Molecular Polarisability. The Electronic Anisotropy of the C_{Ar}–CF_3 Group

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Molar Kerr constants and apparent dipole moments at 25° are recorded for the molecules p-$XC_6H_4{\cdot}CF_3$ (X = H, F, Cl, CF_3), $C_6F_5{\cdot}CF_3$, and m-$C_6H_4{\cdot}(CX_3)_2$ (X = H, F) in carbon tetrachloride and the data have been analysed to provide the anisotropic electron polarisability for the C_{Ar}–CF_3 group. The results are compared with those for C_{Ar}–CX_3 (X = H, CH_3, Cl) for evidence of hyperconjugation.

PREVIOUSLY [1,2] we have investigated the mesomeric and hyperconjugative effects of C_{Ar}–CX_3 systems (X = H, Me, Cl). In this context the C_{Ar}–CF_3 group is of interest since there is much discussion in the literature [3] on the existence and magnitude of any interaction between this group and the benzene ring. We here report the anisotropic electron polarisability of the aromatic trifluoromethyl substituent.

EXPERIMENTAL

Materials, Apparatus, etc.—The solutes were dried and redistilled immediately before use; the b.p.s being in accord with literature values. Apparatus, techniques, and symbols used are given in refs. 4—6. Sulphur-free carbon

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tetrachloride was fractionated and dried with calcium chloride, the following solvent constants apply at 25°: $\varepsilon_1 = 2{\cdot}2270$; $d_1 = 1{\cdot}58454$; $(n_1)_D = 1{\cdot}4575$; $10^7(B_1)_D = 0{\cdot}083$; $10^{14}({}_{S}K_1) = 0{\cdot}894$. N.m.r. spectra were recorded at 40 °C on a Varian A60 spectrometer, tetramethylsilane being used as internal reference.

Previous Measurements.—Apart from *m*-xylene [7] and *p*-dichlorobenzene [8] the molar Kerr constants for these compounds have not previously been recorded as solutes in carbon tetrachloride, nor does McClellan [9] list their dipole moments in this solvent.

DISCUSSION

The determination of molecular polarisabilities b_1, b_2, and b_3 in the general case requires three equations (*e.g.* 22, 23, and 30 on pp. 44—47 of ref. 10) and from these molecular polarisabilities, bond or group polarisabilities b_L, b_T and b_V can be obtained.

Unfortunately light-scattering depolarisation data are available for relatively few simple molecules.[11] In certain cases this limitation may be overcome by choosing molecules of suitable symmetry. For bonds or groups, axial symmetry can sometimes be assumed in order to obtain the bond polarisability parameters.[2] The suitability of this assumption is then verified by the calculation of molar Kerr constants (${}_{m}K_{calc}$) for a similar molecule containing that bond or group and comparison with the observed value.

In previous work we have investigated hyperconjugative effects in C_{Ar}–CX_3 systems by making use of the principle that where there is no electronic interaction between the substituents and the phenyl group in substituted benzenes, then the observed molecular polarisabilities b_i should agree with those obtained by additivity of the isolated component bond and group semi-axes. We now suggest an alternative procedure for the estimation of the anisotropic group polarisabilities where the group is in an aromatic environment. In this approach the three equations used for their derivation are those involving (i) the total group polarisabilities ($b_L + b_T + b_V$) obtained from the electronic polarisation ${}_{E}P$ for the group, (ii) the observed molar Kerr constant ${}_{\infty}({}_{m}K_2)$ of the monosubstituted benzene, and (iii) the ${}_{\infty}({}_{m}K_2)$ value of the *meta*-disubstituted compound. The *meta*-compound is here chosen because it is polar and therefore has a θ_2 term (equation 26 of ref. 10) and further any mesomeric or spatial interaction is minimal.

Calculation of b_L, b_T, *and* b_V *for* C_{Ar}–Cl *and* C_{Ar}–CH_3.—The C_{Ar}–Cl and the C_{Ar}–CH_3 groups have been chosen to illustrate the above procedure because the group polarisability ellipsoid semi-axes have been previously estimated and shown to be reasonable parameters.[12] In the calculation of b_i(C_{Ar}–Cl) the following data are

TABLE 1

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

m-Xylene

10^5w_2	1647	3291	4050	5320	6656	9310
$10^{11}\Delta B$	163	304	371	485	607	835
$10^4\Delta\varepsilon$		82	102	135	170	231
$-10^5\Delta d$	2196	4314	5258	6841	8474	11,608
$10^4\Delta n$	13	27	30	40	49	69

whence $10^7\Delta B = 0{\cdot}951w_2 - 0{\cdot}73w_2^2$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}252$; $\Delta d = 1{\cdot}335w_2 + 0{\cdot}92w_2^2$; $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}075$

Trifluoromethylbenzene

10^5w_2	1085	1706	2164	2438	3172	3608
$10^{11}\Delta B$	1261	2035	2574	2927	3839	4402
$10^4\Delta\varepsilon$	875	1379	1750	1974	2562	2919
$-10^5\Delta d$	607	959	1245	1400	1817	2058
$-10^4\Delta n$	7	12	14	15	22	25

whence $10^7\Delta B = 11{\cdot}45w_2 + 20{\cdot}8w_2^2$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 8{\cdot}09$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}570$; $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}067$

Octafluorotoluene

10^5w_2	577	768	1005	1197	1943
$10^{11}\Delta B$	78	100	133	158	256
$10^4\Delta\varepsilon$	19	30	36	39	51
$-10^5\Delta d$	14	18	19	22	38
$-10^4\Delta n$	7	8	13	15	24

whence $\Sigma 10^7\Delta B/\Sigma w_2 = 1{\cdot}32$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}32$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}020$; $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}122$

p-Fluorotrifluoromethylbenzene

10^5w_2	793	1162	1613	2034	2460
$10^{11}\Delta B$	196	288	409	510	616
$10^4\Delta\varepsilon$	102	148	214	264	316
$-10^5\Delta d$	336	473	669	850	1026
$-10^4\Delta n$	7	11	15	18	22

whence $\Sigma 10^7\Delta B/\Sigma w_2 = 2{\cdot}50$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 1{\cdot}29$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}416$; $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}090$

p-Chlorotrifluoromethylbenzene

10^5w_2	1299	2351	3198	4252	5374	6362
$10^{11}\Delta B$	503	913	1245	1653	2100	2464
$10^4\Delta\varepsilon$	165	296	399	536	675	797
$-10^5\Delta d$	466	812	1073	1426	1783	2111
$-10^4\Delta n$	5	8	9	12	16	17

whence $\Sigma 10^7\Delta B/\Sigma w_2 = 3{\cdot}89$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 1{\cdot}26$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}336$; $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}029$

1,3-Bistrifluoromethylbenzene

10^5w_2	1560	2396	3504	3707	5728
$10^{11}\Delta B$	1096	1672	2442	2586	4006
$10^4\Delta\varepsilon$	804	1242	1821	1925	2976
$-10^5\Delta d$	505	757	1097	1150	1760
$-10^4\Delta n$	18	29	42	46	68

whence $\Sigma 10^7\Delta B/\Sigma w_2 = 6{\cdot}99$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 5{\cdot}19$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}312$; $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}120$

1,4-Bistrifluoromethylbenzene

10^5w_2	1046	1362	1916	2873	3022
$10^{11}\Delta B$		20	25	40	55
$-10^4\Delta\varepsilon$		30	43	60	63
$-10^5\Delta d$	276	436	616	921	965
$-10^4\Delta n$	9	16	25	35	36

whence $\Sigma 10^7\Delta B/\Sigma w_2 = 0{\cdot}15$; $\Sigma\Delta\varepsilon/\Sigma w_2 = -0{\cdot}22$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}315$; $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}118$

p-Dichlorobenzene

10^5w_2	1150	2047	3159	4230	5438	6597
$10^{11}\Delta B$	185	339	543	714	934	1133

whence $10^7\Delta B = 1{\cdot}66w_2 + 0{\cdot}95w_2^2$

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used: for chlorobenzene, $\mu = 1{\cdot}59$ D,[13] $10^{12}\,{}_{\infty}({}_{\mathrm{m}}K_2) = 137$,[14] ${}_{\mathrm{E}}P = 29{\cdot}87$ cm^3 [15] whence $\Sigma b_i = 35{\cdot}52$; * $b_{\mathrm{L}}(C_6H_5) = b_{\mathrm{T}}(C_6H_5) = 10{\cdot}50$, $b_{\mathrm{V}}(C_6H_5) = 6{\cdot}79$,[16] and $b_{\mathrm{L}}(\mathrm{CH}) = b_{\mathrm{T}}(\mathrm{CH}) = b_{\mathrm{V}}(\mathrm{CH}) = 0{\cdot}65$; [17] and for *m*-dichlorobenzene $\mu = 1{\cdot}41$ D and $10^{12}\,{}_{\infty}({}_{\mathrm{m}}K_2) = 64{\cdot}4$.[12] Applying the above data we have three simultaneous equations (1)—(3), where θ_1 and θ_2 have the usual significance.[10] Of

$$\Sigma b_i(\mathrm{C_{Ar}{-}Cl}) = \Sigma b_i(C_6H_5Cl) - \Sigma b_i(C_6H_5) \quad (1)$$

$$({}_{\mathrm{m}}K_2)(C_6H_5Cl) = 2\pi N(\theta_1 + \theta_2)/9 \quad (2)$$

$$({}_{\mathrm{m}}K_2)(m\text{-}C_6H_4Cl_2) = 2\pi N(\theta_1 + \theta_2)/9 \quad (3)$$

the four roots obtained by solving the resulting quartic equation for $b_{\mathrm{L}}(\mathrm{C_{Ar}{-}Cl})$ only one positive value is obtained. Substituting this value back into the above relationships yields b_{T} and b_{V} for the bond. The values thus obtained are $b_{\mathrm{L}}(\mathrm{C_{Ar}{-}Cl}) = 4{\cdot}23$, $b_{\mathrm{T}}(\mathrm{C_{Ar}{-}Cl}) = 1{\cdot}98$, and $b_{\mathrm{V}}(\mathrm{C_{Ar}{-}Cl}) = 1{\cdot}51$, which are in good agreement with the bond polarisability anisotropy obtained previously [11] ($b_{\mathrm{L}} = 4{\cdot}3$, $b_{\mathrm{T}} = 2{\cdot}0_5$, $b_{\mathrm{V}} = 1{\cdot}5$) from polarisation and light scattering. A similar procedure applied to toluene and *m*-xylene can be used for the $\mathrm{C_{Ar}{-}CH_3}$ group, [the relevant data needed: for toluene $\mu = 0{\cdot}37$ D, $10^{12}\,{}_{\infty}({}_{\mathrm{m}}K_2) = 13{\cdot}7$ and $\Sigma b_i = 35{\cdot}55$; [16] and for *m*-xylene $\mu = 0{\cdot}26$ D,[7] $10^{12}\,{}_{\infty}({}_{\mathrm{m}}K_2) = 12{\cdot}4$ (from Table 2)]. The results obtained, $b_{\mathrm{L}}(\mathrm{C_{Ar}{-}CH_3}) = 3{\cdot}39$, $b_{\mathrm{T}}(\mathrm{C_{Ar}{-}CH_3}) = 2{\cdot}04$ and $b_{\mathrm{V}}(\mathrm{C_{Ar}{-}CH_3}) = 2{\cdot}33$ are in close agreement with those earlier derived [16] ($b_{\mathrm{L}} = 3{\cdot}4$, $b_{\mathrm{T}} = 2{\cdot}0$, $b_{\mathrm{T}} = 2{\cdot}3$).

TABLE 2

Polarisations, refractions, dipole moments, and molar Kerr constants (from observations in carbon tetrachloride at 25°)

Solute	$\alpha\varepsilon$	β	γ	δ	${}_{\infty}P_2$/cm^3	R_{D}/cm^3	μ/D *	$10^{12}\,{}_{\infty}({}_{\mathrm{m}}K_2)$
m-Xylene	0·25	−0·843	0·05	11·5	38·7	36·3		12·4
Trifluoromethylbenzene	8·09	−0·360	−0·05	137·9	161·7	31·1	2·52	177
Octafluorotoluene	0·32	−0·013	−0·08	15·9	51·8	32·5	0·93	36
p-Fluorotrifluoromethylbenzene	1·29	−0·263	−0·06	30·2	60·5	30·8	1·17	45
p-Chlorotrifluoromethylbenzene	1·26	−0·212	−0·02	46·8	64·1	35·9	1·14	77
1,3-Bistrifluoromethylbenzene	5·19	−0·197	−0·08	84·2	164·6	35·7	2·49	159
1,4-Bistrifluoromethylbenzene	−0·22	−0·198	−0·08	1·8	39·8	35·7		4·8
p-Dichlorobenzene	0·28 †	−0·225 †	−0·08 †	20·0	37·4 †	36·4 †		27·6

* Calculated on the basis of ${}_{\mathrm{D}}P = 1{\cdot}05\,R_{\mathrm{D}}$. † From ref. 20.

TABLE 3

Calculated molecular polarisabilities and molar Kerr constants for *p*-xylene, *p*-dichlorobenzene, and *p*-chlorotoluene

	b_1 (calc.)	b_2 (calc.)	b_3 (calc.)	$10^{12}\,{}_{\mathrm{m}}K$ (calc.)	$10^{12}\,{}_{\mathrm{m}}K$ (obs.)
p-$C_6H_4Me_2$	16·63	13·93	10·80	12·3	10·8 [a]
p-$C_6H_4Cl_2$	18·31	13·81	9·16	31	28
p-ClC_6H_4Me	17·48	13·89	9·99	237	237 [b]

[a] From ref. 12. [b] From ref. 1.

Table 3 summarises the results of calculations for the molar Kerr constants of *p*-xylene, *p*-dichlorobenzene, and *p*-chlorotoluene using the above group polarisability parameters together with those for the phenyl group listed earlier. In each case the agreement between calculated and observed values is better than those obtained hitherto.[1,8,16]

Calculation of b_{L}, b_{T} *and* b_{V} *for the* $\mathrm{C_{Ar}{-}CF_3}$ *Group*.—Using an analogous equation to (1) $\Sigma b_i(\mathrm{C_{Ar}{-}CF_3})$ is larger than estimates obtained from similar considerations of *p*-fluoro-, *p*-chloro-, *m*- and *p*-trifluoromethyltrifluoromethylbenzene. It would appear that there is an added polarisability of this group in trifluoromethylbenzene. This exaltation of polarisability ($0{\cdot}3 \times 10^{-24}$ cm^3) arising from mesomeric interactions can be readily obtained from $\Sigma b_i(\mathrm{C_{Ar}{-}CF_3})$ observed minus $\Sigma b_i(\mathrm{C_{Ar}{-}CF_3})$ calculated.

Application of the data for trifluoromethylbenzene and 1,3-bistrifluoromethylbenzene from Table 2 yields $b_{\mathrm{L}}(\mathrm{C_{Ar}{-}CF_3}) = 2{\cdot}6$, $b_{\mathrm{T}}(\mathrm{C_{Ar}{-}CF_3}) = 2{\cdot}5$, and $b_{\mathrm{V}}(\mathrm{C_{Ar}{-}CF_3}) = 2{\cdot}2$. The ${}_{\mathrm{m}}K$ values calculated using these values together with the observed quantities are listed in Table 4.

TABLE 4

Calculated molecular polarisabilities and molar Kerr constants for molecules p-$XC_6Y_4{\cdot}CF_3$ in carbon tetrachloride solutions

X	Y	b_1 (calc.)	b_2 (calc.)	b_3 (calc.)	$10^{12}\,{}_{\mathrm{m}}K$ (calc.)	$10^{12}\,{}_{\mathrm{m}}K$ (obs.)
CF_3	H	15·0	14·9	10·5$_5$	9·7	4·8
Cl	H	16·7	14·3$_5$	9·8$_5$	84	77
F	H	13·2$_5$ [a]	13·1$_5$ [a]	8·6$_5$ [a]	46	45
F	F	13·1 [b]	13·5 [b]	7·8$_5$ [b]	38	36

[a] Calc. using $b_i(\mathrm{C_{Ar}{-}F})$ from ref. 11. [b] Calc. using $b_{\mathrm{L}}(C_6F_5) = 11{\cdot}16$, $b_{\mathrm{T}}(C_6F_5) = 11{\cdot}64$, $b_{\mathrm{V}}(C_6F_5) = 6{\cdot}29$, M. J. Aroney, G. Cleaver, and R. J. W. Le Fèvre, unpublished data.

For the $\mathrm{C_{Ar}{-}CH_3}$ group our calculations give $b_{\mathrm{T}} < b_{\mathrm{V}}$, whereas for $\mathrm{C_{Ar}{-}CF_3}$ (where negative hyperconjugation has been postulated) show $b_{\mathrm{T}} > b_{\mathrm{V}}$. This is to be compared with our earlier results [2] for $\mathrm{C_{Ar}{-}CMe_3}$ and $\mathrm{C_{Ar}{-}CCl_3}$ where the assumption that $b_{\mathrm{T}} = b_{\mathrm{V}}$ was satisfactory. If hyperconjugation were to exist to some extent we would expect this to be displayed in the

* The polarisability semi-axes of bonds or groups b_{L}, b_{T}, or b_{V} or of molecules b_1, b_2, or b_3 are quoted throughout in 10^{-24} cm^3 units.

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relative magnitude of b_T to b_V. Kostelnik *et al.*[18] from an n.m.r. study of trifluoromethylbenzene state that the hyperconjugation of the $-CF_3$ group with the aromatic ring is, if not equal, at least comparable (or complementary) to that of the $-CH_3$ group, while Grynkiewicz *et al.*[19] conclude (from a kinetic study) that the $-CCl_3$ group is a substituent without significant hyperconjugative interaction with the ring. Hence it would appear that the sign of $b_V - b_T$ of the group $C_{Ar}-CX_3$ may be an indicator of the type and degree of hyperconjugation.

Trifluoromethylbenzene in Benzene Solution.—Trifluoromethylbenzene has also been studied in benzene solution [$10^{12}{}_{\infty}({}_{m}K_2) = +206$,[20] $10^{12}{}_{\infty}({}_{m}K_2) = +215$ [6]]. Further, the ^1H n.m.r. spectrum for this solute in C_6D_6 shows all the peaks have been shifted up field relative to those in the spectrum with CCl_4 as solvent. This finding is in accord with those of Kostelnik *et al.*[18] for trifluoromethylbenzene, neat liquid (which corresponds to an aromatic environment) and in carbon tetrachloride solution. These results can be attributed to stereospecific solute–solvent interactions [14] involving transient complexes having parallel arrangement of the aromatic rings.

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