Fluorine-19 Nuclear Magnetic Shielding in Some Monofluorinated Compounds

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The chemical shifts in the proton magnetic resonance spectra of aromatic compounds have been studied by several authors both experimentally[1,2] and theoretically[2-8]. The magnetically non-equivalent nature of protons in these compounds has been essentially interpreted in terms of the interaction between a proton magnetic moment and diamagnetic currents induced on aromatic rings by an external magnetic field. On the other hand, Isobe, Inukai and Ito[9] have shown that the fluorine atoms in fluorobenzene, 1- and 2-fluoronaphthalenes are also magnetically non-equivalent. They have concluded tentatively that the non-equivalent nature of the fluorine atoms can not be attributed to the induced diamagnetic ring current mentioned above but may be attributed to the variation in polarity of the C–F σ-bonds. As a criterion for predicting such a variation in polarity of C–F bonds, the π-electron density of McWeeny's sense[10] has been suggested. Recently, however, Fukui and his coworkers[11] have proposed the qualitative assumption that the larger the π-electron conjugation of a fluorine atom with a neighboring atom or group of atoms and consequently the smaller the π-electron density on the fluorine atom, the more the fluorine nucleus is magnetically shielded. The ^{19}F chemical shifts in some aromatic fluoro compounds, including 1- and 2-fluoronaphthalenes, have been interpreted in terms of this assumption, although the variation in polarity of C–F σ-bonds has also been introduced in order to interpret the ^{19}F chemical shifts in *p*-nitrofluorobenzene and 1-fluoro-4-nitronaphthalene for which the assumption predicts results contradictory to those of the experiments.

In the present paper the ^{19}F NMR spectra of 2- and 3-fluoropyridines, 1-fluoropyrene[12] and cyclohexylfluoride are studied and the ^{19}F chemical shifts in these compounds, together with those in fluorobenzene, 1- and 2-fluoronaphthalenes, are discussed. The spectra of 9-fluoroanthracene and 12-fluorochrysene[12] have also been studied but no signal has been obtained.

Experimental

Materials.—The samples of 1-fluoropyrene and 12-fluorochrysene were kindly provided by Prof. G. M. Badger[13] of the University of Adelaide, South Australia, that of 9-fluoroanthracene by Dr. C. F. H. Allen[14], Eastman Kodak Co., Rochester, U. S. A. and that of cyclohexylfluoride by Dr. K. Okuhara of Government Industrial Research Institute, Nagoya, Japan, to whom the authors are much indebted. The samples of fluorobenzene[15], *m*-nitrofluorobenzene[16], 1- and 2-fluoronaphthalenes[15,17], 2- and 3-fluoropyridines[18] were prepared by the method of the Schiemann reaction. Since no NMR signal was found in 9-fluoroanthracene, the preparation of another sample of the compound was attempted by the general method of Garvey, Halley and Allen[14]. The reaction repeated under the conditions given was followed by some yellowing of the solution but no substance with the melting point specified for 9-fluoroanthracene was obtained.

Apparatus and Procedure.—The ^{19}F NMR spectra were measured with a Varian V-4300-B High Resolution Spectrometer operating at a fixed frequency of 40 Mc./sec. and equipped with a Varian Field Stabilizer. The sample was dissolved in

1) H. J. Bernstein and W. G. Schneider, *J. Chem. Phys.*, **24**, 468 (1956).
2) H. J. Bernstein, W. G. Schneider and J. A. Pople, *Proc. Roy. Soc.* (*London*), **A236**, 515 (1956).
3) J. A. Pople, *J. Chem. Phys.* **24**, 1111 (1956).
4) G. Hazato, ibid., **27**, 605 (1957).
5) J. C. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, **79**, 846 (1957).
6) K. Ito, ibid., **80**, 3502 (1958).
7) R. McWeeny, *Molec. Phys.*, **1**. 312 (1958).
8) C. E. Johnson, Jr. and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).
9) T. Isobe, K. Inukai and K. Ito, ibid., **27**, 1215 (1957).
10) R. McWeeny, ibid., **19**, 1614 (1951).
11) K. Fukui, S. Hattori, T. Yonezawa, R. Kusaka and H. Kitano, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zasshi*), **80**, 541 (1959).
12) All compounds are numbered in accordance with A. M. Patterson and L. T. Capell, "The Ring Index", Reinhold Publishing Corp., New York (1940).
13) G. M. Badger and J. F. Stephens, *J. Chem. Soc.*, **1956**, 3637.
14) B. S. Garvey, Jr., L. F. Hally and C. F. H. Allen, *J. Am. Chem. Soc.*, **59**, 1827 (1937).
15) G. Balz and G. Schiemann, *Ber.*, **60**, 1186 (1927).
16) K. Inukai and Y. Maki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 1305 (1957).
17) G. Schiemann, W. Gueffroy and W. Winkelmüller, *Ann.*, **487**, 270 (1930).
18) A. Roy and G. F. Hawkins, *J. Am. Chem. Soc.*, **69**, 2443 (1947).

about the same amount of another fluoro compound, *m*-nitrofluorobenzene in most cases, which provides an internal standard for determining the chemical shift δ of the sample defined as $\delta = 10^5 \times (H_c - H_r)/H_r$ where H_c is the applied magnetic field for the ^{19}F resonance in the sample and H_r is that for the reference. The chemical shift was determined by adjusting that of 1-fluoronaphthalene[9] to +1.32, refered to *m*-nitrofluorobenzene. The value of 1.32 was re-determined for the present work on the basis of the chemical shift of fluorobenzene[19] +0.33, agreeing with the previous one[9].

In the previous work[9], the δ-values obtained from the solutions, 1-fluoronaphthalene+*m*-nitrofluorobenzene, 2-fluoronaphthalene+*m*-nitrofluorobenzene and 1-fluoronaphthalene + 2-fluoronaphthalene, were found to be consistent in themselves. In the present work, the results obtained from the solutions, 2-fluoropyridine+*m*-nitrofluorobenzene, 3-fluoropyridine+*m*-nitrofluorobenzene and 2-fluoropyridine+3-fluoropyridine were, also consistent in themselves. Therefore, the bulk effects[20] for the chemical shifts were assumed to be insignificant in the present experiments.

A 33 mol. per cent solution of 9-fluoroanthracene in *m*-nitrofluorobenzene heated for increasing the solubility gave no signal except that of the solvent which was not greatly deformed compared with that of pure *m*-nitrofluorobenzene. Also no signal was obtained on a solution of 12-fluorochrysene in *m*-nitrofluorobenzene because of its low solubility. Both samples will be examined further.

Results and Discussion

It is known experimentally[21,22] that the magnetic shielding of an ^{19}F nucleus is quite sensitive to the nature of the bond between the fluorine atom in question and the atom to which the fluorine is bound. The simple and direct correlation[23] of ^{19}F magnetic shielding in para-substituted fluorobenzenes with the π-electron densities or Hamett's sigma constants for the para-position in the corresponding non-fluorinated compounds may also be attributed to the dependence of the shielding on the bonding nature of C–F bonds. On the other hand, Saika and Slichter[24] have shown theoretically that the ^{19}F magnetic shielding must have a close relation with the nature of the σ-bond by which the fluorine is bound to another atom. The qualitative extension of their theory suggests readily that a π-bond character in the bond by which the fluorine in question is bound to another atom would also have a significant effect on ^{19}F magnetic shielding. In order to discuss the present results, therefore, it would be necessary to take into account both σ- and π-bonding characters of C—F bonds. Since, however, correct estimations of σ- or π-bonding characters of C—F bonds in the compounds studied are very difficult, the following three molecular indexes which may serve as measures of σ- and π-bonding characters of C–F bonds are taken into account: (1) the π-electron density q on the ring carbon to which the fluorine in question is bound, (2) the π-electron "atom charge" density of McWeeny's sense[10] q' on the ring carbon mentioned above, and (3) the π-electron density q on the carbon atom of a CH_2^- group in a hypothetical molecule in which the fluorine atom of the fluoro compound studied is replaced by a CH_2^- group.

The π-electron densities on ring carbons may serve as a criterion for predicting chemical differences in these carbons and, consequently, differences in the σ-bonding nature of C–F bonds. The π-electron "atom charge" densities may also be usable from the same point of view. The latter, however, may be especially useful in alternant hydrocarbons in which the former fails to interpret chemical differences in ring carbons, being equal to unity on all carbons on the basis of the simple LCAO calculation. It would be worth noting that the π-electron "atom charge" densities on the 1- and 2-positions of naphthalene show a tendency consistent with the experimental observation[25]. The π-electron density on the carbon atom of the CH_2^- group in the hypothetical molecule mentioned above may serve as a measure of the π-conjugation of the fluorine atom substituted at the corresponding position. The smaller the π-electron density on the CH^-_2 group, the greater would be the π-conjugation of the fluorine atom with the remainder of the molecule.

The ^{19}F chemical shifts obtained in the present work are given in Table I, together with those of 1- and 2-fluoronaphthalenes. Three molecular indexes mentioned above are given in Tables II—IV, respectively. The parameters used in these tables for

19) H. S. Gutowsky, D. W. McCall, B. R. McGarvey and L. H. Meyer, ibid., 74, 4809 (1952).
20) B. P. Daily and J. N. Shoolery, ibid., 77, 3977 (1955); H. J. Bernstein and W. G. Schneider, *Nature*, 178, 1328 (1956).
21) H. S. Gutowsky and C. J. Hoffman, *J. Chem. Phys.*, 19, 1259 (1951).
22) L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, 57, 481 (1953).
23) H. S. Gutowsky, D. W. McCall, B. R. McGarvey and L. H. Meyer, *J. Am. Chem. Soc.*, 74, 4809 (1952).
24) A. Saika and C. P. Slichter, *J. Chem. Phys.*, 22, 26 (1954).
25) S. C. Abrahams, J. M. Robertson and J. G. White, *Acta Cryst.*, 2, 238 (1949).

TABLE I. ^{19}F CHEMICAL SHIFTS IN SOME MONOFLUORINATED COMPOUNDS

Compound	2-Fluoro-pyridine	Fluoro-benzene	2-Fluoro-naphthalene	1-Fluoro-pyrene	1-Fluoro-naphthalene	3-Fluoro-pyridine	Cyclohexyl-fluoride
δ	−4.27	0	0.16	0.97	0.99	1.25	5.63

TABLE II. THE π-ELECTRON DENSITIES ON RING CARBONS

Compound Position	Pyridine 2	Benzene	Naphthalene 2	Pyrene 1	Naphthalene 1	Pyridine 3	Ref.
Simple LCAO with[e]							
$\delta_N=1$, $\delta_{C'}=0$	0.855	1.000	1.000	1.000	1.000	1.008	a)
$\delta_N=1$, $\delta_{C'}=0.1$	0.893	1.000	1.000	1.000	1.000	0.984	b)
Jaffe's parameters	0.970	1.000	0.989		0.999	0.977	c)
SCF LCAO		1.000	1.003		0.967		d)

a) K. Higashi and H. Baba, "Quantum Organic Chemistry (Ryoshi Yuki Kagaku)", Asakura Publishing Co., Tokyo (1956).
b) Calculated by the present authors.
c) H. H. Jaffe, *J. Chem. Phys.*, **20**, 279, 778, 1554 (1952).
d) C. M. Moser, *J. chim. phys.*, **52**, 24 (1955).
e) The Coulomb integral of a nitrogen atom is given by $\alpha_N=\alpha_C+\delta_N\beta_{CC}$ where α_C is the Coulomb integral of a carbon atom and β_{CC} is the resonance integral of a C-C bond. The Coulomb integral of the carbon atom bonded to the nitrogen atom is given by $\alpha_{C'}=\alpha_C+\delta_{C'}\beta_{CC}$.

TABLE III. THE π-ELECTRON "ATOM CHARGE" DENSITIES ON RING CARBONS

Compound Position	Pyridine 2	Benzene	Naphthalene 2	Pyrene 1	Naphthalene 1	Pyridine 3
Simple LCAO with						
$\delta_N=1$, $\delta_{C'}=0$	0.644	0.756	0.757	0.771	0.767	0.784
$\delta_N=1$, $\delta_{C'}=0.1$	0.672	0.756	0.757	0.771	0.767	0.767[a]

a) If the inductive effect of nitrogen on β-carbon is taken into account as $\delta_C(\beta)=(0.1)^2$, this value takes 0.770

TABLE IV. THE π-ELECTRON DENSITY ON THE CARBON ATOM OF A CH_2^- GROUP SUBSTITUTED IN AN AROMATIC COMPOUND

Parent compound	Pyridine	Benzene	Naphthalene	Pyrene	Naphthalene	Pyridine
Position of substitution	2		2	1	1	3
Charge density on CH_2^-	1.499[a]	1.571[d]	1.529[d]	1.364[d]	1.450[d]	1.561[a]
	1.485[b]					1.542[b]
	1.464[c]					1.504[c]

a) Calculated with $\delta_N=1$, $\delta_{C'}=0$.
b) Calculated with $\delta_N=1$, $\delta_{C'}=0.1$.
c) Calculated with $\delta_N=2$, $\delta_{C'}=0.25$. This set of parameters was used by H. C. Longuet-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, **43**, 87 (1947). These parameters would overestimate the electronegative effect of nitrogen (see Refs. 26 and 27), but were used here in order to show an extreme case.
d) Calculated by the method of H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 265 (1950).

calculating the indexes of pyridine are their representative values[26,27]. The resonance integral of a C–N bond was assumed to be equal to that of a C–C bond, because small changes in resonance integrals have only negligible effects on the indexes in the tables. The values given in the second and the seventh columns of Table IV were calculated by the use of the mutual atom polarizabilities in a benzyl anion which are shown in Table V.

Fluorobenzene, 1- and 2-Fluoronaphthalenes, 1-Fluoropyrene and 3-Fluoropyridine. — The sequence of δ-values for these compounds is, as shown in Table I, fluorobenzene < 2-fluoronaphthalene < 1-fluoropyrene, 1-fluoronaphthalene < 3-fluoropyridine. As seen from Table II, the π-electron density on the ring carbon to which the fluorine atom is bound fails to explain the

26) R. D. Brown, *Quart. Revs.*, **6**, 63 (1952).
27) L. E. Orgel, T. L. Cottrell, W. Dick and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951).

TABLE V. MUTUAL ATOM POLARIZABILITIES IN A BENZYL ANION

$r-s$[a]	$\pi_{r,s}\times\beta$
1—1′	−0.1324
2—1′	−0.0716
3—1′	−0.0099
4—1′	−0.1162
1′—1′	0.4116

a) 1′ denotes a CH_2^- group, 1 the carbon atom bonded to the CH_2^- group and 2, 3 and 4 denote the α, β and γ carbon atoms, respectively.

sequence of δ, because the densities in benzene, naphthalene and pyrene are all equal to unity. The π-conjugation of fluorine atoms, the rough measure of which is seen from Table IV, fails also to interpret the sequence of δ. As far as one restricts the attention only to fluorobenzene, 1- and 2-fluoronaphthalenes, one may find a possible interpretation in terms of the assumption[11] that the greater the π-electron conjugation of a fluorine atom with a neighboring atom or group of atoms, the greater the value of δ. However, this assumption fails also definitely to interpret the sequence of δ if one takes into account 1-fluoropyrene and 3-fluoropyridine. On the other hand, the sequence of the π-electon "atom charge" density (Table III), benzene<2-position of naphthalene < 1-position of naphthalene < 1-position of pyrene < 3-position of pyridine, shows a fairly good parallel tendency with the sequence of δ mentioned above. Although the parallelism between two sequences is not very good in pyrene, the π-electron "atom charge" density may be rather satisfactory for interpreting the sequence of δ compared with other indexes, in the sense that the "atom charge" densities of the 1-position of pyrene and the 1-position of naphthalene are fairly close to each other and that the "atom charge" density of the 3-position of pyridine can be larger than that of the 1-position of naphthalene within the reasonable limits[26,27] of parameters δ_N and $\delta_{C'}$ (see Table III and footnote e) of Table II). Since the greater the value of q', the more ionic would be the C–F σ-bond, the increasing tendency of δ with q' is reasonable[24].

2-Fluoropyridine.—This compound has the smallest δ-value. This tendency can be interpreted in terms of any index given in Tables II—IV. However, the π-electon density would be rather worthless for this case too, because this index is very poor for interpreting the sequence of δ-values as discussed above. The effect of the π-conjugation of the fluorine atom substituted at the 2-position of pyridine is of interest from the point of view that the ^{35}Cl pure quadrupole resonance of 2-chloropyridine[28] has been explained, emphasizing the larger π-bonding character in the C-halogen bond at the 2-position compared with the π-bonding characters in those at other positions. The π-conjugation of the fluorine atom, however, may not be the main cause of the small δ-value of 2-fluoropyridine. Because, if it is so, the δ-value of 1-fluoronaphthalene must also very small contrary to the experiments. Therefore, the π-electron "atom charge" density and the inductive effect of nitrogen, which has the significant effect on proton NMR spectra of nitrogen heterocycles[29-31], would be responsible for the ^{19}F magnetic shielding of 2-fluoropyridine.

Cyclohexylfluoride.—This compound has a very great δ-value compared with that of benzene. It is obvious that this difference in δ is too great to be interpreted in terms of the diamagnetic ring current induced on benzene[2,3]. The assumption of Fukui et al. on the correlation of δ with the π-conjugation of the fluorine atom fails also to interpret the δ-value of this compound which is greater than that of fluorobenzene. A possible explanation is that the C–F bond in cyclohexylfluoride is more ionic than that in fluorobenzene. Such an explanation may be rather probable, since it is known that[32] the nature of the σ-bonding in a C(sp^3)–Cl bond is more ionic than that in a C(sp^2)-Cl bond and that[32,33] the ring hydrogens of benzene are more protonic than the hydrogens of C(sp^3)–H bonds.

In the arguments given above, it has been shown that the ^{19}F magnetic shielding of the compounds studied in the present work is correlated most probably with the π-electron "atom charge" density. Hereupon, it would be worth while to note

28) P. J. Bray, R. G. Barnes and S. L. Segel, *J. Chem. Phys.*, **28**, 99 (1958).
29) H. J. Bernstein and W. G. Schneider, ibid., **24**, 469 (1956).
30) L. H. Meyer, A. Saika and H. S. Gutowsky, *J. Am. Chem. Soc.*, **75**, 4567 (1953).
31) H. S. Gutowsky, R. L. Rutledge and M. Tamres, ibid., **76**, 4242 (1954).
32) Y. Kurita, *J. Japanese Chem.* (*Kagaku no Ryoiki*), **10**, 24 (1956). See also J. Duchesne, *J. Chem. Phys.*, **19**, 246 (1951).
33) H. W. Thompson, *Trans. Faraday Soc.*, **46**, 103 (1950); G. M. Barrow and D. C. McKean, *Proc. Roy. Soc.* (*London*), **A213**, 27 (1952); I. M. Mills and H. W. Thompson, ibid, **A228**, 287 (1955).

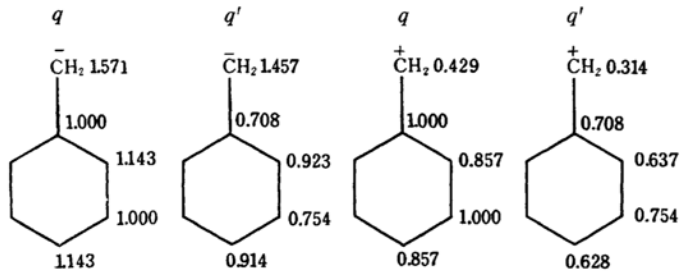

Fig. 1. The π-electron densities (q) and π-electron "atom charge" densities (q') in a benzyl anion and cation

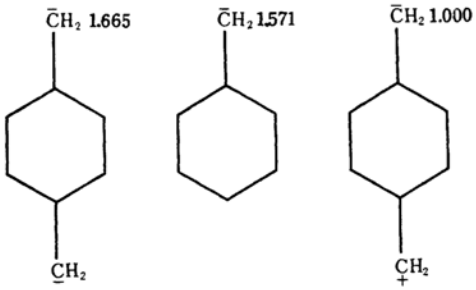

Fig. 2. π-electron densities in some carbions

that the ^{19}F magnetic shielding in substituted fluorobenzenes[23], which has been correlated simply with the π-electron density q, may also be correlated with the π-electron "atom charge" density q', because q and q' have the parallel tendency as shown in Fig. 1. On the other hand, Fig. 2 predicts that the π-conjugation of a fluorine atom, which is represented by CH_2^- in the figure, may be reduced by the para-substitution of $-E$ substituents (halogens, OH, NH_2, etc.) and is increased by that of $+E$ substituents (NO_2, CN, etc.). These predictions suggest that the assumption[11] of Fukui et al. may lead to the contradictory results with the experiments. The pure nuclear quadrupole resonance experiments on para-substituted chlorobenzenes[34] and iodobenzenes[35] have shown that the σ-bond character of a C–halogen bond is made more ionic by the para-substitution of $-E$ substitution and less ionic by that of $+E$ substituents, whereas the double-bond character of the C–halogen bonds is reduced by the para-substitution of $-E$ substituents and is increased by that of $+E$ substituents. These results support the interpretation of ^{19}F magnetic shielding in para-substituted fluorobenzenes in terms of q' or ionicity in C–F bonds, but do not support the interpretation of the same subject in terms of the assumption of Fukui et al. It would also be worth noting that the relative magnetic shielding of CF_4 and CF_3Cl, which has been one of the important experimental evidences for supporting the assumption of Fukui et al., is not necessarily interpreted merely by their assumption, but is also interpreted by the variation in polarity in C–F bonds as argued in the original paper[36].

34) H. C. Meal, *J. Chem. Phys.*, **24**, 1011 (1956); C. Dean, *Phys. Rev.*, **86**, 607 (1952); Y. Kurita, *Chemistry (Kagaku)*, **12**, 556 (1957).
35) G. W. Ludwig, *J. Chem. Phys.*, **25**, 159 (1956).

Summary

The ^{19}F NMR spectra of 2- and 3-fluoropyridines, 1-fluoropyrene, cyclohexyl-fluoride, 9-fluoroanthracene and 12-fluorochrysene were studied. No signal was obtained for the latter two compounds. The magnetic shielding constants obtained were attempted, together with those for fluorobenzene, 1- and 2-fluoronaphthalenes, to be correlated with some molecular indexes. It was found that the π-electron density in McWeeny's sense (π-electron "atom charge" density) on the ring carbon atom, to which the fluorine in question is bound, is must probably correlated with the magnetic shielding of the fluorine nucleus. This result suggests that the variation in ^{19}F magnetic shielding constants in these compounds may be attributed mainly to the variation in polarity in C–F σ-bonds. It was noted that such an idea is supported by nuclear quadrupole resonance experiments.

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