4	9·3	9·4	9·5
C–I	13·9	15·1	14·6	14·6
$C{-}NO_2$	7·4	7·6	7·4	8·2
C–CN	6·2	8·0	6·1	7·1
$C{-}CH_3$	6·5	6·5	6·3	6·6

* Vogel *et al.* annotate their figures for C–F as " preliminary values."

It appears that our figures for b_L^{C-F} and b_T^{C-F} are probably high (the observations on methyl fluoride–carbon tetrachloride mixtures were the most troublesome to make, and therefore the least certain experimentally, of all in this paper); however, Vogel *et al.* call their results for the fluoro-group " preliminary," and we note that their Tables 51 and 53 indicate for fluorobenzene an exaltation of about 0·04 c.c., which is positive, not negative as concluded from other sources by Ingold (*op. cit.*, p. 127) and as shown in our Table 5 under Δb_L. The remaining cases in Table 7 display consistency which is reasonable in view of the larger b_L, b_T, and b_V data involved. Regarding b_L^{C-H} and b_T^{C-H}, the values adopted in this work lead to $R_{C-H} = 1{\cdot}7$ c.c., in satisfactory accord with that reported by Vogel *et al.* for this bond.

The above questions directly concern the degree to which bond polarisability ellipsoids are constant throughout a range of different molecular structures involving them; it is relevant therefore now to consider the *tert.*-butyl halides (included in Table 4) in the same way as we already have the phenyl halides.

From the refractivity of *neo*pentane we estimate R_∞ to be 25·0 c.c., whence $b_1 = b_2 = b_3 = 0{\cdot}986 \times 10^{-23}$ c.c. After subtracting the polarisabilities appropriate for three C–H links and one C–C link (and assuming retention of tetrahedral angles), we obtain for the $(CH_3)_3C$ unit : $b_1 = 0{\cdot}62 \times 10^{-23}$ and $b_2 = b_3 = 0{\cdot}79 \times 10^{-23}$ c.c. Table 8 lists the principal axes which then follow for the carbon–halogen links in the three molecules $(CH_3)_3CX$, together with their differences from the corresponding values for the related CH_3–X structures. Positive exaltations along the axes of the bonds, and negative exaltations across them, thus seem to occur.

TABLE 8. *tert.-Butyl halides.**

Link	b_L	$b_V = b_T$	Δb_L †	$\Delta b_V = \Delta b_T$ †
C–Cl	0·47	0·14	+0·13	−0·06
C–Br	0·67	0·24	+0·18	−0·07
C–I	0·96	0·40	+0·26	−0·07

* Units : 10^{-23} c.c.   † $\Delta b_i = (b_i^{C-X})_{tert.\text{-butyl halide}}$ minus $(b_i^{C-X})_{\text{methyl halide}}$.

Finally, we refer to the case of hexachloroethane. The molar Kerr constant of this substance was determined by Sachsse (*loc. cit.*) who reported it as $4{\cdot}9 \times 10^{-12}$. Our work confirms the low order of this value, and provides estimates of polarisability of $1{\cdot}36 \times 10^{-23}$ c.c. along the C–C direction and of $1{\cdot}66 \times 10^{-23}$ for the two perpendicular directions. In theory, information on the C–C link should now be accessible either *via* data on chloroform ($b_1 = 0{\cdot}59 \times 10^{-23}$, $b_2 = b_3 = 0{\cdot}93_5 \times 10^{-23}$; Le Fèvre and Le Fèvre, *loc. cit.*) and the C–H bond (this paper), or data on carbon tetrachloride ($b_1 = b_2 = b_3 = 1{\cdot}013 \times 10^{-23}$) and the C–Cl bond (this paper). However, the former method produces a negative quantity for b_T^{C-C}. This is probably because the spatial arrangement of the CCl_3 group in chloroform is not retained in hexachloroethane; elementary reasoning from volume requirements would suggest that the Cl–C–Cl angles in C_2Cl_6 should be less than those in $CHCl_3$. The latter route, starting from CCl_4 and C–Cl link data from Table 5, yields $b_L^{C-C} = 0{\cdot}02 \times 10^{-23}$ c.c. and $b_T^{C-C} = 0{\cdot}08 \times 10^{-23}$ c.c.

These values are in marked contrast to those drawn from methane and ethane, although they resemble Sachsse's results, which are $b_L^{C-C} = 0{\cdot}02 \times 10^{-23}$ and $b_T^{C-C} = 0{\cdot}05 \times 10^{-23}$ c.c. It is possible that the electron attracting ($-I$) actions of the six chlorine atoms exert a "polarity" effect on the C–C bond, making its electrons more tightly bound than those between the carbon atoms of ethane, so that a smaller C–C polarisability in C_2Cl_6 than in C_2H_6 merely parallels the general diminishing order known for the polarisabilities of negatively charged, neutral, and positively charged atoms; alternatively, although it seems unlikely, hexachloroethane may be subject to double halogen hyperconjugation. Whatever the explanation, the case is a warning against accepting the anisotropic polarisabilities of bonds as constants throughout all molecular situations.

Conclusions.—Our measurements indicate (1) that changes in average polarisability consequent upon the introduction of a substituent with $\pm M$ character into the benzene ring are not uniformly distributed but tend to be " oriented in the direction along which the hyperconjugative or conjugative electromeric polarisability, allowed by the substituent, should be effective " (Ingold, *op. cit.*, p. 137), and (2) that in the *tert.*-butyl halides each C–Halogen bond shows an enhanced longitudinal polarisability, the increases running I > Br > Cl; such effects may be a manifestation of inductomeric polarisability, for which this order of the halogens, and the greater effect with $(CH_3)_3C$ than with CH_3, is to be expected (cf. Ingold, *op. cit.*, p. 73).

EXPERIMENTAL

Materials.—Carbon tetrachloride and benzene for use as solvents were both sulphur-free. We thank Messrs. I.C.I. (Australia and New Zealand) Ltd. for the gift of a bulk supply of the former, selected specially from a " middle cut." After drying ($CaCl_2$), fractionation, and storage over calcium chloride, it showed B values similar to those of most carefully purified specimens of " AnalaR " grade, and was therefore given no further treatment. Thiophen-free benzene was partially frozen, and the remelted solid kept over clean sodium wire.

The solutes were redistilled or recrystallised, as appropriate, before use and had the b. p.s or m. p.s recorded for pure samples in Beilstein's " Handbuch." The methyl bromide was part of that used for other work (cf. Buckingham and Le Fèvre, *J.*, 1953, 3432). Methyl fluoride was generated as required by heating together potassium fluoride and potassium methyl sulphate (Batuecas and Moles, *J. Chim. phys.*, 1919, **17**, 537). Methyl chloride was obtained from methyl alcohol (Barclay and Le Fèvre, *J.*, 1950, 556). Gases were dissolved by a technique similar to that used by Le Fèvre and Ross (*J.*, 1950, 283) for sulphur dioxide.

Measurements.—These were made by the methods described in our previous paper (*J.*, 1953, 4041), where the symbols used here are defined, and the extrapolation procedure explained. The observations recorded in Table 9 are for either 20° or 25°, at which temperatures the following data for the solvents are taken :

Temp.	10^7B_D	n_D	d_4^t	ε_t	H	J	$10^{14}.K_1$
			Carbon tetrachloride.				
20°	0·072	1·4604	1·5940	2·2360	2·064	0·4721	0·761
25	0·070	1·4575	1·5845	2·2270	2·060	0·4731	0·749
			Benzene				
20	0·424	1·5010	0·8791	2·2825	2·119	0·4670	7·72
25	0·410	1·4973	0·8738	2·2725	2·114	0·4681	7·56

TABLE 9. *Weight-fractions, Kerr constants, refractive indexes, densities, and dielectric constants of solutions.*

10^5w_2	10^7B_{12}	$(n_D^t)_{12}$	$(d_4^t)_{12}$	$(\varepsilon_t)_{12}$	10^5w_2	10^7B_{12}	$(n_D^t)_{12}$	$(d_4^t)_{12}$	$(\varepsilon_t)_{12}$
		Methyl fluoride in carbon tetrachloride at 20°.							
15	$0·072_5$	—	1·5937	2·2366	98	0·081	1·4598	1·5922	2·2540
26	$0·074_5$	—	1·5935	2·2398	101	0·082	1·4600	1·5921	2·2535
29	0·075	—	1·5935	2·2395	119	0·083	1·4598	1·5921	2·2539
34	0·075	—	1·5934	2·2417	185	0·085	1·4595	1·5904	2·2660
		Whence $\Sigma(\Delta B \,.\, w_2)/\Sigma w_2^2 = 8·2_5$.							
		Methyl chloride in carbon tetrachloride at 25°.							
180	0·084	1·4573	1·5821	2·2466	922	0·135	1·4557	1·5745	2·3275
390	0·098	1·4569	1·5804	2·2695	971	0·136	1·4556	1·5739	2·3328
882	0·122	1·4558	1·5749	2·3239	1184	0·153	1·4552	1·5717	2·3568
889	0·133	1·4558	1·5747	2·3240	1441	0·174	1·4547	1·5688	2·3846
		Whence $\Delta B = 6·21w_2 + 67w_2^2$.							
		Methyl bromide in carbon tetrachloride at 25°.							
24	0·080	1·4575	1·5846	2·2284	859	0·115	1·4571	1·5852	2·2754
497	0·095	1·4573	1·5849	2·2555	984	0·122	1·4571	1·5853	2·2829
611	0·101	1·4572	1·5850	2·2617	1004	0·121	1·4571	1·5854	2·2833
732	0·108	1·4572	1·5851	2·2685	1866	0·166	1·4568	1·5858	2·3318
		Whence $\Delta B = 5·20w_2 - 3·0w_2^2$.							
		Methyl iodide in carbon tetrachloride at 25°.							
1148	0·117	1·4580	1·5899	2·2626	6705	0·322	1·4605	1·6153	2·4348
2675	0·167	1·4589	1·5968	2·3126	7689	0·350	1·4608	1·6206	2·4730
2938	0·175	1·4590	1·5980	2·3210	9171	0·408	1·4616	1·6258	2·5296
5502	0·270	1·4598	1·6098	2·4031					
		Whence $\Delta B = 3·63w_2 - 0·23w_2^2$							

TABLE 9. (*Continued.*)

10^5w_2	10^7B_{12}	$(n_D^t)_{12}$	$(d_4^t)_{12}$	$(\varepsilon_t)_{12}$	10^5w_2	10^7B_{12}	$(n_D^t)_{12}$	$(d_4^t)_{12}$	$(\varepsilon_t)_{12}$
Nitromethane in benzene at 25°.									
1019	0·522	1·4961	0·87590	2·4499	2902	0·759	1·4940	0·87978	2·7774
1287	0·559	1·4958	0·87646	2·4951	3277	0·782	1·4936	0·88060	2·8394
2411	0·676	1·4946	0·87879	2·6944	4016	0·885	1·4927	0·88213	2·9713
Whence $\Delta B = 10{\cdot}90w_2 + 22{\cdot}1w_2^2$.									
Acetonitrile in carbon tetrachloride at 25°.									
366	0·266	1·4565	1·5785	2·4283	1423	0·829	1·4538	1·5610	3·0182
485	0·340	1·4562	1·5765	2·4938	2015	1·095	1·4522	1·5510	3·3352
735	0·515	1·4555	1·5724	2·6386	3369	1·894	1·4486	1·5287	4·1136
1073	0·603	1·4547	1·5668	2·8301					
Whence $\Delta B = 51{\cdot}6_5w_2 + 63w_2^2$.									
tert.-Butyl chloride in carbon tetrachloride at 25°.									
104	0·087	1·4574	1·5831	2·2367	1483	0·200	1·4559	1·5645	2·3659
670	0·134	1·4570	1·5753	2·2897	2067	0·255	1·4552	1·5568	2·4208
1020	0·153	1·4562	1·5705	2·3226	2394	0·279	1·4546	1·5524	2·4516
Whence $\Delta B = 8{\cdot}80w_2 - 0{\cdot}20w_2^2$.									
tert.-Butyl bromide in carbon tetrachloride at 25°.									
570	0·130	—	1·5817	2·2657	1957	0·301	1·4574	1·5747	2·3601
1220	0·210	1·4575	1·5785	2·3111	3643	0·576	1·4573	1·5670	2·4765
1791	0·291	1·4574	1·5756	2·3470					
Whence $\Delta B = 10{\cdot}1w_2 + 103w_2^2$.									
tert.-Butyl iodide in carbon tetrachloride at 25°.									
567	0·123	1·4576	1·5834	2·2503	2651	0·331	1·4583	1·5795	2·3516
1734	0·240	$1{\cdot}4579_5$	1·5807	2·2997	3110	$0{\cdot}379_5$	$1{\cdot}4583_5$	1·5786	2·3731
2048	0·273	1·4580	1·5806	2·3273	3706	0·435	1·4586	1·5776	2·4190
Whence $\Delta B = 10{\cdot}4w_2 - 17w_2^2$.									
Hexachloroethane in carbon tetrachloride at 25°.									
607	0·072	1·4579	1·5855	2·2289	2495	0·078	1·4590	1·5890	2·2334
995	0·073	1·4580	1·5862	2·2295	3045	0·080	—	—	—
1146	0·073	1·4581	1·5865	2·2300	5292	0·099	—	—	—
2476	0·078	1·4589	1·5889	2·2332					
Whence $\Delta B = 0{\cdot}131w_2 + 7{\cdot}7w_2^2$.									
Benzene in carbon tetrachloride at 20°.									
2325	0·081	1·4624	1·5761	2·2412	6,832	0·122	1·4669	1·5098	2·2510
3893	0·097	1·4639	1·5444	2·2447	9,064	0·135	1·4694	1·4835	2·2559
4110	0·100	1·4644	1·5424	2·2468	10,806	0·148	1·4714	1·4655	2·2613
6085	0·109	1·4664	1·5198	2·2500	17,673	0·174	1·4779	1·3785	2·2749
Whence $\Delta B = 0{\cdot}756w_2 - 0{\cdot}96w_2^2$.									
Toluene in carbon tetrachloride at 25°.									
1524	0·092	—	—	—	7205	0·165	1·4625	1·4952	2·2687
1593	0·093	1·4586	1·5849	2·2362	7651	0·168	1·4629	1·4893	2·2717
2883	0·104	1·4594	1·5490	2·2437	8666	0·187	—	—	—
2968	0·106	1·4596	1·5480	2·2440	12,276	0·248	—	—	—
4774	0·133	1·4608	1·5237	2·2548	17,707	0·351	—	—	—
6717	0·160	1·4624	1·5012	2·2658	21,185	0·422	—	—	—
6972	0·176	—	—	—					
Whence $\Delta B = 1{\cdot}19w_2 + 2{\cdot}2w_2^2$.									
Fluorobenzene in carbon tetrachloride at 20°.									
1156	0·139	1·4605	1·5833	2·2880	1729	0·175	1·4605	1·5784	2·3103
1458	0·159	1·4605	1·5806	2·2988	1853	0·180	1·4605	1·5770	2·3156
1602	0·164	1·4605	1·5794	2·3049	3637	0·296	1·4607	1·5619	2·3909
Whence $\Delta B = 5{\cdot}628w_2 + 14{\cdot}5w_2^2$.									
Bromobenzene in carbon tetrachloride at 25°.									
806	0·155	—	1·5837	2·2534	2411	0·324	1·4600	1·5822	2·3015
1122	0·188	1·4587	1·5835	2·2615	2599	0·355	1·4603	1·5820	2·3068
1398	0·213	—	1·5832	2·2698	2664	0·361	1·4604	1·5818	2·3083
1700	0·252	1·4594	1·5827	2·2795	3114	0·408	1·4607	1·5812	2·3220
Whence $\Delta B = 10{\cdot}19w_2 + 23{\cdot}6w_2^2$.									
Iodobenzene in carbon tetrachloride at 20°.									
337	0·108	1·4609	1·5947	2·2441	4881	0·492	1·4675	1·6042	2·3512
662	0·131	1·4613	1·5954	2·2509	5302	0·534	1·4680	1·6051	2·3580
2865	0·320	1·4645	1·6002	2·3019	5649	0·566	1·4685	1·6059	2·3654
Whence $\Delta B = 8{\cdot}642w_2 + 1{\cdot}04w_2^2$.									

TABLE 9. (*Continued.*)

10^5w_2	10^7B_{12}	$(n_D^t)_{12}$	$(d_4^t)_{12}$	$(\varepsilon_t)_{12}$	10^5w_2	10^7B_{12}	$(n_D^t)_{12}$	$(d_4^t)_{12}$	$(\varepsilon_t)_{12}$
Benzonitrile in carbon tetrachloride at 20°.									
86	0·171	1·4605	1·5932	2·2632	404	0·512	1·4609	1·5903	2·3633
317	0·433	1·4608	1·5912	2·3363	788	0·930	1·4613	1·5870	2·4838
400	0·508	1·4609	1·5904	2·3623	926	1·141	1·4615	1·5858	2·5271
Whence $\Delta B = 106{\cdot}2w_2 + 778w_2^2$.									
o-Xylene in carbon tetrachloride at 20°.									
1546	0·104	1·4618	1·5742	2·2457	6501	0·206	1·4665	—	—
2465	0·125	1·4626	1·5622	2·2522	8097	0·236	1·4680	1·4956	2·2866
5870	0·193	1·4660	1·5190	2·2730	8299	0·242	1·4681	—	—
Whence $\Delta B = 2{\cdot}14w_2 - 1{\cdot}3w_2^2$.									
m-Xylene in carbon tetrachloride at 20°.									
996	0·079	1·4609	1·5805	2·2395	9,970	0·176	1·4670	1·4695	2·2610
4542	0·119	1·4633	1·5344	2·2486	16,138	0·233	1·4705	1·4013	2·2783
9839	0·174	1·4668	1·4703	2·2601	18,980	0·266	1·4720	1·3725	2·2891
Whence $\Delta B = 1{\cdot}044w_2 - 0{\cdot}16w_2^2$.									
p-Xylene in carbon tetrachloride at 25°.									
1248	0·079	1·4584	1·5677	2·2302	8,711	0·145	1·4634	1·4752	2·2396
2165	0·086	1·4590	1·5564	2·2313	11,461	0·165	1·4662	1·4554	2·2499
3898	0·093	1·4603	1·5336	2·2340	43,240	0·427	1·4817	—	2·3138
Whence $\Delta B = 0{\cdot}816w_2 + 0{\cdot}14w_2^2$.									
p-Dichlorobenzene in carbon tetrachloride at 25°.									
303	0·076	1·4580	1·5836	2·2279	1754	0·108	1·4600	1·5793	2·2325
754	0·090	1·4585	1·5822	2·2293	1939	0·112	1·4603	1·5786	2·2330
1297	0·098	1·4595	1·5806	2·2310	2171	0·118	1·4605	1·5780	2·2338
Whence $\Delta B = 2{\cdot}38_5w_2 - 10w_2^2$.									
p-Dibromobenzene in carbon tetrachloride at 20°.									
1261	0·093	1·4620	1·5980	2·2391	1746	0·101	1·4626	1·5995	2·2404
1521	0·097	1·4623	1·5990	2·2398	1985	0·105	—	—	—
1731	0·100	—	—	—	2081	0·107	—	—	—
Whence $\Delta B = 1{\cdot}57_5w_2 + 4{\cdot}6w_2^2$.									
Mesitylene in carbon tetrachloride at 20°.									
189	0·073	1·4604	1·5915	2·2363	2507	0·090	1·4618	1·5602	2·2403
285	0·073	1·4604	1·5902	2·2366	3432	0·096	1·4624	1·5477	2·2418
955	0·077	1·4610	1·5810	2·2376	5419	0·110	1·4637	1·5222	2·2445
Whence $\Delta B = 0{\cdot}668w_2 + 0{\cdot}69w_2^2$.									
1 : 3 : 5-Trichlorobenzene in carbon tetrachloride at 20°.									
460	0·080	1·4609	1·5930	2·2378	1529	0·100	1·4622	1·5910	2·2424
1148	0·092	1·4617	1·5918	2·2406	2710	0·117	1·4635	1·5887	2·2468
1339	0·096	1·4620	1·5915	2·2414					
Whence $\Delta B = 1{\cdot}90w_2 - 8{\cdot}7w_2^2$.									
1 : 3 : 5-Tribromobenzene in carbon tetrachloride at 20°.									
424	0·075	1·4609	1·5962	2·2375	1413	0·083	—	—	—
1025	0·079	—	—	—	1451	0·083	1·4622	1·6013	2·2407
1149	0·082	1·4618	1·5998	2·2396	1849	0·087	—	—	—
Whence $\Delta B = 0{\cdot}698w_2 + 6{\cdot}0w_2^2$.									

1 : 3 : 5-Trinitrobenzene in benzene at 25°.

10^5w_2	542	713	974	1106	2204	2388
10^7B_{12}	0·428	0·438	0·437	0·455	0·469	0·472
$(n_D)_{12}^{25}$	1·4976	1·4978	1·4979	1·4980	1·4985	1·4987

Whence $\Delta B = 4{\cdot}12_5w_2 - 64w_2^2$.

10^5w_2	10^7B_{12}	$(n_D^t)_{12}$	$(d_4^t)_{12}$	$(\varepsilon_t)_{12}$	10^5w_2	10^7B_{12}	$(n_D^t)_{12}$	$(d_4^t)_{12}$	$(\varepsilon_t)_{12}$
Hexamethylbenzene in carbon tetrachloride at 25°.									
219	0·072	1·4580	1·5821	2·2275	1142	0·081	1·4594	1·5719	2·2299
579	0·075	1·4584	1·5781	2·2276	1732	0·080	1·4608	1·5655	2·2322
691	0·076	1·4585	1·5769	2·2287	2768	0·089	1·4628	1·5540	2·2337
896	0·076	1·4592	1·5746	2·2290					
Whence $\Delta B = 0{\cdot}819w_2 - 5{\cdot}6w_2^2$.									
Hexachlorobenzene in benzene at 20°.									
248	$0{\cdot}428_5$	—	—	—	1351	0·451	1·5020	0·8852	2·2867
878	0·441	1·5016	0·8831	2·2859	1738	0·459	1·5023	0·8870	2·2872
935	0·442	—	—	—	2474	0·547	1·5028	0·8904	2·2905
Whence $\Delta B = 1{\cdot}88w_2 + 7{\cdot}6w_2^2$.									

From the information contained in Table 9, molar Kerr constants at infinite dilution are calculated in Table 10. Since $\alpha\varepsilon_1$, γn_1, and βd_1 do not affect the results very critically they have been estimated in all cases as the quotients: Σ(differences between solutions and solvent)/Σw_2. In deducing the standard errors of $B_1\delta$, the equations quoted by Harris, Le Fèvre, and Sullivan (*J.*, 1953, 1622) have been utilised, the quantities ΔB replacing those written as δQ by these authors.

TABLE 10. *Calculation of molar Kerr constants at infinite dilution.*

Temp.	Solute	Solvent	$\alpha\varepsilon_1$	β	γ	δ	±% Std. error on $B_1\delta$	No. of solns. giving $B_1\delta$	$_\infty(_mK_2) \times 10^{12}$
20°	CH_3F	CCl_4	16	−1·15	−0·34	114	10·5	8	28·3
25	CH_3Cl	,,	10·9	−0·690	−0·130	88·7	6·0	8	32·3
25	CH_3Br	,,	5·72	0·051	−0·028	74·3	1·3	8	51·6
25	CH_3I	,,	3·20	0·290	0·031	51·9	3·8	7	$54{\cdot}2_5$
25	CH_3NO_2	C_6H_6	17·4	0·238	−0·076	26·6	3·5	6	89·0
25	$CH_3{\cdot}CN$	CCl_4	55·7	−1·044	−0·181	738	2·8	7	219·5
25	$(CH_3)_3CCl$	,,	9·37	−0·852	−0·077	126	3·6	6	85·6
25	$(CH_3)_3CBr$	,,	6·81	−0·309	−0·003	144	2·5	5	146
25	$(CH_3)_3CI$	,,	4·77	−0·121	0·019	149	2·6	6	203
25	C_2Cl_6	,,	0·259	0·111	0·039	1·87	6·0	7	4·60
20	C_6H_6	,,	0·227	−0·755	0·067	10·5	5·1	8	7·24
25	$C_6H_5{\cdot}CH_3$	,,	0·511	−0·784	0·048	17·0	1·9	13	12·8
20	C_6H_5F	,,	4·31	−0·567	0·005	78·2	1·4	6	56·8
20	C_6H_5Cl	,,	4·84	−0·431	0·043	170	1	8	145 *
25	C_6H_5Br	,,	3·10	−0·075	0·073	146	1·6	8	171
20	C_6H_5I	,,	2·31	0·132	0·099	120	0·8	6	186
20	$C_6H_5{\cdot}NO_2$	CCl_4	25·6	−0·322	0·063	1156	1	8	1073 *
20	$C_6H_5{\cdot}CN$	,,	31·5	$-0{\cdot}560_5$	0·082	1475	2·5	6	1147
20	$1:2\text{-}C_6H_4(CH_3)_2$	,,	0·631	−0·784	0·064	29·7	1·0	6	$25{\cdot}1_5$
20	$1:3\text{-}C_6H_4(CH_3)_2$	,,	0·266	−0·763	0·043	14·5	1·6	6	13·0
25	$1:4\text{-}C_6H_4(CH_3)_2$	,,	0·193	−0·770	0·052	11·7	4·1	6	10·6
25	$1:4\text{-}C_6H_4Cl_2$	,,	0·310	−0·190	0·098	34·1	4·6	6	38·6
20	$1:4\text{-}C_6H_4Br_2$	,,	0·250	0·201	0·086	21·9	4·9	6	40·3
20	$1:3:5\text{-}C_6H_3(CH_3)_3$	,,	0·165	−0·840	0·004	9·28	2·8	6	10·1
20	$1:3:5\text{-}C_6H_3Cl_3$	,,	0·404	−0·122	0·079	26·4	3·2	5	37·6
20	$1:3:5\text{-}C_6H_3Br_3$	,,	0·324	0·317	0·084	9·69	6·6	6	24·3
25	$1:3:5\text{-}C_6H_3(NO_2)_3$	C_6H_6	0·391	0·472 †	0·039 †	10·1	7·2	6	168
25	$C_6(CH_3)_6$	CCl_4	0·244	−0·695	0·125	11·7	6·8	7	16·0
20	C_6Cl_6	,,	0·315	$0{\cdot}517_5$	0·049	4·43	0·2	6	103·6

* Recalc. from Le Fèvre and Le Fèvre, *J.*, 1953, 4041.

† Calc. from data of Le Fèvre and Le Fèvre, *J.*, 1935, 957.

Molar Kerr constants for eight of the above solutes in carbon tetrachloride are to be found in the literature. The earlier values given for benzene, chlorobenzene, and nitrobenzene are quoted in our previous paper, those for the remaining five substances are noted here (all determined at 4° with light of $\lambda = 5461$ Å):

CH_3Cl	$40{\cdot}8 \times 10^{-12}$	(Sachsse, *Physikal. Z.*, 1935, **36**, 360)
C_2Cl_6	$4{\cdot}9 \times 10^{-12}$	(*idem, ibid.*)
C_6H_5Br	182×10^{-12}	(Otterbein, *ibid.*, 1933, **34**, 646)
C_6H_5I	183×10^{-12}	(*idem, ibid.*)
$1:2\text{-}C_6H_4Cl_2$	22×10^{-12}	(*idem, ibid.*)

Since neither Sachsse nor Otterbein gives B versus concentration figures, we are unable to check the extrapolations of $_mK_2$ to infinite dilution; presumably they evaluated $_mK_2$ for each individual solution—as did Briegleb, Friedrichs, *et al.* (see Le Fèvre and Le Fèvre, *J.*, 1953, 4041, for references)—and then attempted graphical extrapolation. From our experience we suspect the main cause of differences from the results on the right of Table 10 to lie in this procedure.

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