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MAGNETIC SHIELDINGS AND THE ELECTRONIC STRUCTURES OF AROMATIC MOLECULES

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A NUMBER of discussions of the F^{19} and H^1 nuclear magnetic resonance spectra of aromatic compounds have appeared, and it has been demonstrated that the shieldings are closely related to the separated σ-constants of Taft.[1-3] Further correlations with π-electron distributions have been proposed recently for both fluorine[4] and hydrogen[5] shieldings. Our studies of natural abundance C^{13} nuclear magnetic resonance spectra of aromatic hydrocarbons,[6] of phenols and related compounds,[6] of other substituted

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[1] R.W. Taft, Jr., S. Ehrenson, I.C. Lewis, and R.E. Glick, J.Amer.Chem.Soc. **81**, 5352 (1959).

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[3] R.R. Fraser, Canad.J.Chem. **38**, 2226 (1960); which may be consulted for earlier references on H^1 shieldings.

[4] K. Ito, K. Inukai and T. Isobe, Bull.Chem.Soc.Japan **33**, 315 (1960).

[5] G. Fraenkel, R.E. Carter, A.McLachlan and J.H. Richards, J.Amer.Chem.Soc. **82**, 5846 (1960).

[6] P.C. Lauterbur, J.Amer.Chem.Soc. In press.

benzenes[7] and of aromatic heterocyclics[7] show that carbon shieldings in the parent compounds are also closely related to the above parameters and may often be more simply related to the ground state electron distributions than are the fluorine shieldings in their fluorine derivatives. The interpreation of fluorine shieldings is complicated by the possibility of resonance interactions of the fluorine with other substituents[1,2,8] and of other deviations from additivity, especially in the ortho-fluorinated compounds. Hydrogen shieldings are subject to long-range magnetic effects[9] and to large solvent shifts[10,11] and may be expected to be closely correlated with the electronic distribution in the ring only within closely related series of compounds.

The comparison of fluorine[4,12] and carbon[6,7] shieldings in Fig. 1 illustrates the above points. The para substituents, except for the one +R substituent, NO_2, give points falling on a straight line of slope 0.8. The fluorine nucleus in p-nitrofluorobenzene is about 3 p.p.m. less shielded than would have been expected by comparison with the para carbon in nitrobenzene, quantitatively confirming Taft's suggestion[2] that the resonance interaction of the nitro group with the fluorine is responsible for the deviation of the p-nitrofluorobenzene point from his plot of fluorine shieldings against the σ_R^o-parameter. The shieldings of fluorine ortho to

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[7] P.C. Lauterbur, to be published.

[8] R.W. Taft, Jr., R.E. Glick, I.C. Lewis, I.Fox and S. Ehrenson, J.Amer.Chem.Soc. 82, 756 (1960).

[9] For a review, see L.M. Jackman, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry Chap.7. Pergamon Press, London, New York (1959)

[10] T. Schaefer and W.G. Schneider, J.Chem.Phys. 32, 1218, 1224 (1960), and references cited therein.

[11] A.D. Buckingham, T. Schaefer and W.G. Schneider, J.Chem.Phys. 32, 1227 (1960).

[12] H.S. Gutowsky, D.W. McCall, B.R. McGarvey and L.H. Meyer, J.Amer.Chem.Soc. 74, 4809 (1952).

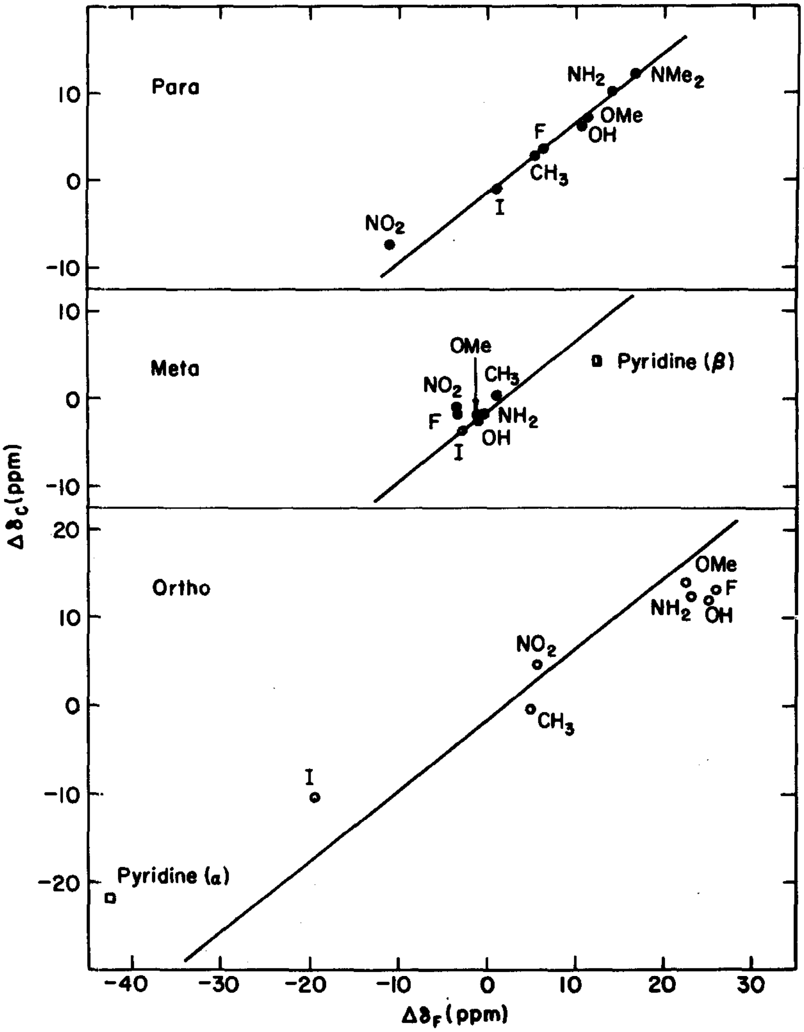

FIG. 1

C^{13} Shieldings (relative to benzene) in substituted benzenes and in pyridine vs. F^{19} shieldings (relative to fluorobenzene) in the corresponding substituted fluorobenzenes and in fluoropyridines.

OH, OMe, NH_2, F and CH_3 are all greater than would be expected on the basis of the para relationship; the smaller shielding of the ortho nitro compound may be the result of the conjugative interaction used to explain the decrease in shielding in the para compound.

The best set of measurements of hydrogen shieldings in a variety of substituted benzenes is that of Fraser[3]. A plot of his hydrogen shieldings against the carbon shieldings in the same compounds is shown in Fig. 2. The meta hydrogen shieldings have been adjusted by Fraser to compensate for the effects of the two methyl groups.

The para points fall close to a straight line with a slope of about 16. Combining this with an estimate[5] of a coefficient of 10 p.p.m. per π-electron for hydrogen shifts, the coefficient for carbon is found to be about 160 p.p.m. per electron, in good agreement with an earlier estimate.[6] It thus appears likely that the π-electron charges play an important role in determining magnetic shieldings in aromatic molecules.

The possibility of determining such charges suggests a number of investigations. One of the most promising is the study of interactions between two or more substituents on the same ring. It has been found that the effects of substituents and of hetero atoms on ring carbon shieldings are usually nearly additive, but that definite small deviations from additivity are found for all relative positions and types of substituents. The deviations are especially pronounced when ortho groups are present, as one would expect. The ortho effects are of two types; those in which only the atoms bearing the ortho groups are affected, and those in which the long-range interactions are changed because of steric inhibition of resonance. The interactions between methyl groups and CH_3, OH, NH_2, F and I are of the former type; in the most extreme example the shielding of the carbon bearing the iodine is decreased by almost 14 p.p.m. by two ortho methyl groups, but there is no anomalous effect at the para position.[7]

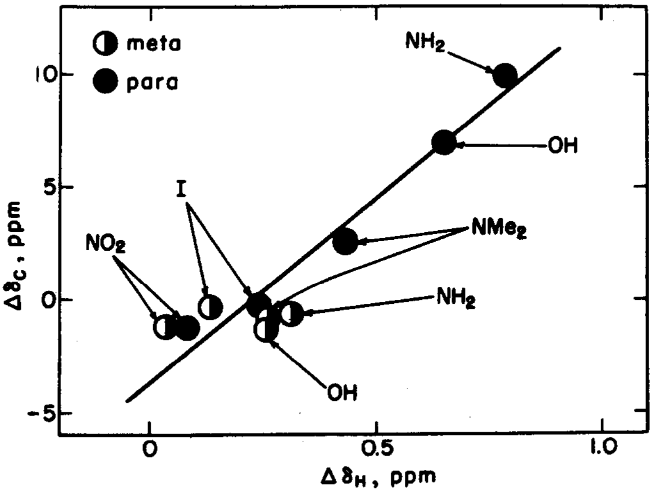

FIG. 2.

C^{13} Shieldings vs. H^1 shieldings in 2,6-dimethyl-1-substituted benzenes (relative to benzene).

The shieldings of para carbons are, however, markedly affected by methyl substitution ortho to groups whose resonance interactions with the ring may be reduced by steric effects. The relative para carbon shieldings in N,N-dimethylaniline, N,N-dimethyl-o-toluidine and N,N,2,6-tetramethylaniline are decreased by ortho methyl substitution,[7] in quantitative agreement with the calculated variation of the electron density[13] with the angle of twist of the dimethylamino group.[14] The para shieldings in nitrobenzene increase with ortho methyl substitution, paralleling the changes in the electronic spectra, dipole moments and molar refractions[15] in very satisfactory fashion. An anomaly in the nitrobenzene shieldings may be noted. Fig. 1 shows that

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[13] E.G. McRae and L. Goodman, J.Chem.Phys. 29, 334 (1958).

[14] E.G. McRae and L. Goodman, Mol.Spectr. 2, 464 (1958).

[15] B.M. Wepster, Rec.Trav.Chim. 76, 335 (1957).

both fluorine and carbon are more shielded at the *ortho* position than are the reference compounds, implying that there is a π-electron density greater than unity on the *ortho* carbons. No theoretical calculations support this possibility and it may be that major distortions of the σ-bond framework[16] can affect the shieldings.

A number of unexpected deviations from additivity of the carbon shieldings in polysubstituted benzenes have been observed and will be reported in detail elsewhere. It seems certain that the ability to detect the magnetic shielding effects of substituents and their interactions at *each* carbon atom will lead to a more detailed understanding of aromatic molecules.

J. Trotter, *Tetrahedron* **8**, 13 (1960).