Electric Dipole Moments of Some Tetra- and Penta-fluorobenzenes

By **Hsing Hua Huang,** Chemistry Department, University of Singapore, Singapore 10

The mutual electronic interactions between electron-withdrawing and -releasing substituents and the penta- and 2,3,5,6-tetra-fluorophenyl systems are evaluated from the electric dipole moments of sixteen 2,3,5,6-tetra- and penta-fluorobenzenes.

FLUORINE exerts a number of interesting electronic effects when bonded to a phenyl group. First, its Hammett–Taft σ inductive constant (σ_I) indicates that it is a better electron-withdrawing agent than the other halogens,[1,2] in the order $F > Cl > Br > I$. On the other hand, its σ_R value shows that it drives π-electrons into the benzene ring by resonance interaction or a mesomeric ($+M$) effect (involving the back donation of fluorine lone-pair electrons) to a greater extent than any other halogen ($F > Cl > Br > I$).[2] This confirms earlier theoretical predictions made by Groves and Sugden [3] and explains the order of ionization constants of *para*-substituted halogeno-phenols.[4] Finally, fluorine has also been shown to possess the unique ability of suppressing the mesomeric effects of substituents *para* to it, if they conflict with its own.[5] Thus, we may expect that in penta- and tetra-fluorophenyl derivatives, the electronic character of the benzene ring will be grossly affected by the replacement of hydrogen by fluorine. The overall extent to which this occurs will undoubtedly be reflected in their physical molecular properties (spectroscopic [6,7] and dielectric) and chemical reactivity.[8] Here, we report the electric dipole moments of sixteen substituted tetra- and penta-fluorobenzenes and interpret these results in terms of electronic interactions between the fluorine atoms and various electron-withdrawing and -releasing substituents.

---

[1] (*a*) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 1964, **2**, 323; (*b*) R. W. Taft, jun., and I. G. Lewis, *J. Amer. Chem. Soc.*, 1959, **81**, 5343; (*c*) R. W. Taft, jun., *J. Phys. Chem.*, 1960, **64**, 1805.

[2] R. W. Taft, jun., E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, 1963, **85**, 709, 3146.

[3] L. G. Groves and S. Sugden, *J. Chem. Soc.*, 1937, 1992.

[4] G. M. Bennett, G. L. Brooks, and S. Glasstone, *J. Chem. Soc.*, 1935, 1821.

[5] N. J. Leonard and L. E. Sutton, *J. Amer. Chem. Soc.*, 1948, **70**, 1564.

[6] D. W. Davies, D. A. Shirley, and T. D. Thomas, *J. Amer. Chem. Soc.*, 1973, **94**, 6565.

[7] I. J. Lawrenson, *J. Chem. Soc.*, 1965, 117.

[8] R. D. Chambers, W. K. R. Musgrave, J. S. Waterhouse, and D. L. H. Williams, *J.C.S. Chem. Comm.*, 1974, 239.

EXPERIMENTAL

Measurements of dielectric constants, refractive indices, and densities were carried out by standard procedures[9] using benzene and carbon tetrachloride as solvents. The purified solutes were obtained commercially and had the refractive indices (n_D) and densities (d) quoted in Table 1 which also summarises the experimental results.

DISCUSSION

A simple way of seeing the effect of replacing the four hydrogens in the 2,3,5,6-positions by fluorine atoms in *para*-substituted fluorobenzenes and in mono-substituted benzenes, is to compare the moments of the derivatives of penta- and 2,3,5,6-tetra-fluorobenzene with those of fluorobenzene and benzene respectively. This is done in Table 2, but the halogenopentafluorobenzenes have not been included partly because some of the halogenated tetrafluorobenzenes were not available and because the literature values of the moments of *p*-chloro- and *p*-iodo-fluorobenzene were obtained under different conditions from the present work.[10] In the absence of interaction between 2,3,5,6-fluorines and the ring substituents, the moments of the pentafluorobenzenes should be equal to those of the corresponding *p*-fluorobenzene derivatives because the moments of the four C–F bonds should mutually cancel one another. Similarly, the moments of the 2,3,5,6-tetrafluorobenzenes should be equal to those of the benzene derivatives.

TABLE 1

Polarisations, refractive indices, refractions densities, and dipole moments at infinite dilution at 25 °C

Compound	Solvent	$\alpha\varepsilon_1$	β	γ	${}_2P$/cm^3	R_D/cm^3	n_D^{25}	d^{25}	μ/D [a]
Methylpentafluorobenzene	C_6H_6	2.20	0.371		114.3	30.8	1.4016	1.4357	20.00
									(1.98)
	CCl_4	3.42	−0.110		103.0	30.8			1.86
Pentafluoroanisole	C_6H_6	2.34	0.408		127.0	32.9	1.4085	1.4886	2.16
Pentafluorobenzonitrile	C_6H_6	2.88	0.390	−0.093	144.0	31.8	1.4402	1.5584	2.33
Pentafluorobenzaldehyde	C_6H_6	1.85	0.539	−0.136	98.9	18.9	1.4488	1.7518	1.97
Pentafluoroaniline	C_6H_6	4.97	0.513	−0.092	201.6	22.7			2.95
Pentafluorophenol	C_6H_6	3.60	0.475	−0.089	157.5	24.9	1.4273	1.7519	2.54
Pentafluorobenzene	C_6H_6	1.08	0.408		68.0	26.2	1.3881	1.5175	1.40
									(1.38)
	CCl_4	1.66	−0.064		62.3	26.2			1.30
Hexafluorobenzene	C_6H_6	−0.16	0.493		30.5	26.5	1.3743	1.6076	0.36
Chloropentafluorobenzene	C_6H_6	−0.08	0.405	−0.110	40.5	30.8	1.4205	1.6360	0.63
Bromopentafluorobenzene	C_6H_6	0.11	0.544	−0.080	43.6	29.3	1.4480	1.9413	0.80
Iodopentafluorobenzene	C_6H_6	0.40	0.616	−0.014	60.6	36.0	1.4947	2.2055	1.06
1,2,4,5-Tetrafluorobenzene	C_6H_6	−0.11	0.359	−0.122	29.8	27.0	1.4044		0.26
2,3,5,6-Tetrafluorotoluene	C_6H_6	0.12	0.342	−0.105	40.4	28.8	1.4173		0.70
									(0.66)
	CCl_4	0.29	−0.166	−0.086	40.1	29.4			0.67
									(0.63)
2,3,5,6-Tetrafluoroanisole	C_6H_6	1.25	0.390	−0.078	79.6	30.8	1.4266		1.52
2,3,5,6-Tetrafluoroaniline	C_6H_6	2.12	0.427	−0.049	98.0	28.2			1.83
2,3,5,6-Tetrafluorophenol	C_6H_6	1.85	0.451	−0.077	88.8	25.1			1.75
1,4-Fluorotoluene	CCl_4	5.27	−0.548		92.7	30.7	1.4653	0.9921	1.72
	C_6H_6	3.09	0.128		96.7	30.7			1.77

[a] Dipole moments are calculated assuming that the distortion polarisation (P_D) is 105% of the electronic polarisation as given by the molar refraction (R_D). Dipole moments in parentheses are based on the P_D obtained by adding the apparent moment of 1,2,4,5-tetrafluorobenzene to the R_D of the compound concerned.

TABLE 2

Comparison of moments (in benzene at 25 °C) of derivatives of penta- and 2,3,5,6-tetra-fluorobenzene with those of fluorobenzene and benzene

Substituent X	Penta-fluorobenzene derivatives	*p*-Fluorobenzene derivatives	$\Delta\mu_1$ [a]	2,3,5,6-Tetrafluoro-benzene derivatives	Benzene derivatives	$\Delta\mu_2$ [a]
NO_2	1.94 [b]	2.62 [c]	−0.68	3.28 [b]	4.01 [d]	−0.73
CN	2.33	2.67 [b]	−0.34	3.62 [b]	4.05 [d]	−0.43
NH_2	2.95	2.46 [c]	+0.49	1.83	1.53 [d]	+0.30
OMe	2.16	2.04 [c]	+0.12	1.52	1.23 [15]	+0.22
CHO	1.97	1.96 [c]	+0.01			
OH	2.54	2.08 [c]	+0.46	1.75	1.45 [d]	+0.30
CH_3	2.00	1.77	+0.23	0.70	0.34 [d]	+0.36
CH_3 (in CCl_4)	1.86	1.72	+0.14	0.67	0.35 [e]	+0.32

[a] $\Delta\mu_1$ is defined as $\mu(C_6F_5X) - \mu(p\text{-}FC_6H_4X)$; $\Delta\mu_2$ is defined as $\mu(C_6F_4HX) - \mu(C_6H_5X)$. [b] W. A. Sheppard in ' The Chemistry of the Cyano Group,' ed. Z. Rappoport, Interscience, New York, 1970, p. 215. The solvent is unknown. However the agreement between the moment of pentafluorobenzonitrile found in this work (2.33 D) and that quoted by Sheppard (2.34 D) suggests that conditions of measurement are the same. [c] N. J. Leonard and L. E. Sutton, *J. Amer. Chem. Soc.*, 1948, **70**, 1564. [d] J. W. Smith, ' Electric Dipole Moments,' Butterworths, London, 1955, pp. 215, 221. [e] C. G. Le Fèvre and R. J. W. Le Fèvre, *Austral. J. Chem.*, 1954, **7**, 33.

---

[9] R. J. W. Le Fèvre, ' Dipole Moments,' Methuen, London, 1953, 3rd edn., ch. 2.

[10] (*a*) C. R. Murty, *J. Sci. Ind. Res.* (*India*), 1956, **153**, 230; (*b*) R. J. W. Le Fèvre and M. Kemp, *J. Chem. Soc.*, 1965, 3463.

Electron-attracting (—I, —M) *Nitro, Cyano, and Formyl Substituents*.—An interesting feature of the results in Table 2 is that the deviations from the expected values, as given by $\Delta\mu_1$ and $\Delta\mu_2$, fall into two distinct categories: for powerful electron-withdrawing substituents such as NO_2 and CN, they are negative; whereas for electron-releasing substituents such as NH_2, OMe, OH, and Me, they are positive. The position of CHO is ambiguous.

The $\Delta\mu_1$ and $\Delta\mu_2$ values for NO_2 and CN indicate that in the penta- and 2,3,5,6-tetra-fluorobenzene derivatives, the effect of the five or four fluorines is to reduce the effective moments of the two substituents. In general, this can occur in three possible ways: (a) by steric inhibition of resonance interaction between the substituent and the aromatic system; (b) by a competitive mechanism whereby the fluorine atoms decrease the charge density in both the π- and σ-framework of the ring system so effectively that the mesomeric effect of the substituent is suppressed; and (c) by mutual induction (electrostatic field effect) between the substituents (which have high moments) and *o*-fluoro-atoms.

The cyano group, with its essentially cylindrical cloud of π-electrons, has relatively small steric requirements (between those of chlorine and bromine) and can interact with an adjacent π-system regardless of rotatory orientation.[11] It seems unlikely therefore, that its coplanarity, and hence its ability to conjugate with the fluoro-aromatic ring will be affected by the comparatively modest volume requirements of *o*-fluorine atoms. On the other hand, as scale drawings show, the molecular dimensions and planar triangular shape of the nitro-group will undoubtedly prevent it from being coplanar with the ring and accordingly, its $-M$ effect will be considerably reduced. The fact that the moments of pentafluoro- and 2,3,5,6-tetra-fluoro-nitrobenzene are 0·3—0·4 D lower than their cyano-counterparts is consistent with this view. We may thus regard the $\Delta\mu_1$ and $\Delta\mu_2$ values for the cyano-compounds, and approximately half the $\Delta\mu_1$ and $\Delta\mu_2$ values for the nitro-compounds, as constituting the combined effects of (b) and (c).

Table 2 also shows that the moments of pentafluoro- and *p*-fluoro-benzaldehyde are virtually the same. However, the three factors discussed above would lead us to expect a lowering of moment in pentafluoro- relative to *p*-fluoro-benzaldehyde. Hydrogen bonding between the formyl hydrogen and an *o*-fluorine could enhance the transmission of the $-M$ effect of the formyl group by stabilising the coplanar structure, but it is not clear whether this will be sufficient to offset the three factors mentioned.

Electron-releasing (—I, +M) *Amino, Methoxy, and Hydroxy Substituents*.—The positive sign and appreciable $\Delta\mu_1$ and $\Delta\mu_2$ values for the NH_2 group show that its group moment (as found in aniline) is increased when it is attached to the penta- or 2,3,5,6-tetra-fluorophenyl systems. Evidence that *ortho*-induction[12] makes only a minor contribution to this exaltation of moment comes from earlier work in which it was found that the moments of *o*-chloro- (1·77 D) and *o*-bromo-aniline (1·77 D) are almost the same as the values calculated by vectorial addition of group moments (1·71 and 1·69 D respectively). Since fluorine is less polarisable than either chlorine or bromine, *ortho*-inductive effects are likely to be even smaller, perhaps negligible, when the amino-group is flanked by fluorine atoms. Hence, we confirm n.m.r. evidence[13] that the ability of NH_2 to donate π-electrons is further stimulated by the strongly electron-withdrawing penta- and tetra-fluorophenyl groups. This occurs in spite of the possibility that the NH_2 group may not be quite coplanar with the benzene ring, as in the case of aniline.[14]

From Table 2, we see that $\Delta\mu_1$ and $\Delta\mu_2$ for the methoxy-group are smaller than the corresponding values for the amino-group. This suggests only a slight enhancement of the mesomeric $+M$ effect of methoxy when the four 2,3,5,6-hydrogens in *p*-fluoroanisole or anisole are replaced by fluorines. Electric birefringence measurements[15] have shown that the C_{ar}–O–C group in *p*-XC_6H_4OMe is virtually coplanar with the aromatic ring if $X = NO_2$ or CN; when X = H, Me, or halogen, this group is non-coplanar with a dihedral angle of *ca.* 20°. There is also some evidence from the n.m.r. chemical shifts of fluorine nuclei in pentafluoroanisole that the methoxy-group does not lie in the plane of the benzene ring.[16] Thus the slight enhancement of moment may be attributed to the power of the pentafluorophenyl group in withdrawing electrons and thus stimulating the $+M$ effect, rather than to any increase in overlap between the orbitals of the oxygen lone pair and the π-molecule orbitals of the ring.

When the methyl group in methoxy is replaced by hydrogen, there is an apparent increase in $\Delta\mu_1$ and $\Delta\mu_2$. Electric birefringence measurements[17] have shown that in phenol and *p*-cresol the OH link lies effectively slightly out of the plane of the benzene ring whereas with *p*-Cl, *p*-Br, and *p*-NO_2 substituents, the molecules are effectively flat. In penta- and 2,3,5,6-tetra-fluorophenol, intramolecular hydrogen bonding involving the *o*-fluorines and hydroxy-hydrogen may be expected. This should tend to further stabilise the planar structure with a consequent increase in mesomeric interaction. Thus the increase in $\Delta\mu_1$ and $\Delta\mu_2$ could be attributed to the operation of this factor as well as to the influence of the electron-withdrawing power of the penta- or tetra-fluorophenyl group. These observations are consistent

---

[11] W. A. Shappard, 'The Chemistry of the Cyano Group,' ed. Z. Rappoport, Interscience, New York, 1970, ch. 5.

[12] C. P. Smyth, 'Dielectric Behaviour and Structure,' McGraw-Hill, New York, 1955, p. 332.

[13] M. G. Hogben, R. S. Gay, A. J. Oliver, J. A. J. Thompson, and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1969, **91**, 291.

[14] M. J. Aroney and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1956, 2775.

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

[16] J. W. Emsley, *J. Chem. Soc. (A)*, 1968, 2018.

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

with ionisation constant results which show that pentafluorophenol is much more acidic than its hydrocarbon counterpart.[18]

Halogen (−I, +M) *Substituents*.—In principle, the effect of the halogens on the pentafluorophenyl group can be seen in the moments of the series, hexafluorobenzene, chloropentafluorobenzene, bromopentafluorobenzene, iodopentafluorobenzene (Table 1). The apparent moment of 0·36 D in hexafluorobenzene is probably due to higher than average atomic polarisations arising from the presence of three pairs of *para*-substituted fluorine atoms. As we ascend the series, the moment apparently increases. It is likely that there is a steady increase of atom polarisation (P_A) in the order $F < Cl < Br < I$ because the increasing mass of the halogen and, probably, the decreasing bending force constant of the carbon–halogen bond will cause the polar out-of-plane bending frequencies of the *para*-C–F and –halogen bonds to decrease in the order $F > Cl > Br > I$. Because of the dependence [19,20] of P_A on $1/\nu^2$ (where ν is the position of the appropriate absorption band in the i.r. vibrational and torsional region), this decrease in frequency could cause a marked increase in P_A. The actual magnitude of this effect can be discovered by careful measurements of intensities and frequencies of absorption bands in the sub-millimeter region,[21,22] or by gas-phase measurements of the distortion polarisation. Dielectric dispersion measurements would also indicate whether the polarities of these molecules are real or apparent. However, judging by the magnitude of the atomic polarisation of hexachlorobenzene,[23] it is not certain that the whole of the apparent moments observed can be attributed to this cause.

It is also possible that as the polarisability of the halogen increases from chlorine through bromine to iodine, so too will the effective moment of the carbon–halogen bond be increasingly reduced. It has been suggested [13] that in the monohalogenobenzene, the high polarity of the carbon–halogen bond (with the halogen atom negative) will favour the transfer or back-donation of halogen lone-pair electrons to the benzene ring. In the pentafluorophenyl compounds, however, the relatively high electronegativity of the C_6F_5 group could lower the polarity of the ring substituent σ-bond so that the tendency of the halogen to donate its lone-pairs will be correspondingly reduced.

Steric repulsion is another possible contributing factor. It could produce some widening of angle between the C–I and C–F dipole axes and possibly cause the iodine atom to be bent out of the plane of the ring. This effect is likely to be relatively small because the results of electron-diffraction measurements [24] have indicated no measurable angle widening in *o*-dichloro- and a widening of only 10° in *o*-di-iodo-benzene. However, there is some spectroscopic evidence [25] that bromine in *o*-dibromo- and chlorine in *o*-dichloro-benzene are bent out of the plane of the ring by 18°.

Methyl (+I, +M) *substituent*.—In the absence of steric effects and of induction between *o*-fluorine atoms and between methyl and fluorine, the dipole moment of pentafluorotoluene should be equal to that of *p*-fluorotoluene. We have remeasured the moment of *p*-fluorotoluene as a range of values has been reported.[5,26,27] In view of some evidence that benzene forms complexes with polyfluorinated aromatic compounds,[28] we have also determined the moment in carbon tetrachloride. Our values (1·72 in benzene and 1·77 D in carbon tetrachloride) agree closely with those of Le Fèvre and his co-workers.[27] Alternatively, the moment of pentafluorotoluene may be expected to be equal to the sum of the moments of toluene (0·34 D) and pentafluorobenzene (1·3—1·4 D), *i.e.* 1·64—1·74 D. The observed moment of pentafluorotoluene is however some 0·2—0·3 D higher than the expected values. Similarly the moment of 2,3,5,6-tetrafluorotoluene is *ca.* 0·3 D higher than the value obtained by vectorial addition of the moments of toluene (0·34 D) and tetrafluorobenzene (taken as zero). Hence, it seems reasonable to conclude that these results provide evidence for hyperconjugation in tetra- and penta-fluorotoluenes.[29]

[4/1557 *Received*, 26*th July*, 1974]

---

[18] (*a*) J. M. Birchall and R. N. Haszeldine, *J. Chem. Soc.*, 1959, 3653; (*b*) R. D. Chambers, F. G. Drakesmith, and W. K. R. Musgrave, *ibid.*, 1965, 5045.

[19] D. H. Whiffen, *Trans. Faraday Soc.*, 1958, **54**, 327.

[20] J. Haigh, K. M. Jinks, A. G. Leach, B. D. Mulligan, L. E. Sutton, and D. Waddington, *J.C.S. Faraday II*, 1974, 779.

[21] G. J. Davies, J. Chamberlain, and M. Davies, *J.C.S. Faraday II*, 1973, 1223.

[22] G. J. Davies and J. Chamberlain, *J.C.S. Faraday II*, 1973, 1739.

[23] R. J. W. Le Fèvre and D. A. A. S. N. Rao, *Austral. J. Chem.*, 1955, **8**, 39.

[24] S. B. Hendricks, L. R. Maxwell, V. L. Mosley, and M. E. Jefferson, *J. Chem. Phys.*, 1933, 549.

[25] P. W. Allen and L. E. Sutton, *Acta Cryst.*, 1950, **3**, 46.

[26] A. L. Myers and T. De Vries, *J. Amer. Chem. Soc.*, 1951, **73**, 1813.

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

[28] E. Mchaughlin and C. E. Messer, *J. Chem. Soc.* (*A*), 1966, 1106.

[29] H. H. Huang, *J.C.S. Chem. Comm.*, 1973, 723.