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ESR LINE-SHAPE EFFECTS IN THE PRESENCE OF SECOND-ORDER SPLITTINGS OBSERVED FOR 4,4'-DIFLUOROBIPHENYL CATION

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ESR spectra of 4,4'-difluorobiphenyl cation in solution show resolved second-order splittings and marked line-broadening attributable to the modulation of tumbling motion of the ^{19}F anisotropic hyperfine interactions. This dipolar broadening is mainly observed for the line associated with the triplet state of the two equivalent ^{19}F nuclei and at -90°C, only the singlet line is readily detectable.

ESR studies of line-shape effects in the presence of second-order splittings have been booming on the fluorinated alkyl radicals, but there is no detailed studies on the fluoro aromatic radicals. We wish to report here the second-order splitting of ^{19}F and the temperature dependent broadening of ^{19}F splitting noted for the 4,4'-difluorobiphenyl cation radical.

The cation radical was generated by $SbCl_5$ oxidation in CH_2Cl_2 in the manner described before.1) The ESR spectra of 4,4'-difluorobiphenyl cation radical were observed in the temperature range from +20°C to -90°C.

The spectrum at +10°C (Fig. 1-a) consists of a large triplet of 19.20 G due to two ^{19}F nuclei, each line of which splits into quintet of 2.76 G due to the four ring ortho-protons and the central components ($M^F=0$ lines) of the triplet are further split by second-order effect into doublet of ~250 mG corresponding to the two possible values of the resultant nuclear angular momentum for two ^{19}F nuclei $I^F=1$, 0.2) The analyzed hyperfine coupling constants were nearly comparable with the values already reported by Fisher.3)

The relative amplitudes of the ^{19}F-splittings, however, deviate from the expected ratio. Upon lowering temperature, the wing lines of the triplet due to two ^{19}F, and the downfield second order components ($I_F=1$, $M_F=0$) become broad, while the central quintet ($I_F=0$ lines) is unaffected, as shown in Fig.1-b.

The viscosity-dependent selective lines broadening is, mainly, due to a relaxation process brought about by the modulation of the anisotropic component of the hyperfine coupling tensor for the two ^{19}F nuclei by the rotational Brownian motion.

The dipolar contribution to the line width of the (M_F, I_F) hyperfine components can be calculated as a function of the molecular rotatinal correlation time τ_2 using a spin Hamiltonian for a system undergoing dipolar relaxation.4,5,6)

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

$$T_2^{-1} = \frac{A_{/\!/}^2}{40}\left[(3I_F(I_F+1)+5M_F^2)J_0 + (7I_F(I_F+1)-M_F^2)J_1\right]$$

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.

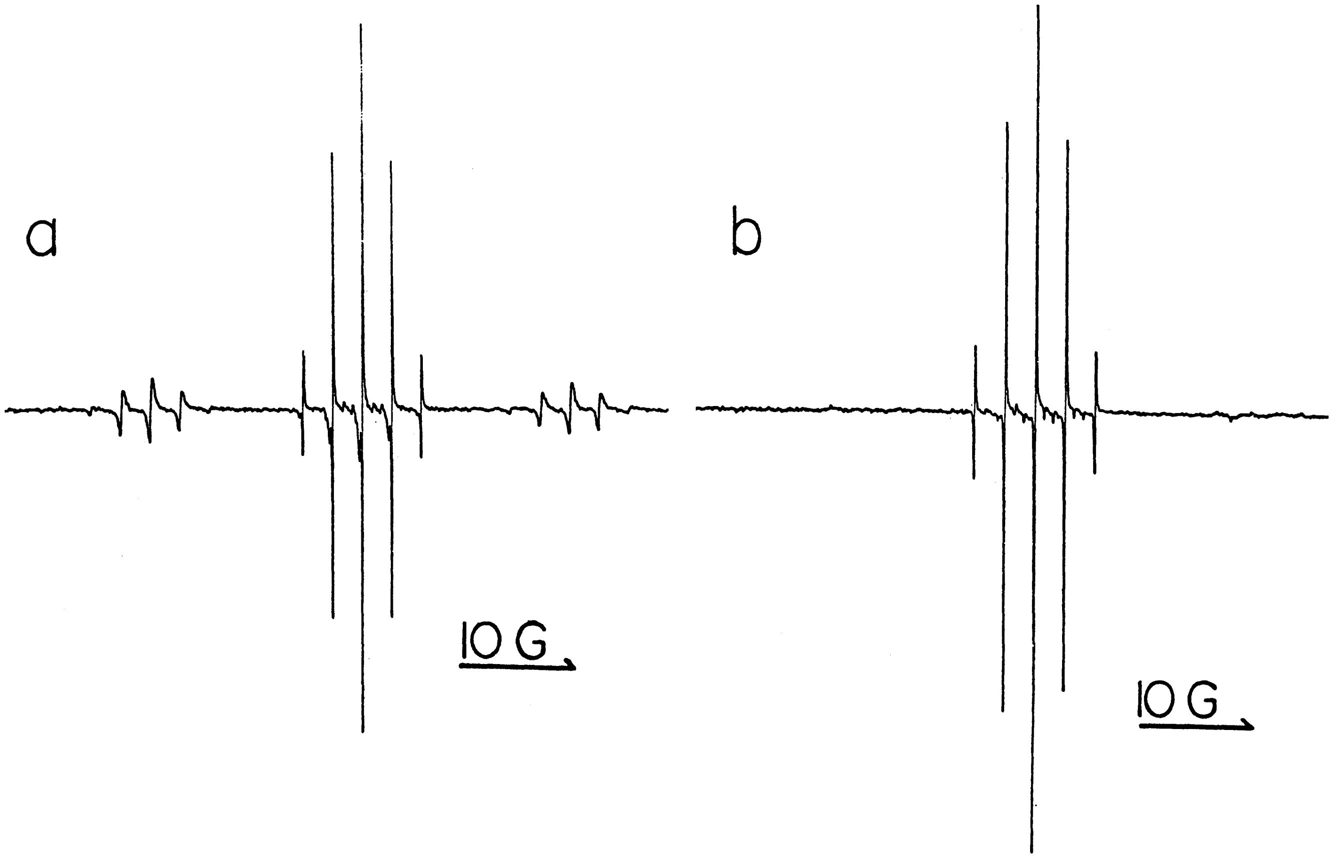

Fig. 1. ESR spectra of 4,4'-difluorobihenyl cation radical.
a) +10°C.
b) -80°C.

This equation shows that the singlet state line is unaffected by the dipolar mechanism, but the other triplet state lines are broadened as the temperature is lowered and furthermore, that line width would be greatest for the $M_F=\pm1$ components. Our experimental results are in good accordance with the theoretical analysis of the ESR line shape of the radicals.

The detailed treatments of the line width, T_2, related with the correlation time, τ_2, for the rotational Brownian motion are now under way.

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