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# FLUORINE-19 RESONANCE IN MONOFLUORO AROMATIC COMPOUNDS[1]

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SINCE nuclear screening in molecules is determined by the electron distribution in the vicinity of the nucleus, chemical shift measurements provide a basis for evaluating electronic theories of molecules. Proton and carbon-13 chemical shifts in aromatic hydrocarbons and ions have been linearly correlated with charge densities[3]. Proton[4] and fluorine[5] shifts in benzenoid compounds have been interpreted using the Hammett sigma-rho equation. Fluorine shifts are potentially valuable

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[3] G. Fraenkel, R.E. Carter, A. McLachlan and J.H. Richards, J. Am. Chem. Soc. **82**, 5846 (1960); P.C. Lauterbur, ibid. **83**, 1838 (1961); H. Spiesecke and W.G. Schneider, Tetrahedron Letters 468 (1961).

[4] R.E. Klinck and J.B. Stothers, Canad. J. Chem. **40**, 1071 (1962).

[5] H.S. Gutowsky, D.W. McCall, B.R. McGarvey and L.H. Meyer, J. Am. Chem. Soc. **74**, 4309 (1952); R.W. Taft, ibid. **79**, 1045 (1957); R.W. Taft and I.L. Lewis, ibid. **81**, 5352 (1959).

for probing electron distribution in monofluoro aromatic compounds. The only evidence available has been that of Ito, Inukai and Isobe[6] on fluorobenzene, 1- and 2-fluoronaphthalene, 1-fluoropyrene and 2- and 3-fluoropyridine. Accordingly, we have undertaken the measurement of fluorine shifts in a wide variety of systems and here report results for sixteen monofluoro aromatic hydrocarbons.

Materials were purchased or prepared by the known procedures referenced in column three of Table 1. Samples were prepared as 15% w/v solutions in chloroform containing 15% v/v $\alpha,\alpha',\alpha''$-trifluorotoluene as internal standard with the exception of 6-fluorochrysene and the fluorotriphenylenes which were not soluble to this extent and were measured as saturated solutions in chloroform at 25°C. Shifts were measured relative to the standard on a Varian V-4300 spectrometer operating at 40 Mc by the sideband technique. Results were corrected by difference to give the shift, $\delta_F$, relative to fluorobenzene.

Values of $\delta_F$ are given in Table 1. Since ring current effects make negative contributions to the shifts, it is necessary to correct for this effect. A suitable method consists of adding the proton shift, $\delta_H$, relative to benzene observed for the corresponding position in the hydrocarbon, as these are determined primarily by the ring current effect. The corrected fluorine shift, $\delta_F'$, is given by

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

TABLE 1

Fluorine Chemical Shifts in Monofluoro Aromatic Compounds

| Fluoro Compound | Position | Source | Shift (cps) | | | $\pi_{rr}$[7] |
|---|---|---|---|---|---|---|
| | | | $\delta_F$ | $\delta_H$ | $\delta'_F$ | |
| Benzene | - | [a] | 0 | 0 | 0 | 0.398 |
| Naphthalene | 1 | [b] | 413 | 22[c] | 435 | 0.443 |
| | 2 | [b] | 67 | 8[c] | 75 | 0.405 |
| Phenanthrene | 1 | ref. 8 | 370 | 22[d] | 392 | 0.439 |
| | 2 | ref. 8 | 83 | 8[d] | 91 | 0.403 |
| | 3 | ref. 8 | 14 | 8[d] | 22 | 0.409 |
| | 4 | ref. 8 | -130 | 58[c] | -72 | 0.429 |
| | 9 | ref. 8 | 486 | 18[c] | 504 | 0.443 |
| Biphenyl | 2 | ref. 9 | 195 | 0[d] | 195 | 0.424 |
| | 3 | ref. 9 | -2 | 0[d] | -2 | 0.396 |
| | 4 | ref. 9 | 107 | 0[d] | 107 | 0.411 |
| Triphenylene | 1 | ref. 8 | -190 | 52[c] | -138 | 0.427 |
| | 2 | ref. 8 | 40 | 14[c] | 54 | 0.400 |
| Pyrene | 1 | [e] | 406 | 32[c] | 438 | 0.466 |
| Chrysene | 6 | ref. 10 | 407 | 18[d] | 425 | 0.451 |
| Fluoranthene | 3 | [f] | 387 | 22[d] | 409 | 0.462 |

[a] Eastman Organic Chemicals

[b] Columbia Organic Chemicals Co., Inc.

[c] Experimental values of reference 11.

[d] Experimental values not available. Value shown is an estimate based on similar position in compound with one less ring.

[e] Sample kindly provided by Dr. J. Blackwell who prepared it by the method of reference 8.

[f] K and K Laboratories, Inc.

$$\delta_F' = \delta_F + \delta_H \ . \qquad (1)$$

Since the corrections are small compared with the range of $\delta_F$ observed, any errors in this procedure will be negligible.

The theory of fluorine shielding in fluoroaromatic molecules has been considered by Karplus and Das[12] and by Prosser[13]. A detailed calculation of the chemical shift requires a knowledge of the LCAO-MO wave function for the molecule concerned. As these are not now available for the compounds studied, we consider the approximate equation derived by Karplus and Das[12]

$$\delta_F' = 0.765\Delta I - 0.777\Delta\rho \ , \qquad (2)$$

which relates the shift, $\delta_F'$, to the change in ionic character, $\Delta I$, of the C-F sigma bond and the change in double bond character, $\Delta\rho$, for the bond, all relative to fluorobenzene.

The ionic character, I, may be related to $\pi_{rr}$, the atom polarizability calculated by MO theory for the appropriate position in the parent hydrocarbon. It can be seen that I increases as $\pi_{rr}$ increases by considering the definition of $\pi_{rr}$,

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[7] A.J. Streitwieser, Jr., Molecular Orbital Theory for Organic Chemists pp. 330, 347. John Wiley and Sons, Inc., New York (1961).

[8] P.M.G. Bavin and M.J.S. Dewar, J. Chem. Soc. 4486 (1955).

[9] G. Schiemann and W. Roselius, Ber. 62B, 1805 (1929).

[10] G.M. Badger and J.F. Stephens, J. Chem. Soc. 3638 (1956).

[11] N. Jonathan, S. Gordon and B.P. Dailey, J. Chem. Phys. 36, 3443 (1962).

[12] M. Karplus and T.P. Das, J. Chem. Phys. 34, 1683 (1961).

[13] F.P. Prosser, Diss. Abs. 22 3873 (1962).

$$\pi_{rr} = \delta q_r/\delta\alpha_r \ , \qquad (3)$$

where $q_r$ is the charge at atom r and $\alpha_r$ is the coulomb integral for atom r and varies with the electronegativity of that atom. If fluorine is substituted at carbon atom r, electrons will be withdrawn from carbon toward fluorine in the C-F sigma bond causing $\alpha_r$ to increase. This increase in $\alpha_r$ is offset by polarization of the pi electrons giving an increased $q_r$ on atom r. The greater the increase in $q_r$ for a unit change in $\alpha_r$, that is, the greater is $\pi_{rr}$, the more effective fluorine will be in polarizing the C-F sigma bond and the greater will be the ionic character of the bond.

The double bond character is determined by the bond order of the C-F bond. Coulson and Longuet-Higgins[14] have shown that the bond order, $p_{rs}$, between atom r in R and atom s in S of the system R-S is related to the atom polarizability by

$$p_{rs} = K + K'\sqrt{\pi_{rr}\pi_{ss}} \qquad (4)$$

where $\pi_{rr}$ and $\pi_{ss}$ are the atom polarizabilities in the isolated systems R and S. If the C-F bond may be treated in this fashion, then $p_{rs}$, and hence $\rho$, should increase with increasing $\pi_{rr}$. The same would hold for differences in this quantities with benzene taken as standard and equation (2) could be written in the form

$$\delta_F' = K_1\Delta\pi_{rr} - K_2\sqrt{\Delta\pi_{rr}} \ . \qquad (5)$$

While the gross approximations involved may cast doubt on the validity of this expression, it cannot be doubted that both

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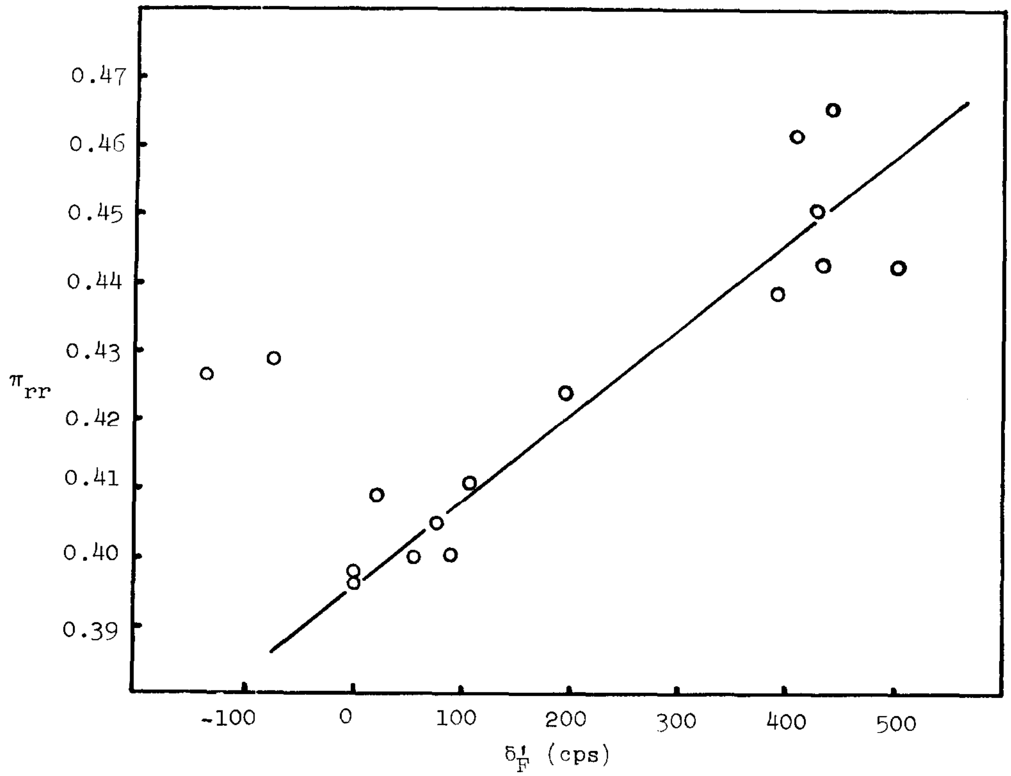
[14] C.A. Coulson and J.C. Longuet-Higgins, Proc. Roy. Soc. (London) A195, 188 (1948).

I and $\rho$, and hence $\Delta I$ and $\Delta\rho$, increase with $\pi_{rr}$. Since $\Delta I$ and $\Delta\rho$ appear in equation (2) with opposite signs, the relative importance of the two terms will determine the sign of the correlation with $\pi_{rr}$.

FIGURE 1



From the plot of $\delta_F'$ versus $\pi_{rr}$ in Figure 1 it is seen that the points for the 4-position in phenanthrene and the 1-position in triphenylene deviate badly. In the case of phenanthrene, the fluorine in the 4-position interacts strongly with the proton in the 5-position. This interaction is expected to disturb the axial symmetry of the C-F bond, reducing diamagnetic currents in the bond, and causing a paramagnetic shift to lower field as is observed. The 1-position in triphenylene is an analogous case.

Neglecting the points for 4-fluorophenanthrene and 1-fluorotriphenylene a fair linear relationship between $\delta_F^!$ and $\pi_{rr}$ is observed. A positive slope is evident indicating that the ionic term dominates and that changes in double bond character are of less importance. This implies that the degree of resonance interaction between fluorine and the aromatic system to which it is attached is not very sensitive to the nature of the aromatic system involved.

The observed qualitative correlation between $\delta_F^!$ and $\pi_{rr}$ is another example of the usefulness of the simple Huckel MO method. Detailed calculations taking fluorine explicitly into account are in progress in order to determine whether application of the more rigorous equations for chemical shifts will give an improved correlation. We have also measured fluorine shifts in a number of monofluoro heteroaromatic compounds and these will be published at a later date.