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An ESR Study of the 4,4'-Difluorobiphenyl Cation Radical[*]

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The ESR spectra of the 4,4'-difluorobiphenyl cation show resolved second-order splittings and a marked line-broadening attributable to the modulation of the ^{19}F anisotropic hyperfine interactions by the tumbling motion. This dipolar broadening is mainly observed for the lines associated with the triplet state ($I=1$) of the two equivalent ^{19}F nuclei. When the temperature is lowered, the wings of the triplet due to the two ^{19}F and the downfield second-order components become broad and finally disappear. The dipolar contributions to the line widths are calculated as a function of the correlation time for the molecular motion, τ_2. Furthermore, the ESR observation of the ^{13}C hyperfine structures is carried out, and the spin densities on each ring carbon and the fluorine atoms are experimentally determined. From the spin densities thus determined, the parameters in the equation

$$a_F = Q^F_{CF}\rho^\pi_C + Q^F_{F(FC)}\rho^\pi_F,$$

in which the ^{19}F hyperfine coupling constant is correlated to the π spin densities on the fluorine atom and the adjacent carbon atom, are estimated to be $Q^F_{CF}=39$ and $Q^F_{F(FC)}=324$ G.

Recently there have been a number of ESR and NMR studies of fluoro-substituted alkyl and aromatic radicals in solution. The objectives of these studies may mainly be classified as follows; (1) The ESR spectra of fluoro-substituted radicals show a viscosity-dependent selective line-width effect due to a relaxation process brought about by the modulation of the relatively large anisotropic fluorine splitting by the tumbling motion. The information about the motion of molecules in solution was extracted from the analysis of their temperature-dependent selective line width. The fluorinated alkyl radicals ordinarily have simple ESR spectra and show large fluorine hyperfine coupling constants, so that the line width of the spectra can be determined with great precision. Consequently, the temperature dependence and selective variations in line widths were studied in detail for fluorinated alkyl radicals.1—3) There has been no detailed study of the fluoro aromatic radicals, however, because of the small values of the ^{19}F hyperfine splitting. (2) The hyperfine coupling constants, a_F, of fluorine atoms in fluoro-substituted aromatic radicals depend on both the spin density, ρ^π_C, at the adjacent carbon atom and the spin density, ρ^π_F, at the fluorine atom. There have been numerous investigations of the fluoro aromatic radicals, and a consistent functional relationship between the isotropic fluorine splitting and the π spin densities has been proposed.11—19) Mainly, two types of equations have been examined;

$$a_F = Q^F_{CF}\rho^\pi_C \qquad (1)$$

$$a_F = Q^F_{CF}\rho^\pi_C + Q^F_{F(FC)}\rho^\pi_F \qquad (2)$$

Here, Q^F_{FC} is the π–σ contribution analogous to that of the aromatic C–H fragment. $Q^F_{F(FC)}$ is the contribution from the π–σ polarization of the 1s and 2s electrons of fluorine by the spin density centered on the 2p$_\pi$ orbital of fluorine.

The results of the ESR and NMR investigations indicate that the simple linear relationship, Eq. 1, may be inadequate to describe the data of fluorinated compounds. Equation 2 seems more realistic than Eq. 1 in that it allows for conjugation on the fluorine 2p$_\pi$ orbital with the π electrons in the aromatic ring. The previously determined values of Q's in Eq. 2 are, however, scattered over a wide range because the π fluorine spin densities are usually not obtained by solution ESR studies; the simple LCAO MO approach to the calculation of the ρ^π_F is, then, not necessarily valid.

In the present paper, we wish to report the results of ESR studies of the 4,4'-difluorobiphenyl cation radical. The value of the ^{19}F hyperfine coupling constant is quite large (19.20 G) compared with those of the fluoro aromatic radicals, and a second-order splitting of ^{19}F and a temperature-dependent broadening of ^{19}F splitting were observed. Furthermore, the spin densities on each ring carbon and fluorine atom were experimentally determined based on the observation of the ^{13}C hyperfine splittings for ring carbons, and the Q values of Eq. 2 were discussed.

Experimental

4,4'-Difluorobiphenyl (mp 88—89 °C) was synthesized and recrystallized from ethanol. The cation radicals was generated by SbCl$_5$ oxidation in CH$_2$Cl$_2$ in a manner described before.7) The ESR spectrum of the 4,4'-difluorobiphenyl cation radical was observed using a JEOL-ME-3X spectrometer operating with a 100 kHz magnetic field modulation. The magnetic field was calibrated by means of a perylene cation radical prepared in concentrated sulfuric acid.

Results and Discussion

Temperature-dependent Line Broadening of the ^{19}*F Splittings.* The high-resolution ESR spectrum of the 4,4'-difluorobiphenyl cation radical was observed in the temperature range from −90 to +20 °C. The spectrum observed at +10 °C is shown in Fig. 1-a. This spectrum consists of a large triplet of 19.20 G due to two ^{19}F nuclei (a_F), each line of which splits into a quintet of 2.76 G due to the four ring ortho-protons (a^H_2)8); the central component ($I_z=0$ lines) of the triplet further splits, by means of the second-order effect, into a doublet of 250 mG corresponding to the possible values ($I=1$, 0) of the resultant nuclear angular momentum for the two

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equivalent ^{19}F nuclei. As is well known, the second-order splitting of the $I_z=0$ component of the first-order triplet is $(a_F)^2/H_0$, where H_0 is the position of the center of the spectrum.6) The expected value of $(a_F)^2/H_0$ is about 100 mG, taking $a_F=19.20$ and $H_0=3300$ G, but the observed splitting is larger than that theoretically expected. This is probably due to the line broadening attributed to the modulation of the ^{19}F anisotropic hyperfine interactions as a result of the tumbling motion, which makes the accurate measurement of the hyperfine splittings difficult.

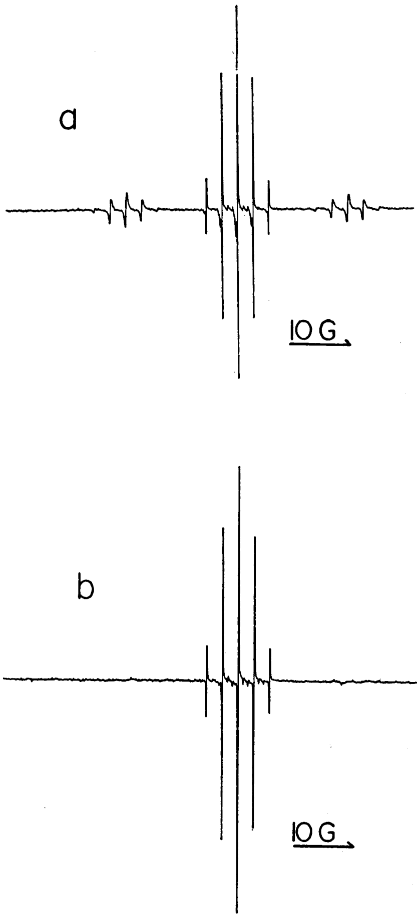


Fig. 1. The ESR spectra of 4,4′-difluorobiphenyl cation radical. a) +10 °C. b) −80 °C.

Upon a lowering of the temperature, the wing lines of the triplet due to the two ^{19}F, and the downfield second-order components ($I=1$, $I_z=0$) become broad and finally disappear, while the central quintet ($I=0$ lines) is unaffected, as is shown in Fig. 1-b.

For organic radicals in solution, it is well known1−3) that the line width variations in the various second-order components are mainly due to a relaxation process brought about by the modulation of the anisotropic hyperfine coupling tensor by rotational Brownian motion; this theory is well established.4,5)

The dipolar contribution to the line width of the (I, I_z) hyperfine components can be calculated as a function of the molecular rotational correlation time τ_2, using a spin Hamiltonian for a system undergoing dipolar relaxation.

Assuming a set of completely equivalent ^{19}F nuclei with an axially symmetric hyperfine tensor, the main term of the dipolar contribution to the line width is given by:4,5)

$$T_{2d}^{-1} = \frac{A_{//}^2}{40}[(3I(I+1)+5I_z^2)J_0+(7I(I+1)-I_z^2)J_1] \tag{3}$$

where $J_0=\tau_2$, $J_1=\tau_2(1+\omega^2\tau_2{}^2)^{-1}$, and $A_{//}$ is the parallel component of the anisotropic part of the hyperfine tensor. From the line widths of the $I_z=\pm 1$ lines, the correlation times, τ_2, are estimated using Lorentzians with line widths given by:

$$[T_2(I, I_z)]^{-1} = [T_{2d}(I, I_z)]^{-1} + T_{20}^{-1} \tag{4}$$

where T_{20} accounts for the other relaxation processes and T_{20}^{-1} is assumed to be 80 mG. The experimental value of $A_{//}$ is not known for the cation radical of 4,4′-difluorobiphenyl. Therefore, the estimation of $A_{//}$ was performed in the following way.

The anisotropic component of the ^{19}F hyperfine tensor for a $\gg$C–F fragment may be described by the following equation9,23):

$$\boldsymbol{B}_F = \boldsymbol{B}_C^\pi \rho_C^\pi + \boldsymbol{B}_F^\pi \rho_F^\pi + \boldsymbol{B}_F^\sigma \rho_F^\sigma \tag{5}$$

where $\boldsymbol{B}_C^\pi$, $\boldsymbol{B}_F^\pi$, and $\boldsymbol{B}_F^\sigma$ are the anisotropic tensors due to the interaction of a fluorine nucleus with carbon $2p_\pi(\rho_C^\pi=1)$, fluorine $2p_\pi(\rho_F^\pi=1)$, and fluorine $2p_\sigma(\rho_F^\sigma=1)$ electrons respectively. The principal values of $\boldsymbol{B}_C^\pi$ and $\boldsymbol{B}_F^\pi$ have been calculated by Cook *et al.*9) and Morton *et al.*24) respectively. According to Iwasaki *et al.*,23) Eq. 5 may be represented in this form:

$$\boldsymbol{B}_F = (\boldsymbol{B}_C^\pi + \boldsymbol{Q}_{CF}^F)\rho_C^\pi + (\boldsymbol{B}_F^\pi + \boldsymbol{Q}_{CF}^F)\rho_F^\pi \tag{6}$$

where $\boldsymbol{Q}_{CF}^F$ and $\boldsymbol{Q}_{FC}^F$ are the tensor polarization factors of the $F_{2p\sigma}$ electrons arising from the unit spin density in $C_{2p\pi}$ and $F_{2p\pi}$ respectively, and where the parameters, $\boldsymbol{Q}_{CF}^F$ and $\boldsymbol{Q}_{FC}^F$, have been experimentally determined.

Using Eq. 6, the value of $A_{//}$ in Eq. 4 was estimated to be 41 G based on the spin densities, ρ_C^π and ρ_F^π, determined from the ^{13}C hyperfine splittings for the ring carbons (see Table 2 and the following section). The values of τ_2 obtained are 1.5×10^{-10} s at −60 °C and 0.8×10^{-10} s at +10 °C. These correlation times are typical of those found for similar molecules in liquids by a study of the relaxation mechanism of ENDOR.10)

Estimate of Q *Values.* As is shown in Fig. 2, four kinds of ^{13}C hyperfine splitting were recorded. The absolute values of these hyperfine coupling constants are much like those of the ring carbon atoms of the 4,4′-bitolyl cation radical, as has already been reported7) (see Table 1). In previous works, it has been reported that the substitution of fluorine for hydrogen has little effect on the spin-density distribution.9,11−14) The ^{13}C hyperfine coupling constants, therefore, can more easily be assigned than those of the 4,4′-bitolyl cation radical; $a_1^C=-0.78$, $a_2^C=1.90$, $a_3^C=-3.57$, and $a_4^C=6.92$ G. The experimental values of the ring spin densities were obtained from the ring proton hyperfine splittings, a_2^H, and the ^{13}C hyperfine splittings, a_1^C, based on the Colpa-Bolton20) and the Karplus-Fraenkel21) formulae:

$$a_i^H = Q_{CH}^H \rho_i^\pi + K_{CH}^H[\rho_i^\pi]^2 \tag{7}$$

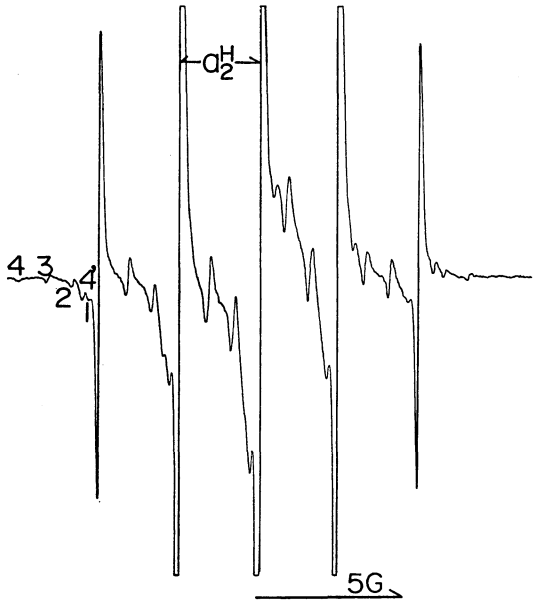


Fig. 2. The ^{13}C splitting of the ring carbon atoms of 4,4′-difluorobiphenyl cation radical. The figures denote the ring position.

$$a_i^C = (S^C + \sum_{k=1}^{3} Q_{C_iX_k}^C)\rho_i^\pi + \sum_{k=1}^{3} Q_{X_kC_i}^C \rho_k^\pi \tag{8}$$

The parameters in Eq. 7 were taken as $Q_{CH}^H = -27$ and $K_{CH}^H = -12$ G, while the parameters in Eq. 8 were taken as $S^C = -12.7$ G, $Q_{C_iX_k}^C (Q_{C_iH}^C = 19.5$, $Q_{C_iC_k}^C = 14.4$ G), and $Q_{C_iC_k}^C = -13.9$ G. The experimental values of the spin density are summarized in Table 2. Here, the fluorine spin densities were obtained by the normalization of the total spin density. For comparison, Hückel- and McLachlan-type calculations were carried out, taking the Coulomb integral and resonance integral to be $\alpha_F = \alpha_C + 2.5\beta_C$ and $\beta_{CF} = 0.62\beta_C$.[11] The results are summarized in Table 2. As may be seen in Table 2, the values of the spin densities for the 4,4′-difluorobiphenyl cation radical are nearly the same as those for the 4,4′-bitolyl cation radical, and the similarity in the spin densities on the ring carbon atoms shows that the substitution of fluorine for hydrogen does not produce a large perturbation in the overall spin densities.

The evaluation of Q_{CF}^F and $Q_{F(CF)}^F$ in Eq. 2 requires the values of ρ_C^π and ρ_F^π. Nevertheless, there have been few studies in which ρ_C^π and ρ_F^π were experimentally determined, and the simple LCAO MO approach to the estimation of ρ_F^π is not necessarily valid.

Recently Icli and Kreilick[12,13] experimentally determined the values of both ρ_C^π and ρ_F^π for a series of fluorinated phenoxyl radicals based on the measurement of the paramagnetic chemical shift in NMR; they also examined Eq. 2. For a series of fluorinated phenoxyl radicals, the ratios of ρ_C^π to ρ_F^π at the adjacent carbon are nearly constant (0.07). This situation is not feasible for determining the individual values of Q_{CF}^F and $Q_{F(FC)}^F$, because two sets of data on ρ_F^π and ρ_C^π with very different ratios (ρ_F^π/ρ_C^π) should be chosen for obtaining accurate Q values.

On the other hand, for the 4,4′-difluorobiphenyl cation radical the ratio of ρ_F^π to ρ_C^π at the adjacent carbon is much larger (0.27) than those for other fluorinated aromatic radicals, and this situation is very favorable for estimating the values of Q_{CF}^F and $Q_{F(FC)}^F$ accurately. The estimation of the values of Q's was carried out using a_F and the spin densities, ρ_C^π and ρ_F^π, obtained for the 4,4′-difluorobiphenyl cation, together with those for the 4-(*p*-fluorophenyl)-2,6-di-*t*-butylphenoxyl radical.[13] The estimated values of the parameters are $Q_{F(FC)}^F = 324$ and $Q_{CF}^F = 39$ G.

In order to examine the validity of our parameters, we applied the present Q values to the fluorine coupling constants of several compounds previously studied. In Table 3, the experimental and calculated fluorine coupling constants are summarized. We found that our two-parameter equation, $a_F = 324\rho_F^\pi + 39\rho_C^\pi$, gives a consistent explanation in every case.

Based on the experimental finding that fluorine substitution has little effect on the ring spin densities except for the at the adjacent carbon,[9,11-14] we assumed that the original spin density, ρ_C^0, on the carbon atom in the parent molecule is shared by the carbon atom and the fluorine atom;

$$\rho_C^\pi + \rho_F^\pi = \rho_C^0 \tag{9}$$

By substituting Eq. 9 into Eq. 2, we obtain:

$$a_F = [(Q_{F(FC)}^F - Q_{CF}^F)K + Q_{CF}^F]\rho_C^0 = Q_{eff}\rho_C^0 \tag{10}$$

TABLE 1. THE OBSERVED VALUES OF THE PROTON AND ^{13}C HYPERFINE COUPLING CONSTANTS (G)

		a_2^H	a_3^H	$a_4^F(a_4^{CH_3})$	a_1^C	a_2^C	a_3^C	a_4^C
4,4′-Difluorobiphenyl	Cation	2.76	—	19.20	−0.78	1.90	−3.57	6.92
	Anion[22]	2.28	—	3.13				
4,4′-Bitolyl	Cation[7]	2.64	—	8.79[a]	—	1.83	−3.59	8.47

a) Methyl proton hyperfine coupling constant.

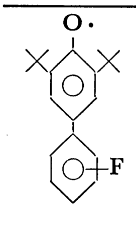
TABLE 2. EXPERIMENTAL AND THEORETICAL SPIN DENSITIES

Position		1	2	3	4	F
4,4′-Difluorobiphenyl cation	Exptl	0.1171	0.0980	−0.0028	0.1517 (0.1925)[a]	0.0408
Hückel		0.1190	0.0800	0.0269	0.1514	0.0167
McLachlan	$\lambda = 1.2$	0.1265	0.0905	−0.0108	0.1975	0.0165
4,4′-Bitolyl cation[7]	Exptl	—	0.0939	0.0172	0.1945	

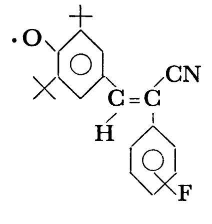
a) This value is the sum of the ρ_4^π and ρ_F^π values experimentally determined.

Table 3. Carbon and fluorine spin densities and calculated and experimenal fluorine coupling constants

	$\rho_C^\pi \times 10^2$	$\rho_F^\pi \times 10^3$	$\left(\frac{\rho_F^\pi}{\rho_C^\pi}\right) \times 10^2$	a_F (G) Exptl	a_F (G) Calcd	Lit
4,4′-Difluorobiphenyl	15.17	40.08	26.9	19.20	19.14	55)
I	−2.45	−1.70	7.0	−1.42	−1.48	13)
II	7.11	5.28	7.4	4.45	4.48	
A	3.64	2.23	6.1	1.66	2.14	12)
B	−1.77	−1.68	9.5	−1.11	−1.23	
C	5.31	4.61	8.6	3.60	3.56	



I: *m*-fluoro
II: *p*-fluoro



A: *o*-fluoro
B: *m*-fluoro
C: *p*-fluoro

where K is the ratio of ρ_F^π to ρ_C^π and $Q_{eff}=(285K+39)$ G, using our estimated values. This equation corresponds to Eq. 1.

In respect of Eq. 1, many investigators have reported that the experimentally or semiempirically determined values of Q are scattered over a wide range from molecule to molecule.[11–23] This is not surprising, because the K ratio is certainly not a constant for different molecules. Perhaps the K ratio depends on the double-bond character of the C–F bond, as has previously been proposed by Eaton *et al.*[11] For example, the fluorine hyperfine coupling constant of the 4,4′-difluorobiphenyl cation radical is about six times as large as that of the 4,4′-difluorobiphenyl anion radical,[22] but the spin densities of the anion and cation, based on the LCAO MO calculations, are nearly identical with each other. These results are analogous to the case of the hyperconjugation of the methyl group (see Tables 1 and 2). We can, therefore, consider that the value of Q_{eff} in Eq. 10 is related to the degrees of π-conjugation between the $2p_z$ orbital of fluorine atom and the $2p_z$ orbital of carbon which is adjacent to fluorine. That is, the large value of Q_{eff} represents the strong conjugation of the π system on the C–F fragment. As a result of this strong conjugation, the spin density on the fluorine atom and the K ratio increase. Indeed, the estimated value of Q_{eff} for the 4,4′-difluorobiphenyl cation is very large (100 G), and the corresponding K value reaches 0.21.

The numerical calculations were carried out mainly at the Computing Center of Ehime University.

References

1) J. Cooper, A. Hudson, R. A. Jackson, and M. Townson, *Mol. Phys.*, **23**, 1155 (1972).

2) P. Meakin and P. J. Krusic, *J. Am. Chem. Soc.*, **95**, 8186 (1973).

3) K. S. Chen, P. J. Krusic, P. Meakin, and J. K. Kochi, *J. Phys. Chem.*, **78**, 2014 (1974).

4) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 326 (1963).

5) A. D. McLachlan, *Proc. R. Soc. London, Ser. A.*, **280**, 271 (1964).

6) R. W. Fessenden, *J. Chem. Phys.*, **37**, 747 (1962).

7) K. Ishizu, M. Ouchi, F. Nemoto, and M. Suga, *Bull. Chem. Soc. Jpn.*, **46**, 2932 (1973).

8) P. H. Fisher and H. Zimmerman, *Tetrahedron Lett.*, **1969**, 797; M. J. Shaw, J. A. Weil, H. H. Hyman, and R. Filler, *J. Am. Chem. Soc.*, **92**, 5096 (1970).

9) R. J. Cook, J. R. Rowlands, and D. H. Whiffen, *Mol. Phys.*, **7**, 31 (1963).

10) K. Ishizu, M. Ohnishi, and H. Shikata, *Bull. Chem. Soc. Jpn.*, **50** 76 (1977).

11) D. R. Eaton, A. D. Josey, W. D. Phillips, and E. Benson, *Mol. Phys.*, **5**, 407 (1962).

12) W. G. Esperson and R. W. Kreilick, *Mol. Phys.*, **16**, 577 (1969).

13) S. Icli and R. W. Kreilick, *J. Phys. Chem.*, **75**, 3462 (1971).

14) S. V. Kulkarni and C. Trapp, *J. Am. Chem. Soc.*, **92**, 4801 (1970).

15) H. Konishi and K. Morokuma, *J. Am. Chem. Soc.*, **94**, 5603 (1972).

16) J. Sinclair and D. Kivelson, *J. Am. Chem. Soc.*, **90**, 5074 (1968).

17) A. Carrington, A. Hudson, and H. C. Longuet-Higgins, *Mol. Phys.*, **9**, 377 (1965).

18) W. E. Geiger, Jr. and W. M. Gulick, Jr., *J. Am. Chem. Soc.*, **91**, 4657 (1969).

19) W. R. Knolle and J. B. Bolton, *J. Am. Chem. Soc.*, **91**, 5411 (1969).

20) J. P. Colpa and J. R. Bolton, *Mol. Phys.*, **6**, 273 (1963).

21) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

22) A. L. Allred and L. W. Bush, *Tetrahedron*, **24**, 6883 (1968).

23) M. Iwasaki, S. Noda, and K. Toriyama, *Mol. Phys.*, **18**, 201 (1970).

24) J. R. Morton, J. R. Rowlands, and D. H. Whiffen, *Circ. Nat. Phys. Lab.*, No. BPR13 (1962).