Molecular Polarisability. The Anisotropy of the C_{ar}–F Group

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Electric dipole moments and molar Kerr constants are reported for the following fluoroaromatic compounds examined as solutes in cyclohexane: fluorobenzene, 1,2-, 1,3-, and 1,4-difluorobenzene, 1,3,5-trifluorobenzene, 1,2,3,4- and 1,2,4,5-tetrafluorobenzene, pentafluorobenzene, hexafluorobenzene, and octafluoronaphthalene. The data are analysed to specify the anisotropic electron polarisabilities for the molecules and for the C_{ar}–F grouping.

We are currently investigating the conformational preferences of a series of substituted fluoroaromatic compounds in order to gauge the effects of non-bonded interactions involving fluorine atoms. The electro-optical Kerr effect, in particular, may be used to obtain such information. However, a necessary precursor to an analysis of this physical property is the specification of the anisotropic polarisabilities of component groups within the molecular system.[1] This paper is concerned primarily with the measurement of the molar Kerr constants and electric dipole moments of ten fluoroaromatic compounds of fixed geometry and the derivation from this data of polarisability semi-axes for the molecules and for the C_{ar}–F grouping.

EXPERIMENTAL

Materials, Apparatus, etc.—The solutes were purified immediately before use to give: fluorobenzene, b.p. 85°; 1,2-difluorobenzene, b.p. 93°; 1,3-difluorobenzene, b.p. 82°; 1,4-difluorobenzene, b.p. 88·5°; 1,3,5-trifluorobenzene, b.p. 77°; 1,2,3,4-tetrafluorobenzene, b.p. 90·5°; 1,2,4,5-tetrafluorobenzene, b.p. 89°; pentafluorobenzene, b.p. 85°; hexafluorobenzene, b.p. 80°; octafluoronaphthalene, m.p. 88°. Cyclohexane, as solvent, was dried over sodium, distilled, and then stored with fresh sodium. The following constants apply for the solvent at 25°: $\varepsilon_1 = 2{\cdot}0199$, $d_1 = 0{\cdot}77389$, $(n_1)_D = 1{\cdot}4235$, $10^7(B_1)_D = 0{\cdot}054$, $10^{14}({}_sK_1) = 1{\cdot}35$. The apparatus, techniques, symbols used, and methods of calculation have been described before.[2-5] The experimental results are summarised in Table 1.

DISCUSSION

From the experimental molecular refractions in column 8 of Table 1, the C_{ar}–F group refractivity may be derived by subtraction of the appropriate number of C_{ar}–C_{ar} and C–H bond equivalents[6] (2·688 and 1·676

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cm^3, respectively), for each of the nine fluorobenzenes examined. The mean value for R_D (C_{ar}–F) is 1·58 cm^3 which is a little higher than that (1·48 cm^3) extracted by Vogel *et al.*[6] from the pure liquid refractivity of fluorobenzene. Refractivity dispersion data are not available for many of these substances and evaluation of the molecular electron polarisations ${}_{\mathrm{E}}P$ as $[R]_\infty$ and hence of ${}_{\mathrm{E}}P(C_{ar}\text{–F})$ is not always possible. We assume in this work that for the C_{ar}–F group ${}_{\mathrm{E}}P = 0{\cdot}95\ [R]_{\mathrm{D}} = 1{\cdot}50$ cm^3 (*cf.* the molecular refractivity data of ref. 7 for fluorobenzene and the difluorobenzenes which yield a mean $[R]_\infty : [R]_{\mathrm{D}}$ ratio of 0·96). It follows that the sum of the polarisability semi-axes [*] $\Sigma b_i(C_{ar}\text{–F})$ is 1·78 Å^3. The molecular Σb values obtained by additivity of the component group parameters using $\Sigma b_i(C_6H_6) = 29{\cdot}75$[8] and Σb_i(C–H) = 1·95,[9] are as follows: 29·58 (fluorobenzene), 29·41 (difluorobenzene), 29·24 (trifluorobenzene), 29·07 (tetrafluorobenzene), 28·90 (pentafluorobenzene, and 28·73 (hexafluorobenzene).

TABLE 1

Polarisations, refractions, dipole moments, and molar Kerr constants (from observations on cyclohexane solutions at 25°)

Solute	Concentration range $10^5 w_2$	$\alpha\varepsilon_1$ *	β *	γ *	δ *	${}_\infty P_2$/cm^3	R_D/cm^3	μ/D †	$10^{12}{}_\infty({}_{\mathrm{m}}K_2)$ ‡
Fluorobenzene	501—3395	2·04	0·211	−0·010	51·3	71·9	25·9	1·48	66·0
1,2-Difluorobenzene	281—4018	4·77	0·303	−0·004	122	157	25·8	2·51	184
1,3-Difluorobenzene	560—3883	1·69	0·292	−0·003	45·7	72·8	26·2	1·49	70·0
1,4-Difluorobenzene	629—5119	0·09	0·304	−0·002	5·85	28·6	26·0	0	10·0
1,3,5-Trifluorobenzene	707—4744	0·026	0·348	−0·017	6·17	29·1	26·2	0	12·1
1,2,3,4-Tetrafluorobenzene	1015—4037	3·26	0·417	−0·022	87·5	146	25·5	2·41	174
1,2,4,5-Tetrafluorobenzene	1272—4669	0·029	0·407	−0·026	6·50	30·2	25·6	0	14·3
Pentafluorobenzene	1027—5028	0·91	0·438	−0·029	28·3	67·7	26·4	1·40	64·3
Hexafluorobenzene	1515—8666	−0·063	0·479	−0·033	5·74	29·0	26·0	0	15·8
Octafluoronaphthalene	907—3869	0·085	0·519	0·005	16·2	48·4	44·5	0	61·0

* Incremental changes in the dielectric constants, densities, refractive indices, and Kerr constants ($\Delta\varepsilon$, Δd, Δn, and ΔB, respectively) were measured for solutions having solute weight fractions w_2. The coefficients, $\alpha\varepsilon_1$, β, γ, and δ, were derived from the relations: $\alpha\varepsilon_1 = \Sigma\Delta\varepsilon/\Sigma w_2$; $\beta = \Sigma\Delta d/d_1\Sigma w_2$; $\gamma = \Sigma\Delta n/n_1\Sigma w_2$; $\delta = \Sigma\Delta B/B_1\Sigma w_2$. In the case of 1,2,3,4-tetrafluorobenzene, the variation of B_{12} with w_2 was non-linear over the concentration range studied and the experimental ΔB values were fitted to a regression equation of the form $\Delta B = aw_2 + bw_2^2$; subsequent extrapolation to $w_2 = 0$ resulted in the coefficient δ here recorded for this solute. † Calculated on the basis that ${}_{\mathrm{D}}P = 1{\cdot}05\ R_{\mathrm{D}}$. ‡ The term ${}_\infty({}_{\mathrm{m}}K_2)$ refers to the solute molar Kerr constant at infinite dilution.

The Anisotropic Polarisabilities of 1,3,5-*Trifluorobenzene and of Hexafluorobenzene*.—For each of these molecules the ellipsoid of polarisability is one of revolution with $b_1 = b_2 \neq b_3$ where b_1 and b_2 are the in-plane polarisabilities. Since the sum $2b_1 + b_3$ is known, b_1 can, in each case, be expressed in terms of b_3 and substitution into the modified Langevin–Born equation (1)

$${}_{\mathrm{m}}K = 4\pi N\,{}_{\mathrm{D}}P(b_1 - b_3)^2/405kT\,{}_{\mathrm{E}}P \qquad (1)$$

appropriate for an axially symmetric, non-polar molecule leads to a quadratic equation in b_3. The solutions are shown in Table 2. The term ${}_{\mathrm{D}}P$ refers to the distortion polarisation which for these substances is equal to the measured ${}_\infty P_2$. For each molecule two sets of molecular polarisabilities are mathematically possible. However, those listed in columns 3 and 5 of Table 2 appear highly improbable (see the footnotes to Table 2). Further, they lead to impossibly large estimates of the vertical polarisability of the C_{ar}–F bond. In the calculations we use the benzene polarisability semi-axes given in Table 2 together with the C–H bond parameters b_{L}(C–H) = b_{T}(C–H) = b_{V}(C–H) = 0·65 (from ref. 9). The two independent determinations of $b_{\mathrm{V}}(C_{ar}\text{–F})$ are in reasonable accord yielding a mean value of 0·35 (± 0·03). Le Fèvre and Rao[10] reported an estimate of $b_{\mathrm{V}}(C_{ar}\text{–F})$ of 0·3 from measurements of the depolarisation ratio of transverse scattered light for fluorobenzene (in carbon tetrachloride) using a molar Kerr constant of $56{\cdot}8 \times 10^{-12}$ (from ref. 11).

TABLE 2

Polarisability semi-axes of 1,3,5-trifluorobenzene and hexafluorobenzene

	$C_6H_3F_3$		C_6F_6	
$b_1 = b_2$	11·38	8·10 *	11·45	7·70 †
b_3	6·46	13·02 *	5·83	13·32 †
$b_{\mathrm{V}}(C_{ar}\text{–F})$	0·32	2·51	0·38	1·63
$b_{\mathrm{L}}(C_{ar}\text{–F}) + b_{\mathrm{T}}(C_{ar}\text{–F})$	1·46	−0·73	1·40	0·15

* These values are highly unlikely; the group C_6H_3 alone has $b_{\mathrm{L}} = b_{\mathrm{T}} = 9{\cdot}20$, $b_{\mathrm{V}} = 5{\cdot}49$ (ref. 8). † These estimates are also improbable; *cf.* $b_1(C_6H_6) = b_2(C_6H_6) = 11{\cdot}15$, $b_3(C_6H_6) = 7{\cdot}44$ (ref. 8).

Specification of the Longitudinal and Transverse Polarisabilities of the C_{ar}–F *Group*.—For the fluorobenzenes which have a lower than C_3 symmetry, $b_1 \neq b_2 \neq b_3$ and three equations are required to evaluate the semi-axes for each molecule. Since scattered light data are not available (except for fluorobenzene[10]), we adopt the alternative procedure of calculating the molecular b_3 polarisability in each case by additivity of the appropriate group polarisability vertical components quoted earlier. This reduces the unknowns for each molecule to b_1 and b_2 and since the sum $b_1 + b_2 + b_3$ is

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[*] Polarisability semi-axes of bonds and groups b_{L}, b_{T}, or b_{V} or of molecules b_1, b_2, or b_3 are quoted throughout in Å^3 units.

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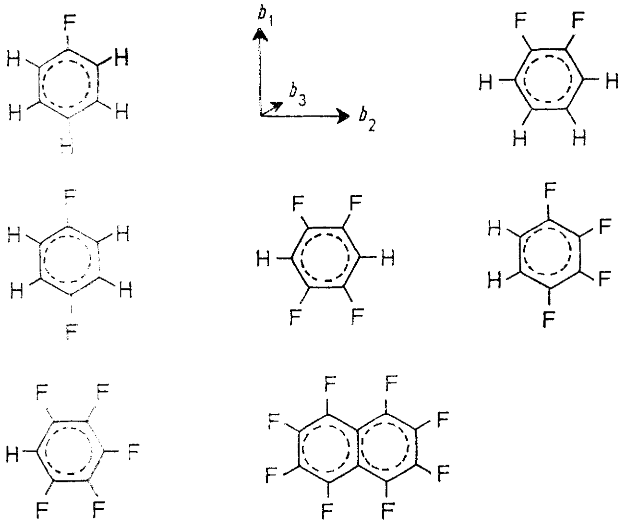
known, b_1 can be expressed in terms of b_2. Substitution for b_1 and b_3 in equation (2) results in a quadratic

$${}_{\mathrm{m}}K = 2\pi N\{{}_{\mathrm{D}}P[(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2]/405kT_{\mathrm{E}}P + [(\mu_1^2 - \mu_2^2)(b_1 - b_2) + (\mu_2^2 - \mu_3^2)(b_2 - b_3) + (\mu_3^2 - \mu_1^2)(b_3 - b_1)]/405k^2T^2\} \qquad (2)$$

equation in b_2, the solution of which yields the two mathematically possible sets of molecular in-plane polarisabilities listed in Table 3. The terms μ_1, μ_2, and μ_3 refer to the vector components of the permanent electric moment along the principal axes. The locations of these axes are indicated as b_1, b_2, and b_3, respectively, in the Figure. The ratios ${}_{\mathrm{D}}P : {}_{\mathrm{E}}P$ were taken as 1·1 throughout. The solutions b_1 and b_2 thus obtained are shown in columns 2 and 3, respectively, of Table 3. Column 4 lists the corresponding b_3 values derived by calculation. In the case of 1,3-difluorobenzene the equation could not be solved to give real roots for b_1 and b_2. Columns 5 and 6 contain the C_{ar}–F longitudinal and transverse polarisability semi-axes derived from the molecular b_1 and b_2 values in that row (assuming 120° angles about the benzene carbon atoms). With fluorobenzene, 1,2-difluorobenzene, and pentafluorobenzene, the alternative solutions shown in the second row can clearly be discounted and a unique set of molecular b_i values, and thence $b_i(C_{ar}\text{–F})$ estimates, is obtained for each molecule. In all three cases $b_{\mathrm{L}}(C_{ar}\text{–F}) > b_{\mathrm{T}}(C_{ar}\text{–F})$. The C_{ar}–F bond polarisabilities in columns 5 and 6 which are italicised best provide a consistent set of data for the series of model compounds examined. The mean values are: $b_{\mathrm{L}}(C_{ar}\text{–F}) = 0·94$ and $b_{\mathrm{T}}(C_{ar}\text{–F}) = 0·49$; the standard deviation is $\pm 0·11$. The six individual estimates of b_{L} and b_{T} are in fair, though by no means perfect, accord with each other. This is not surprising as they are extracted from the molecular parameters as relatively small quantities in combination with the larger polarisability tensor components of the aromatic C_6 grouping. We note also that the polarisability anisotropy now reported for C_{ar}–F is greater than that previously published; *cf.* $b_{\mathrm{L}}(C_{ar}\text{–F}) = b_{\mathrm{T}}(C_{ar}\text{–F}) = 0·8$, $b_{\mathrm{V}}(C_{ar}\text{–F}) = 0·3$, from ref. 10. Finally we apply our C_{ar}–F bond polarisabilities to a test situation in which they are used to calculate molecular polarisability semi-axes and thence the molar Kerr constant of octafluoronaphthalene. The b_i values for naphthalene[8] are $b_1 = 16·60$, $b_2 = 21·80$, $b_3 = 11·30$; the locations of b_i are shown in the Figure. Assuming 120° angles about each carbon atom, we calculate for octafluoronaphthalene $b_1 = 17·57$, $b_2 = 21·87$, $b_3 = 8·90$, and ${}_{\mathrm{m}}K(\mathrm{calc}) = 64 \times 10^{-12}$; the latter is in reasonable agreement with the experimental ${}_{\infty}({}_{\mathrm{m}}K_2)$ value of $61·0 \times 10^{-12}$.



FIGURE

TABLE 3

Molecular and C_{ar}–F group polarisabilities

	b_1	b_2	b_3	$b_{\mathrm{L}}(C_{ar}\text{–F})$	$b_{\mathrm{T}}(C_{ar}\text{–F})$
Fluorobenzene	11·44	10·99	7·14	*0·94*	*0·49*
	−13·22	35·65	7·14	−23·72	25·15
1,2-Difluorobenzene	11·47	11·09	6·84	*0·91*	*0·52*
	−58·52	81·08	6·84	−69·09	70·52
1,4-Difluorobenzene	11·59	10·97	6·84	*0·87*	*0·56*
	10·97	11·59	6·84	0·56	0·87
1,2,4,5-Tetrafluoro-	12·18	10·64	6·24	*1·10*	*0·33*
benzene	10·64	12·18	6·24	0·33	1·10
1,2,3,4-Tetrafluoro-	11·47	11·35	6·24	*0·78*	*0·65*
benzene	11·35	11·47	6·24	0·65	0·78
Pentafluorobenzene	11·82	11·13	5·94	*1·05*	*0·38*
	32·79	−9·84	5·94	22·03	−20·60

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