Molecular Polarisability. The Conformations of Some Substituted Pentafluorobenzenes

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Electric dipole moments and molar Kerr constants are reported for molecules C_6F_5R (R is CH_3, OH, NH_2, CHO, $COCH_3$, OCH_3, SCH_3, or CH_2CN), examined as solutes in cyclohexane at 25°. The experimental data are analysed to deduce the preferred solution state conformations.

THIS paper is concerned with the application of considerations of polarity and polarisability to determining the preferred solution state conformations of the fluoroaromatic compounds C_6F_5R (R = OH, NH_2, CHO, $COCH_3$, OCH_3, SCH_3, or CH_2CN). The degree of deflection of the groups R from the resonance favoured ' planar ' form is determined and comparison is made in each case with the corresponding C_6H_5R compounds.

EXPERIMENTAL

Materials, Apparatus, etc.—The solutes were commercial samples which were purified immediately before use; their purity was checked by g.l.c. Cyclohexane was fractionated and stored over sodium wire. The apparatus, techniques, symbols used, and methods of calculation have been described before.[1-3] The experimental results are summarised in Table 1. The dipole moments (μ) and molar Kerr constants (${}_{\mathrm{m}}K$) are expressed in S.I. units throughout. The conversion factors from the electrostatic (c.g.s., e.s.u.) system are respectively: 1 C m = 0.299 8 × 10^{30} D, 1 m^5 V^{-2} mol^{-1} = 0.898 8 × 10^{15} e.s.u. mol^{-1}.

DISCUSSION

Our procedure is to choose suitable molecule-fixed orthogonal axes, x,y,z and to specify the molecular polarisability tensor for a particular structure by transforming the known bond and group polarisability components into this axis system.[4] The polarisability parameters used in the calculations are shown in Table 2. For all molecules studied, refractivity exaltations ΔR_D, estimated as R_D (observed) $-R_D$ (calculated by addi-

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[1] R. J. W. Le Fèvre and D. J. Millar, *Chem. and Ind.*, 1971, 399.

[2] R. J. W. Le Fèvre and G. L. D. Ritchie, *J. Chem. Soc.*, 1963, 4933.

[3] C. G. Le Fèvre and R. J. W. Le Fèvre, ' The Kerr Effect,' in ' Techniques of Chemistry,' ed. A. Weissberger, Wiley–Interscience, New York, 1972, vol. I, part IIIC, ch. VI, p. 399.

[4] R. J. W. Le Fèvre, *Adv. Phys. Org. Chem.*, 1965, **3**, 1.

tivity of the refractivities [5,12-14] of the component bonds and groups of Table 2) were zero or near zero except for pentafluorobenzaldehyde which had ΔR_D 1.0 cm^3, and hence a polarisability correction Δb_{xx} of 1.3 (polarisabilities are expressed throughout as $10^{40}b$/C m^2 V^{-1}).

TABLE 1

Molar polarisations and 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	$10^{30}\mu$/ C m †	$10^{27}{}_\infty({}_mK_2)$/ m^5 V^{-2} mol^{-1} ‡
Pentafluorotoluene	882—2 272	1.81	0.416	−0.029	72.2	114.1	29.9	6.70	196
Pentafluorophenol	634—3 284	2.05	0.488	−0.022	68.1	121.3	27.0	7.11	186
Pentafluoroaniline	1 018—4 521	4.02	0.478	−0.004	156	207.8	30.7	9.77	423
Pentafluoro-benzaldehyde	999—5 104	1.36	0.478	−0.009	35.5	97.5	32.0	5.90	103
Pentafluoro-acetophenone	1 330—4 809	2.30	0.445	−0.014	−35.6	154.3	35.5	7.97	−113
Pentafluoroanisole	1 042—4 639	2.18	0.445	−0.020	42.3	139.6	32.3	7.57	124
Pentafluorothioanisole	439—2 614	1.63	0.443	0	35.2	122.8	39.3	6.67	112
Pentafluorobenzyl cyanide	698—3 093	4.06	0.453	−0.016	−114	238.7	34.1	10.5	−357

* Incremental changes in the relative permittivities, 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: $\alpha\varepsilon_1 = \Sigma\Delta\varepsilon/\Sigma w_2$; $\beta = \Sigma\Delta d/d_1\Sigma w_2$; $\gamma = \Sigma\Delta n/n_1\Sigma w_2$; $\delta = \Sigma\Delta B/B_1\Sigma w_2$. † Calculated on the basis that $_DP = 1.05\ R_D$. ‡ The term $_\infty({}_mK_2)$ refers to the solute molar Kerr constant at infinite dilution.

The molar Kerr constant predicted for each geometric form of a molecule was calculated [4] by substitution of the elements of the molecular polarisability matrix b_{xx}, b_{yy}, *etc.* into the Langevin–Born equations (1)—(3) together with μ_x, μ_y, and μ_z, the resolved parts of the permanent molecular dipole moment vector along x, y, and z respectively; the ratio $_DP : {}_EP$, *i.e.* distortion polarisation : electron polarisation, was taken as 1.1 throughout.

$$_mK = \mathrm{N}(\theta_1 + \theta_2)/18\epsilon_0 \qquad (1)$$

$$\theta_1 = {}_DP[(b_{xx} - b_{yy})^2 + (b_{yy} - b_{zz})^2 + (b_{zz} - b_{xx})^2 + 6(b_{xy}{}^2 + b_{xz}{}^2 + b_{yz}{}^2)]/45kT_EP \qquad (2)$$

$$\theta_2 = [\mu_x{}^2(2b_{xx} - b_{yy} - b_{zz}) + \mu_y{}^2(2b_{yy} - b_{xx} - b_{zz}) + \mu_z{}^2(2b_{zz} - b_{xx} - b_{yy}) + 6(b_{xy}\mu_x\mu_y + b_{xz}\mu_x\mu_z + b_{yz}\mu_y\mu_z)]/45k^2T^2 \qquad (3)$$

N is Avogadro's number; ε_0 is the permittivity of a vacuum.

Pentafluorotoluene.—The polarisability parameters for the pentafluorophenyl group were tested with pentafluorotoluene which, for our purposes, is conformationally unambiguous. The polarisability semi-axes calculated from $b_i(C_6F_5)$ and $b_i(C_{ar}$–$CH_3)$ are $b_{xx} = 15.44$, $b_{yy} = 14.66$, and $b_{zz} = 8.45$ where x lies along the C_{ar}–C bond axis and z is perpendicular to the aromatic ring plane. The off-diagonal elements are zero. We have also $\mu_x = 6.70$, $\mu_y = \mu_z = 0$. Substitution into equations (1)—(3) leads to a theoretical $_mK(C_6F_5CH_3)$ of 194 × 10^{-27} in very good agreement with the experimental value of 196 × 10^{-27}.

Conformations of Molecules C_6F_5R (R = OH, NH_2, CHO, $COCH_3$, OCH_3, SCH_3, CH_2CN).—For each molecule C_6F_5R molar Kerr constants were calculated for conformations defined by dihedral angles ϕ within the range $0° \leqslant \phi \leqslant 90°$, where $\phi = 0°$ corresponds to the resonance favoured 'planar' model (except for $C_6F_5NH_2$ where $\phi = 0°$ describes the conformer having the H $\cdots$ H line parallel to the aromatic ring plane).

TABLE 2

Anisotropic polarisabilities of bonds and groups (expressed as $10^{40}b$/C m^2 V^{-1})

	b_L	b_T	b_V	Ref.
C_6F_5	11.66	12.43	5.89	5
C_{ar}–CH_3	3.78	2.23	2.56	6
C–O	0.99	0.51	0.51	4
O–H	1.06	0.56	0.56	7
C_{ar}–NH_2	4.73	1.28	1.56	8
C=O	2.56	1.56	0.51	4
C–C	1.08	0.29	0.29	9
C–H	0.72	0.72	0.72	9
C_{ar}–S	5.27	0.67	1.18	10
C–S	2.09	1.88	1.88	4
C–CN	4.05	1.95	1.95	11

Regular angles (110 or 120°) were assumed about the central atoms of R; the overall molecular polarisability anisotropy is insensitive to variations in these angles. The $_mK$(calc.) values can, however, be sensitively dependent on the direction of action of the permanent electric dipole moment within the molecular framework. In each case the location of μ was obtained by vector analysis on the basis that μ(observed) for C_6F_5R is the

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[5] M. J. Aroney, G. Cleaver, R. K. Pierens, and R. J. W. Le Fèvre, *J.C.S. Perkin II*, 1974, 3.

[6] M. J. Aroney, K. E. Calderbank, R. J. W. Le Fèvre, and R. K. Pierens, *J. Chem. Soc.* (*B*), 1969, 159.

[7] C. G. Le Fèvre, R. J. W. Le Fèvre, B. Purnachandra Rao, and A. J. Williams, *J. Chem. Soc.*, 1960, 123.

[8] M. J. Aroney, K. E. Calderbank, R. J. W. Le Fèvre, and R. K. Pierens, *J. Chem. Soc.* (*B*), 1968, 561.

[9] C. L. Cheng, I. G. John, G. L. D. Ritchie, and P. H. Gore, *J.C.S. Perkin II*, 1974, 1318.

[10] M. J. Aroney, G. M. Hoskins, and R. J. W. Le Fèvre, *J. Chem. Soc.* (*B*), 1968, 1206.

[11] R. J. W. Le Fèvre, G. L. D. Ritchie, and P. J. Stiles, *J. Chem. Soc.* (*B*), 1967, 819.

[12] A. I. Vogel, W. T. Cresswell, G. H. Jeffery, and J. Leicester, *J. Chem. Soc.*, 1952, 514.

[13] R. J. W. Le Fèvre, B. J. Orr, and G. L. D. Ritchie, *J. Chem. Soc.*, 1965, 2499.

[14] M. J. Aroney, R. J. W. Le Fèvre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc.* (*B*), 1968, 507.

vector sum of $\mu(C_6H_5R)$[14-20] and a component μ', directed along the 1,4-axis and into the aromatic ring, which in turn is the sum of the p-C_{ar}–F group moment and μ(interaction), the latter arising mainly from electromeric interactions between the substituent groups. Theoretical ${}_{m}K$ values for the conformations $\phi = 0$ and 90° are shown in Table 3. Column 4 of this Table lists the dihedral angles for which agreement between theoretical and experimental ${}_{m}K$ values is achieved. In the case of pentafluoro-benzaldehyde and -acetophenone alternative determinations of the electric moment direction were made assuming that μ(observed) is composed of μ(pentafluorobenzene)[5] and a second vector component μ'' directed along the $\overrightarrow{C=O}$ bond axis. The estimates of ${}_{m}K$(calc.) and ϕ shown in Table 3 for each of these two molecules are mean values; the uncertainty in the location of μ results in a $\pm 4°$ error contribution to the overall uncertainty in each ϕ. Trial calculations were made with the other molecules C_6F_5R to gauge the effect on ϕ of possible μ locations; this constitutes the major component of the error estimates specified in Table 3. In column 5 of this table are listed for comparison the ϕ estimates previously derived for the analogous C_6H_5R molecules. The present results indicate restricted rotation of the R groups in C_6F_5R; the ϕ values describe the preferred time-averaged conformations.

Pentafluorophenol and pentafluoroaniline, in common with the non-fluorinated analogues, exist as solutes in the resonance favoured ϕ *ca.* 0 forms; such conformers are possibly stabilised in the case of C_6F_5OH and $C_6F_5NH_2$ by hydrogen-bond formation with the *o*-fluoro-groups. With molecules C_6F_5R, where R is OCH_3, SCH_3, or CH_2CN, the apparent dihedral angles ϕ are in each case substantially greater than for the corresponding C_6H_5R molecules clearly indicating the greater steric–electrostatic repulsiveness of F over H *with respect to these groups*. The deflection of the formyl and acetyl groups away from the aromatic ring plane in C_6F_5CHO and $C_6F_5COCH_3$ may be attributed to coulombic repulsions between the highly electronegative oxygen and fluorine atoms, to methyl–fluorine steric repulsions in the case of $C_6F_5COCH_3$, and to lower resonance energies, relative to the C_6H_5R compounds, through inductive drain of π-electrons by fluoro-substituent groups.

TABLE 3

Calculated molar Kerr constants and conformations ϕ for molecules C_6F_5R

	$10^{27}\,{}_{m}K$(calc.)/$m^5\,V^{-2}\,mol^{-1}$			
R	$\phi = 0°$	$\phi = 90°$	$\phi°(C_6F_5R)$	$\phi°(C_6H_5R)$
OH	199	−59	*ca.* 0 [a]	*ca.* 0 [b]
NH_2	431	542	*ca.* 0 [a]	0 [c]
CHO	181	−154	28 ± 6	0 [d]
$COCH_3$	341	−269	58 ± 7	0 [d]
OCH_3	185	48	47 ± 5	*ca.* 18 [e]
SCH_3	240	80	64 ± 5	*ca.* 23 [f]
CH_2CN	512	−524	68 ± 4	*ca.* 32 [g]

[a] The rate of change of ${}_{m}K$(calc.) is slow in the range 0—*ca.* 12° so it may be concluded that ϕ is zero or near zero (*i.e.* <12°). [b] Ref. 21. [c] Ref. 14. [d] Ref. 16. [e] Ref. 22. [f] Ref. 19. [g] Ref. 20.

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[15] J. B. Bentley, K. B. Everard, R. J. B. Marsden, and L. E. Sutton, *J. Chem. Soc.*, 1949, 2957.

[16] P. H. Gore, P. A. Hopkins, R. J. W. Le Fèvre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc. (B)*, 1971, 120.

[17] E. V. Goode and D. A. Ibbitson, *J. Chem. Soc.*, 1960, 4265.

[18] M. J. Aroney, M. G. Corfield, and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1964, 2954.

[19] M. J. Aroney, R. J. W. Le Fèvre, R. K. Pierens, and M. G. N. The, *J. Chem. Soc. (B)*, 1971, 1132.

[20] R. J. W. Le Fèvre, B. J. Orr, and G. L. D. Ritchie, *J. Chem. Soc.*, 1965, 3619.

[21] R. J. W. Le Fèvre and A. J. Williams, *J. Chem. Soc.*, 1960, 1825.

[22] M. J. Aroney, R. J. W. Le Fèvre, R. K. Pierens, and M. G. N. The, *J. Chem. Soc. (B)*, 1969, 666.