Dipole Moment Evidence for Hyperconjugation in Tetrafluoro- and Pentafluoro-toluenes

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Summary Dipole moments of various polyfluorinated toluenes and benzenes have been measured; they give evidence for hyperconjugation in tetrafluoro- and pentafluoro-toluenes.

PHYSICAL and chemical evidence bearing on the importance of hyperconjugation in organic systems has been found to be either unsound or inconclusive.[1] The dipole moment of toluene[2] itself (0·34 D), which was originally thought to be due to hyperconjugative interaction between the methyl group and the benzene ring, can be partly if not completely explained in terms of the intrinsic polarity of the sp^3–sp^2 C–C bond. Other dipole moment evidence which has been cited in the past in favour of hyperconjugation has been shown to be equally inconclusive.[1]

Since hyperconjugation, if it exists, is not normally expected to be a large effect, it is possible that in toluene at least, the effect can be stimulated only by attaching several powerful electron-withdrawing groups to the benzene ring. Fluorine appears to be suitable for this; it is the most electronegative element and has low polarisability and small size.

We have now measured the electric dipole moments of a number of polyfluorinated toluenes and benzenes in benzene solution at 25 °C with the following results: pentafluorotoluene, 1·94 D; 2,3,5,6-tetrafluorotoluene, 0·66 D; pentafluorobenzene, 1·38 D; hexafluorobenzene, 0—0·36 D; 1,2,4,-5-tetrafluorobenzene, 0—0·26 D. It seems unlikely that the last two compounds should have non-zero dipole moments because of their symmetry. It is much more likely that the presence of three and two pairs respectively of polar groups in *para*-positions in the benzene ring has caused higher than average atomic polarisations.[3] Due allowance has therefore been made for these atomic polarisations in calculating the moments of the first three compounds.

In the absence of steric effects and of induction between *ortho*-fluorine atoms and between methyl and fluorine, the dipole moment of pentafluorotoluene should be equal to that of *p*-fluorotoluene[4] (1·68 D). Alternatively, the moment may be expected to be equal to the sum of the moments of toluene (0·34 D) and pentafluorobenzene (1·38 D), *i.e.* 1·72 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 calculated by adding the moments of toluene (0·34 D) and tetrafluorobenzene (taken as zero).

Induction between *ortho*-fluorine atoms decreases the value of the moment. (*ortho*-Difluorobenzene has a moment of 2·38 D instead of the value of 2·53 D expected from vectorial addition.[5] Pentachlorobenzene[5] has a moment of 0·88 D instead of the chlorobenzene value of 1·58 D). Induction between fluorine and methyl is expected to be negligible since the moments of chloromesitylene, bromomesitylene, chlorodurene, and bromodurene are experimentally indistinguishable from those of chlorobenzene and bromobenzene.[5]

It may be argued that the five fluorine atoms in pentafluorotoluene or the four in 2,3,5,6-tetrafluorotoluene increase the electronegativity of the carbon atom to which the methyl group is attached and so increase the CH_3–C_{ar}. moment. While this is not implausible, the moment of pentafluorobenzene (1·38 D) is slightly less than that of fluorobenzene[4] (1·53 D) whereas if the carbon with hydrogen on it were made more electronegative, pentafluorobenzene also should have a larger moment than fluorobenzene. The smaller value for pentafluorobenzene is what one would expect from the F · · · · F induction effects. Since there is, furthermore, no evidence of distortion from planarity arising from steric requirements of *ortho*-fluorine atoms,[6] the discrepancies between expected and observed values of pentafluorotoluene and 2,3,5,6-tetrafluorotoluene seem best attributed to resonance interaction between the methyl group and the electron-depleted C–C bond framework of the phenyl ring.

Another interesting aspect of our results is that the elevated moments observed for 2,3,5,6-tetrafluorotoluene and pentafluorotoluene suggest that the negative inductive (−I) effect of fluorine outweighs its positive mesomeric (+M) effect, although fluorine has been shown to have the unique power to suppress the mesomeric effect of groups *para* to it if they conflict with its own[4]. This unusual behaviour is another example of the dual ability of halogen atoms to attract electrons or release them according to circumstances, an effect which has been observed particularly clearly in the pyridine *N*-oxide system.[7]

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[1] M. J. S. Dewar, 'Hyperconjugation,' Ronald Press, New York, 1962.
[2] C. W. N. Cumper and A. I. Vogel, *J. Chem. Soc.*, 1959, 3521.
[3] J. W. Smith, 'Electric Dipole Moments,' Butterworths, London, 1955 p. 272.
[4] N. J. Leonard and L. E. Sutton, *J. Amer. Chem. Soc.*, 1948, **70**, 1564.
[5] C. P. Smyth, 'Dielectric Behaviour and Structure,' McGraw-Hill, New York, 1955, p. 334—335.
[6] L. E. Sutton, ed., 'Interatomic Distances,' Chemical Society, London, 1958.
[7] C. M. Bax, A. R. Katrizky, and L. E. Sutton, *J. Chem. Soc.*, 1958, 1254.