*On the Fluorine Shift of Aromatic Fluorine Compounds**

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Numerous experimental data on fluorine chemical shifts of various organic compounds have been presented[1-5]. To explain the general trend of these shifts, some empirical interpretations based upon the electronegativity of the atom to which the fluorine is bonded[2], and upon the Hammett constant of a substituent in fluorobenzene have been proposed[3]. These interpretations, however, rest upon no clear basis of electronic configuration around the nucleus.

Ramsey[6] has derived a general expression of nuclear magnetic shielding constant, σ, in a molecule which has no orbital or spin angular momentum and contains only one nucleus of non-zero magnetic moment. The nuclear magnetic shielding is written by his expression

$$\begin{aligned} A_{v_\lambda}\sigma = & \left(\frac{e^2}{3mc^2}\right)\left(0\left|\sum_k \frac{1}{r_k}\right|0\right) \\ & -2A_{v_\lambda}\Bigg[\sum_{n_\lambda}{}' \frac{1}{E_n-E_0}\Bigg\{(0_\lambda|\sum \mathbf{m}^0{}_{kz}|n_\lambda{}') \\ & \qquad \times\left(n_\lambda{}'\left|\sum_k \frac{\mathbf{m}^0{}_{kz}}{r_k{}^3}\right|0_\lambda\right) \\ & +\left(0_\lambda\left|\sum_k \frac{\mathbf{m}^0{}_{kz}}{r_k{}^3}\right|n_\lambda{}'\right)(n_\lambda{}'|\sum_k \mathbf{m}^0{}_{kz}|0_\lambda)\Bigg\}\Bigg] \end{aligned} \tag{1}$$

where r_k is the distance between the kth electron and the nucleus in question, $A_{v\lambda}$ implies an average over all molecular orientations, each of which is specified by the subscript λ; and $\mathbf{m}^0{}_{kz}$ is the z component of the operator for the kth electron

$$\mathbf{m}^0{}_k = \left(\frac{ieh}{4\pi mc}\right)(\mathbf{r}_k \times \nabla_k) \tag{2}$$

The application of this formula to calculate the nuclear magnetic shielding of the nucleus in a complex molecule has been considered to be almost impossible due to the lack of our knowledge of the energies and wave functions of all excited states. Furthermore, as Ramsey[6] pointed out, the formula contains many terms which cancel each other, and this might bring about a considerable error in the numerical calculation.

An important contribution to develop the procedure of obtaining shielding constants was proposed by Saika and Slichter[7]. According to them the screening was divided into three terms.

1. The diamagnetic correction for the atom in question.

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* This study was presented at the Symposium on Electronic Structures of Molecules, Tokyo, September, 1959.

1) L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953).

2) H. S. Gutowsky and C. J. Hoffman, *J. Chem. Phys.*, **19**, 114 (1951).

3) H. S. Gutowsky, D. W. McCall, B. R. McGarvey and L. H. Meyer, *J. Am. Chem. Soc.*, **74**, 4509 (1952).

4) T. Isobe, K. Inukai and K. Ito, *J. Chem. Phys.*, **27**, 1215 (1957); This Bulletin, **33**, 315 (1960).

5) K. Fukui, S. Hattori, T. Yonezawa, R. Kusaka and H. Kitano, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 541 (1959).

6) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950).

7) A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

2. The paramagnetic term for the atom in question.
3. The contribution from other atoms.

Based upon these divisions, they concluded that the F^{19} nuclear magnetic shielding is mainly determined by the paramagnetic contribution of the electrons belonging to the fluorine atom in question. This conclusion was shown to be successful in calculating the chemical shift between HF and F_2. The equation developed by them remained, however, only available for evaluating fluorine shifts in some aliphatic compounds. Further application of their procedure to fluorine shifts in aromatic compounds seems never to have been attempted.

In the present paper, an extension of their analysis to more complex conjugated compounds is presented by using a molecular orbital treatment.

Theoretical

The second order paramagnetic term of Ramsey[6] is approximated referring to the treatment by Saika and Slichter[7]. In the present paper, we have chosen the coordinate system of Fig. 1 whose origin is set at the fluorine atom in question. Considering the paramagnetic contribution of electrons belonging to the fluorine, the paramagnetic shielding term, σ_p, in a conjugated molecule can be given by the mean of three principal components as

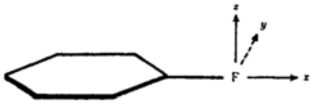

Fig. 1. The coordinate system adopted in the present treatment.

$$\sigma_{\rm p}=\frac{1}{3}(\sigma_{l-\pi}+\sigma_{l-\sigma}+\sigma_{\sigma-\pi}) \tag{3}$$

These three components are obtained as

$$\left.\begin{aligned}
\sigma_{l-\pi}&=-\left(\frac{eh}{2\pi mc}\right)^2\left\langle\frac{1}{r^3}\right\rangle\sum^{\rm unocc}\frac{2}{\varepsilon_i-\varepsilon_l}(c_{\rm F}{}^i)^2\\
\sigma_{l-\sigma}&=-\left(\frac{eh}{2\pi mc}\right)^2\left\langle\frac{1}{r^3}\right\rangle\frac{2}{\varepsilon_\sigma{}^*-\varepsilon_l}(a^*)^2\\
\sigma_{\sigma-\pi}&=-\left(\frac{eh}{2\pi mc}\right)^2\left\langle\frac{1}{r^3}\right\rangle\left[\sum_i^{\rm unocc}\frac{2}{\varepsilon_i-\varepsilon_\sigma}\right.\\
&\qquad\times\left\{a^2(c_{\rm F}{}^i)^2+\sqrt{\frac{2}{3}}abc_1{}^ic_{\rm F}{}^i\right\}\\
&\left.+\sum_j^{\rm occ}\frac{2}{\varepsilon_\sigma{}^*-\varepsilon_j}\left\{(a^*)^2(c_{\rm F}{}^j)^2+\sqrt{\frac{2}{3}}a^*b^*c_{\rm F}{}^jc_1{}^j\right\}\right]
\end{aligned}\right\} \tag{4}$$

respectively, where $\langle 1/r^3\rangle$ is the average of $1/r^3$ for 2p electron of fluorine, ε_i and ε_l are the energies of the ith π molecular orbital and of the lone pair electrons of the fluorine atom, $c_F{}^i$ and $c_1{}^i$ are the coefficients of the ith π electronic LCAO MO, whose energy is $\alpha+\lambda_i\beta$, at the fluorine atom and its adjacent carbon atom, and $\overset{\rm occ}{\sum}$, $\overset{\rm unocc}{\sum}$ indicate summation over all occupied and unoccupied orbitals, respectively. The wave functions of bonding and antibonding C–F σ orbitals, φ_σ and $\varphi_\sigma{}^*$, whose energies are denoted by ε_σ and $\varepsilon_\sigma{}^*$ in Eq. 4, respectively, may be expressed by the following linear combinations of two atomic orbitals, χ_F and χ_C, which are the 2p σ AO of fluorine and the sp^2 hybridized orbital of the adjacent carbon atom*.

$$\left.\begin{aligned}\varphi_\sigma&=a\chi_{\rm F}+b\chi_{\rm C}\\ \varphi_\sigma{}^*&=a^*\chi_{\rm F}+b^*\chi_{\rm C}\end{aligned}\right\} \tag{5}$$

The coefficients a, b, a^* and b^* are those appearing in Eq. 4. Three components in the right side of Eq. 3, $\sigma_{l-\pi}$, $\sigma_{l-\sigma}$ and $\sigma_{\sigma-\pi}$, can be obtained, as is shown by Eq. 4, by calculating the matrix elements in Eq. 1 between the ground state and the various singlet excited states resulting from one electron transition between MO's designated by each subscript, l, σ and π, denoting the orbital of fluorine lone pairs, C–F σ orbitals and π molecular orbitals, respectively. In the last component $\sigma_{\sigma-\pi}$ which appears only when the π conjugation takes place, the cross term arises from the circumstances that we take account of matrix elements of χ_C and π AO on the adjacent carbon atom in $(0|\mathbf{m}^0{}_{ky}|n)$ and neglect $(0|\mathbf{m}^0{}_{ky}/r_k{}^3|n)$ terms on that carbon, as was done in Ref. 7. Equation 3 is easily shown to coincide with the equation given by Saika and Slichter[7] when one considers that no conjugation takes place. It can be shown also, that Eq. 3 in the present paper is also derivable by an alternative procedure proposed by Pople[8], in which attention was paid to the paramagnetic shielding resulting from the local paramagnetic current of the fluorine.

In the present paper, a chemical shift parameter, δ, is defined as

$$\delta=\frac{H_{\rm r}-H_{\rm c}}{H_{\rm r}} \tag{6}$$

where H_r and H_c are the resonance field for the reference compound and the sample compound, respectively.

The chemical shift, δ, can be represented in terms of the paramagnetic shielding constant obtained by Eq. 3 whenever σ is small and the change of diamagnetic shielding constant can be neglected. Thus the shift between the

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* χ_C is written as $\sqrt{1/3}\chi_s+\sqrt{2/3}\chi_{2p\sigma}$, where χ_s and $\chi_{2p\sigma}$ are 2_s and $2_{p\sigma}$ AO's of carbon atom, respectively.

[8] J. A. Pople, *Proc. Roy. Soc.*, **A239**, 541, 550 (1957).

compound in question and the reference one can be expressed as[*1]

$$\delta=\delta_p(\text{reference})-\sigma_p(\text{sample}) \tag{7}$$

Numerical Calculation

In order to carry out calculation, the information on the energies of the molecular orbitals and the coefficients involved in Eq. 4 is indispensable. The π molecular orbital energies and the coefficients are settled by the simple LCAO MO method. The values of the Coulomb integrals and the resonance integral representing the characteristics of a fluorine atom and a carbon atom adjacent thereto are taken as

$$\left.\begin{aligned}\alpha_F&=\alpha+1.8\beta\\ \alpha_{adj}&=\alpha+0.18\beta\\ \beta_{C-F}&=0.8\beta\end{aligned}\right\} \tag{8}$$

where α is the Coulomb integral of a carbon atom and β is the resonance integral for a C–C bond in a benzene molecule. The values of α and β are taken to be -7.25 eV. and -2.3 eV., respectively, in numerical calculation[*2]. Other Coulomb and resonance integrals used for amino and nitro groups in the present calculation are as follows:

$$\begin{aligned}\alpha_{-NH_2}&=\alpha+0.4\beta\\ \beta_{C-NH_2}&=0.4\beta\\ \alpha_N&=\alpha+\beta\\ \alpha_O&=\alpha+\beta\end{aligned}$$

Since the simple LCAO MO studies for a σ electron system have not been sufficiently copious for providing reliable numerical values of various parameters, an attempt to estimate these parameters is necessary for our calculation. Hereupon, the values of Coulomb and resonance integrals are determined on the basis of some experimental data in the following way. At first, the energies of σ-bonding and antibonding orbitals for the reference compound are put to -14 eV. and -4 eV., respectively. The energy of bonding orbital is equal to the absolute value of ionization potential of an electron localized in a C–F bond in methyl fluoride assigned by McDowell9). The energy of the antibonding orbital is estimated by the spectroscopic data on other methyl halides. The molecular orbital coefficients, a and b, are determined from the magnitude of the bond moment, μ, with the aid of simplified formulas[*3]

$$\left.\begin{aligned}\mu&=\frac{\lambda^2-1}{1+\lambda^2}eR\\ a&=\frac{-\lambda}{(1+\lambda^2)^{1/2}}\\ b&=\frac{1}{(1+\lambda^2)^{1/2}}\end{aligned}\right\} \tag{9}$$

where R is a C–F bond distance, e is the charge of an electron, and $\lambda(\lambda>0)$ is a coefficient representing the polarity of the molecular orbital. The bond moment, μ, is adopted as 1.51 D and C–F distance as 1.39 Å. Inserting these values into Eq. 9, we obtain: $a=-0.783$ and $b=0.622$[*4]. The coefficients a^* and b^* are then obtained as 0.622 and -0.783, respectively.

Coulomb and resonance integrals in a C–F σ electron system might be determined in such a way that in solving the secular determinant these integrals give the values of energies and orbital coefficients estimated above. It may be more reasonable, then, to consider that, as the character of the C–F σ bond alters according to the change of molecular structure, the values adopted for the integrals may change. In this connection it may be recollected that in π electron approximation a π electron is considered to move in a resultant electric field from all other π electrons and the σ skeleton. Hence, in the treatment of σ electrons, the electronic structure is naturally recognized to be affected by π electronic distribution conversely.

Referring to the facts stated above, the Coulomb and resonance integrals available for a C–F σ electron system are expressed as[*5]

$$\left.\begin{aligned}h_{FF}&=-10.16-\gamma_F(q_F{}^0-q_F)\\ h_{CC}&=-7.84-\gamma_C(q_C{}^0-q_C)\\ h_{CF}&=+4.84^{*6}\end{aligned}\right\} \tag{10}$$

[*1] The shielding constant σ is represented by the sum of diamagnetic and paramagnetic shielding constant σ_d, σ_p as $\sigma=\sigma_d+\sigma_p$. Then the shift becomes $\delta=\{\sigma_d(\text{reference})-\sigma_d(\text{sample})\}+\{\sigma_p(\text{reference})-\sigma_p(\text{sample})\}$. Neglecting the first term, we obtain Eq. 7.

[*2] These values are determined so that the calculated highest occupied orbital energy of fluorobenzene ($\alpha+0.8441\beta$) becomes equal to the negative value of ionization potential of the compound, 9.19 eV. (V. J. Hammond, W. C. Price, J. P. Teeganand and A. D. Walsh, *Faraday Soc. Discuss.*, **9**, 53 (1950)). The value of α is not so unreasonable compared with the value -7.18 eV. adopted by Mulliken (*Phys. Rev.*, **74**, 736 (1948)). The value of β is equal to that determined by Pariser and Parr (*J. Chem. Phys.* **21**, 767 (1953)).

9) C. A. McDowell and B. A. Cox, *Proc. Roy. Soc.*, **A241**, 194 (1957).

[*3] Cf. C. A. Coulson, "Valence", Oxford Univ. (1952), p. 103; In the present formulas, the overlap integral is neglected.

[*4] The minus sign of a is determined so as to correspond with the coefficient of bonding σ MO in the present coordinate system (see Fig. 1).

[*5] These equations resemble those used in a semi-empirical SCF treatment carried out in a π electron system. (Cf. e. g., R. S. Mulliken et al., *J. Am. Chem. Soc.*, **76**, 4770 (1954)). The present procedure, however, represents a reciprocal interaction of σ electrons with π electrons in a bond.

[*6] The exchange integral is taken to be positive since the overlap integral between carbon and fluorine AO's in a C-F σ bond is found to be negative in the present coordinate system (see Fig. 1).

TABLE I. TOTAL π ELECTRON DENSITY, σ-ELECTRONIC ENERGY AND MOLECULAR ORBITAL COEFFICIENT

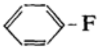
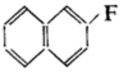
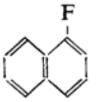
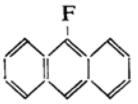
	q_F	q_C	ε_σ	$\varepsilon_\sigma{}^*$	ε_l	a^2	b^2
	1.9330	1.0204	−13.977	−4.023	−10.000	0.6166	0.3834
	1.9318	1.0196	−13.993	−4.033	−10.024	0.6176	0.3824
	1.9306	1.0216	−14.008	−4.043	−10.048	0.6187	0.3813
	1.9268	1.0162	−14.057	−4.075	−10.124	0.6220	0.3780
	1.9198	1.0128	−14.147	−4.132	−10.264	0.6283	0.3717

TABLE II. TOTAL π ELECTRON DENSITY, σ-ELECTRONIC ENERGY AND MOLECULAR ORBITAL COEFFICIENT

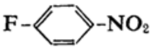
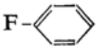
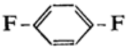
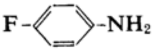
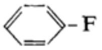
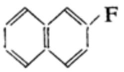
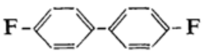
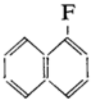
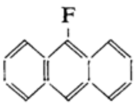
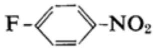
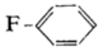
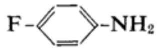
	q_F	q_C	ε_σ	$\varepsilon_\sigma{}^*$	ε_l	a^2	b^2
	1.9204	0.9686	−14.173	−4.183	−10.252	0.6235	0.3765
	1.9330	1.0204	−13.977	−4.023	−10.000	0.6166	0.3834
	1.9344	1.0342	−13.949	−3.995	− 9.972	0.6165	0.3835
	1.9352	1.0410	−13.934	−3.987	− 9.956	0.6164	0.3836

TABLE III. CALCULATED SHIELDING CONSTANTS AND CHEMICAL SHIFTS

	$-\sigma_{l-\sigma}$	$-\sigma_{l-\pi}$	$-\sigma_{\sigma-\pi}$	$-\sigma_p$	δ_{calcd}	δ_{obs} (a)
	165.398	15.761	146.921	1/3×328.080	0	0
	164.590	16.400	146.914	1/3×327.904	−0.06	−0.18
	163.731	16.632	146.875	1/3×327.238	−0.28	−0.26
	161.144	18.462	147.262	1/3×326.868	−0.40	−1.02
	156.305	22.273	147.623	1/3×326.201	−0.63	−

(a) Ref. 5; in units of 10 p. p. m.

TABLE IV. CALCULATED SHIELDING CONSTANTS AND CHEMICAL SHIFTS

	$-\sigma_{l-\sigma}$	$-\sigma_{l-\pi}$	$-\sigma_{\sigma-\pi}$	$-\sigma_p$	δ_{calcd}	δ_{obs} (b)
	159.962	20.738	152.238	1/3×332.938	+1.62	+1.08
	165.398	15.761	146.921	1/3×328.080	0	0
	165.453	15.505	145.714	1/3×326.672	−0.47	−0.64
	165.537	15.214	144.889	1/3×325.640	−0.78	−1.46

(b) Ref. 3; in units of 10 p. p. m.

where these matrix elements are represented in units of eV., $q_F{}^0$ and $q_C{}^0$ denote the total π electron densities at the fluorine and the adjacent carbon atom in the reference, respectively, and q_F and q_C are those in the sample compound. Parameters γ_F and γ_C are tentatively put at 20 and 2, respectively, in the present treatment. Using the integrals in Eq. 10, the energies of bonding and antibonding orbitals as well as the coefficients are calculated.

Finally the energy of lone pair electrons of fluorine, ε_l, is assumed to be[*]

$$\varepsilon_l = -10 - \gamma_F(q_F{}^0 - q_F) \qquad (11)$$

in which the second term has a similar meaning in Eq. 10. The value of $\langle 1/r^3 \rangle$ is put at $8.89/a_H{}^3$, where a_H is the Bohr radius[7].

Result and Discussion

It was discussed qualitatively by the present authors[5] that the two factors, the polarity of C–F bond and the π electron density on fluorine, had a dominant role in determining a paramagnetic term in a conjugated molecule. The two empirical rules were proposed[5], whereby a qualitative analysis of magnetic shielding parameter δ was made. Further we pointed out that in polycondensed aromatics the magnitude of total π electron more density decreases with the decrease of fluorine chemical shifts, while in some fluorobenzene derivatives this correlation is reversed. More precisely, the fluorine chemical shift seems to be governed by the polarity of a C–F σ bond in fluorobenzene derivatives.

In the present paper an investigation on fluorine chemical shifts in these compounds is made quantitatively by making use of Eqs. 3 and 4.

In Tables I and II, the total densities at the fluorine and the adjacent carbon atom, the energies of bonding and antibonding orbitals, and the values of a^2 and b^2 for benzene derivatives and condensed aromatics are cited. One should note that the polarity of a C–F bond which is measured by the magnitude of a^2 seems to increase with the decrease of q_F in Table I, while in Table II the polarity seems to increase with the increase of q_F.

In Tables III and IV, there are listed three principal components of the paramagnetic shielding constant, the mean of the constants and the calculated values of chemical shift together with observed ones.[3,5] With regard to 9-fluoroanthracene, there are unfortunately no data to be compared with the theoretical result. Though there remain many points to be modified in future, the good agreement observed between the present results and experimental data may be sufficiently valuable to be stressed.

Summary

In order to make a quantitative analysis of the F^{19} magnetic shielding parameters in conjugated molecules, an extension of the idea previously proposed by Saika and Slichter is made. Calculations are carried out with respect to several fluorobenzene derivatives and fluorinated polycondensed aromatic compounds by using the molecular orbital method. The agreement of our calculated shifts with observed shielding data is almost satisfactory.

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[*] In a rough estimation, it may be assumed that this energy can be obtained by the equation, $\varepsilon_l = -I_F + 1/2(I_F - A_F)$, where I_F and A_F are the ionization potential and the electron affinity of the fluorine in its valence state. Using the published data, $I_F = 17.481$ eV., $A_F = 3.78$ eV., we can obtain $\varepsilon_l = -10.5$ eV. Therefore the value of -10 in Eq. 11 seems not to be so unreasonable.