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ESR Studies of the Conformational Interconversion of the 9,10-Dihydrophenanthrene Radical Anion and Its Related Compounds

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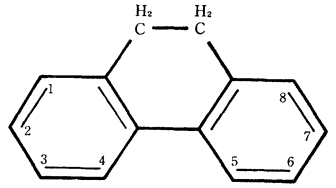
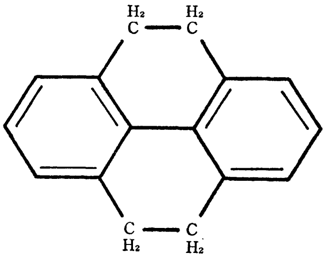
The ESR spectra of the 9,10-dihydrophenanthrene radical anion change drastically with the temperature, and at temperatures around −30°C the spectra show a marked line-width alternation effect. These temperature-dependent ESR spectra and the line-width alternation effect have been interpreted in terms of the conformational interconversion of the 9,10-dihydrophenanthrene radical anion molecule. From an analysis of the spectra, the activation energy of the inversion has been estimated to be 6.3 ± 0.6 kcal/mol. It has also been estimated, from the ratio of the axial and equatorial proton splittings, that the dihedral angle of the axial protons is about 11°. These data are compared with those of the 4,5,9,10-tetrahydropyrene radical anion. The ESR of the 4,5-dihydropyrene radical anion is also presented.

The conformational interconversion of several bridged biphenyls has been investigated by means of NMR[1,2] and ESR,[3] and also by the observation of the racemization of optically-active biphenyls.[4–7] The inversional motion of the neutral molecule of 9,10-dihydrophenanthrene (I) has been studied by the NMR[1] and the optical methods.[6] However, the techniques of NMR or optical measurements were not effective in obtaining information about the inversion process of the 9,10-dihydrophenanthrene molecule, because the inversion process was too fast to be treated by the NMR or optical measurements. In a previous paper,[3] we observed a line-width alternation effect in the ESR of the radical anion of 4,5,9,10-tetrahydropyrene (II) and explained it in terms of the inversional motion of the molecule. The ESR technique is sometimes quite effective in the study of fast rate processes; it makes possible the measurements of much faster rate processes than in the case of the NMR and optical methods.



[I]



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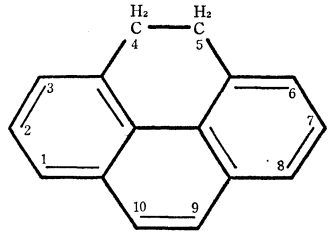

[III]

In this paper, we wish to report on the inversion process of the radical anion of 9,10-dihydrophenanthrene as studied by the ESR method. We observed a line-width alternation effect in the ESR similar to that of the 4,5,9,10-tetrahydropyrene radical anion. This line-width alternation effect can be explained as arising from the rapid modulation of the methylene proton hyperfine splitting constants due to exchange between an axial and equatorial state by means of the inversional motion of the molecule. The data obtained for this inversion process and the structure of the molecule are compared with those of the 4,5,9,10-tetrahydropyrene radical anion. In connection with these compounds, the 9,10-dihydropyrene radical anion has also been studied by the ESR method.

Experimental

The 9,10-dihydrophenanthrene and 4,5-dihydropyrene were obtained commercially. The 9,10-dihydrophenanthrene was purified by recrystallization from ethyl alcohol (mp 34—35°C), and the 4,5-dihydropyrene, by column chromatography (mp 130—131°C). The radical anions were prepared by alkali metal reduction in ethereal solvents by the previously-established technique.[8] ESR measurements were carried out by means of a Hitachi X-band ESR spectrometer. Variable temperature experiments were performed using a gas-flow temperature control method previously described.[3] The temperature of the samples was monitored by means of a copper-constantan thermocouple which was fixed just below the sample tube.

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1) M. Ōki, H. Iwamura, and N. Hayakawa, This Bulletin, **36**, 1542 (1963); **37**, 1865 (1964).

2) R. J. Kurland, M. B. Rubin, and W. B. Wise, *J. Chem. Phys.*, **40**, 2426 (1964).

3) M. Iwaizumi and T. Isobe, This Bulletin, **38**, 1547 (1965).

4) K. Mislow and M. A. W. Glass, *J. Amer. Chem. Soc.*, **83**, 2780 (1961).

5) K. Mislow and H. B. Hopps, *ibid.*, **84**, 3018 (1962).

6) K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon, and G. H. Wahl, Jr., *ibid.*, **86**, 1710 (1964).

7) K. Mislow, R. Graeve, A. J. Gordon, and G. H. Wahl, Jr., *ibid.*, **86**, 1733 (1964).

8) J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 3307 (1964).

Results and Discussion

Line-width Alternation Effect in the ESR spectra of the 9,10-Dihydrophenanthrene Radical Anion and the Inversional Motion of the Molecule. As Fig. 1 shows, the hyperfine structure of the ESR spectra of the 9,10-dihydrophenanthrene radical anion changes markedly with the temperature. This change in the hyperfine structure with the temperature comes mainly from the change in the hyperfine components due to the methylene protons. The spectrum at low temperatures (Fig. 1a, 4) can be analyzed in terms of the difference in the splitting constant for the axial and the equatorial methylene protons, and the four sets of triplet splittings due to the four sets of two equivalent ring protons. A typical set of splittings due to the methylene protons are shown with arrows in Fig. 1. As the temperature increases, this methylene proton hyperfine splitting changes extensively; at temperatures around −27°C (Fig. 1a, 1) it becomes a three-line pattern with an intensity ratio of about 1 : 4.2 : 1 and with line separation of $(a_{eq}+a_{ax})$, where the a_{eq} and a_{ax} are the splitting constants of the equatorial and axial protons obtained at low temperatures. This hyperfine pattern is a typical line-width alternation phenomenon, and the intensity ratio coincides well with the one expected, 1 : 4 : 1, from the theory of the line-width-alternation effect[9] for an extremely broadened case.

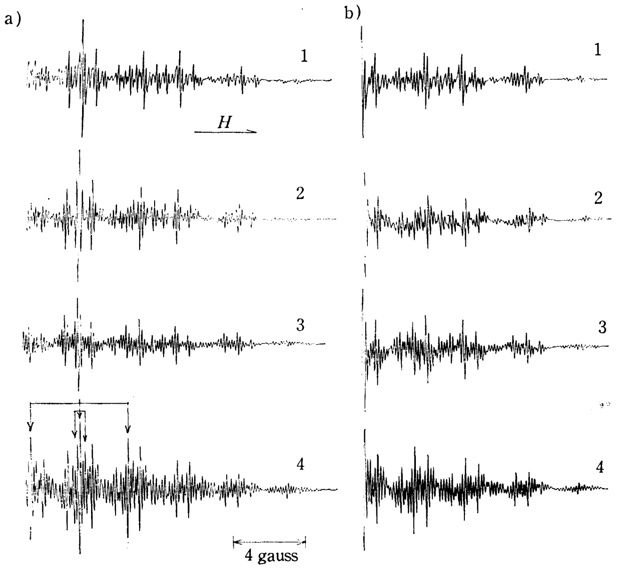


Fig. 1. ESR spectra of the 9,10-dihydrophenanthrene radical anion in tetrahydrofuran with lithium ion as a counter ion.
(a) Spectra observed 1) at −27°C, 2) at −71°C, 3) at −81°C, and 4) at −102°C.
(b) Computer simulation; 1) $\tau=1.4\times10^{-7}$ sec 2) $\tau=2.0\times10^{-6}$ sec, 3) $\tau=5.0\times10^{-6}$ sec 4) $\tau=4.0\times10^{-5}$ sec.

As has been reported in the previous paper,[3] the line-width alternation effect observed here can be attributed to the inversional motion of the 9,10-dihydrophenanthrene anion molecule. At low temperatures, the rate of the inversional motion is slow and the axial and equatorial splitting constants can be separately observed. On the other hand, at high temperatures the inversional motion becomes rapid and it becomes impossible to distinguish the axial and the equatorial protons by rapid exchange between the two states.

This rate process has, therefore, been analyzed by using a modification for the two-jump model of Bloch's equation.[10] The computer-simulated ESR spectra obtained on the basis of this model are compared with the observed spectra in Fig. 1. Although the ring proton hyperfine splitting constants change slightly with the temperature, the neglect of such slight changes in the splitting constants does not result in serious errors in the evaluation of the life-time of the conformation, τ. Therefore, the changes in the hyperfine splitting constants with the temperature were ignored and the hyperfine splitting constants obtained at −102°C were used throughout the ESR

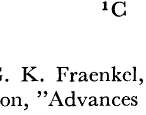
Table 1. Hyperfine splitting constants and spin densities for the 9,10-dihydrophenanthrene radical anion[a] (in gauss)

Position	1,8	2,7	3,6	4,5	CH_2	
					Axial	Equatorial
Hyperfine splitting constants at −102°C[b]	0.161	5.363	0.708	3.359	2.674	0.289
Spin densities[c]	−0.0064	0.2041	−0.0262	0.1154	—	—

a) The radical was prepared with lithium in tetrahydrofuran.
b) Absolute values.
c) The values were obtained by the McLachlan's calculation (*Mol. Phys.*, **3**, 233 (1960)) using the following parameters and $\lambda=1$.

$\delta_{\alpha_1}=-0.1\,\beta$ $\delta_{\alpha_2}=\delta_{\alpha_3}=-0.1\,\beta$ $\delta_{\alpha_4}=-0.5\,\beta$

$\beta_{12}=\beta_{23}=0.7\,\beta$ $\beta_{24}=2.5\,\beta$



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9) J. H. Freed and G. K. Fraenkel, *ibid.*, **39**, 326 (1963); P. D. Sullivan and J. R. Bolton, "Advances in Magnetic Resonance," Vol. 4, ed. by J. S. Waugh, Academic Press, New York, N. Y. (1970), p. 39.

10) H. S. Gutowski and C. H. Holm, *J. Chem. Phys.*, **25**, 1288 (1956).

simulation. In Table 1 the hyperfine splitting constants obtained at $-102°C$ are listed. The assignment of the observed splitting constants to the respective proton positions was made on the basis of the calculated spin distribution.

By applying the estimated τ values to the following relation:

$$k = 1/\tau = k_0 \exp(-E_a/\boldsymbol{R}T) \qquad (1),$$

the activation energy, E_a, of the inversional motion can be evaluated. Here, k is the rate constant of the inversion, and k_0 is the frequency factor. Figure 2 shows the plot of $\log_{10} 1/\tau$ against $1/T$. E_a and k_0 were calculated to be 6.3 ± 0.6 kcal/mol and $3.5 \pm 2.9 \times 10^{12}$ sec^{-1} respectively from the figure.

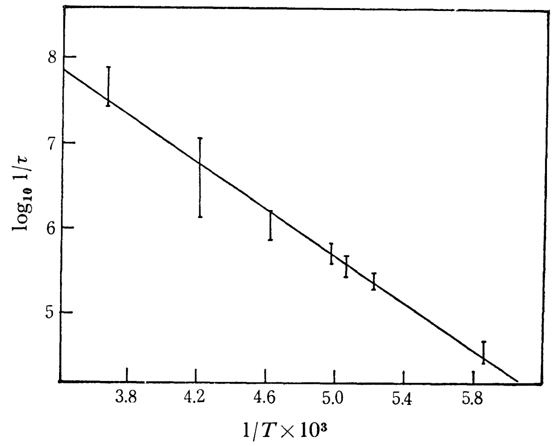

Fig. 2. Plot of $\log_{10} 1/\tau$ against $1/T \times 10^3$ for the 9,10-dihydrophenanthrene radical anion.

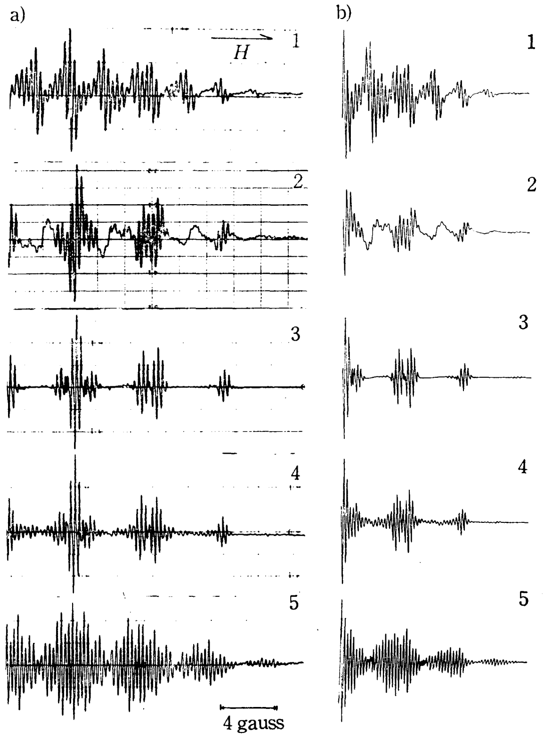

Fig. 3. Comparison of the computer simulated ESR spectra with the observed ones of the 4,5,9,10-tetrahydropyrene radical anion in 1,2-dimethoxyethane with potassium ion as a counter ion.

(a) Spectra observed 1) at $+63°C$, 2) at $+23°C$, 3) at $-35°C$, 4) at $-58°C$, and 5) at $-81°C$.

(b) Computer simulation; 1) $\tau = 1.2 \times 10^{-9}$ sec, 2) $\tau = 1.2 \times 10^{-8}$ sec, 3) $\tau = 7.0 \times 10^{-8}$ sec, 4) $\tau = 1.6 \times 10^{-6}$ sec, 5) $\tau = 9.0 \times 10^{-6}$ sec.

The observed spectra are taken from Ref. 3.

For a comparison of the activation energy with that of the inversion of the 4,5,9,10-tetrahydropyrene radical anion, the inversion process of the 4,5,9,10-tetrahydropyrene radical anion previously reported was reexamined through a computer simulation of the spectra. The calculated spectra are compared with the observed ones in Fig. 3. From the plot of $\log_{10} 1/\tau$ against $1/T$ (Fig. 4), the activation energy of the inversion of the molecule was obtained as 8.7 ± 0.6 kcal/mol, and k_0, as $4.4 \pm 2.8 \times 10^{14}$ sec^{-1}.[11] That is, the increase in the activation energy of the inversion from the singly-bridged form to the doubly-bridged form is 2.4 kcal/mol. Milsow estimated, by a simple theoretical consideration, an activation energy of 7—8 kcal/mol for the 4,5,9,10-tetrahydropyrene and one of 4 kcal/mol for the 9,10-dihydrophenanthrene molecules.[6] These predictions are in agreement with our experimental results, although his calculation was made for neutral molecules and gave a larger difference in the activation energies between the two compounds.

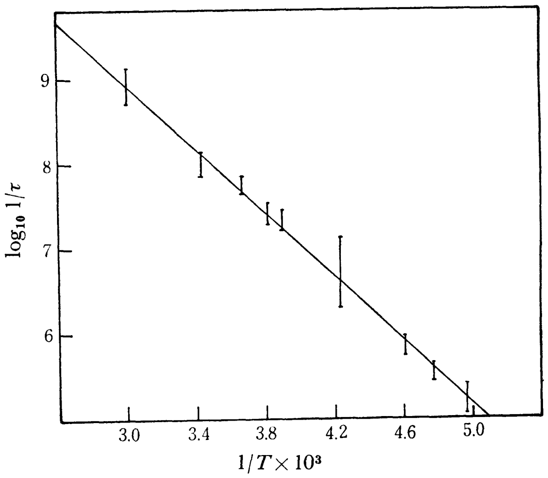

Fig. 4. Plot of $\log_{10} 1/\tau$ against $1/T \times 10^3$ for the 4,5,9,10-tetrahydropyrene radical anion.

The Conformation of the 9,10-Dihydrophenanthrene Anion Molecule. β proton hyperfine splitting constants have a pronounced orientation dependence, which is given by the well-known formula:[12]

$$a_\beta = (B_0 + B_2 \cos^2\theta)\rho_i. \qquad (2)$$

Here, ρ_i represents the spin density at the trigonal carbon(i), θ is the dihedral angle between the C–H$_\beta$

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[11] In a previous paper[3] the activation energy was estimated without attempting a computer simulation of the whole hyperfine pattern of the spectra, but by observing the behavior of the pair of lines with spin states (1,0) and (0,1) or (−1,0) and (0,−1). Here, the numbers in the parentheses correspond to the quantum numbers for the total angular momenta of the axial and equatorial protons respectively. In this work adopting the computer simulation of the whole hyperfine pattern of the spectra, it was found that the estimated activation energy in the previous paper contains a large error. The value reported previously must, therefore, be revised.

[12] C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).

bond and the $2p_z$ orbital on the ith carbon, and B_0 and B_2 are constants. In the 9,10-dihydrophenanthrene molecule, if the molecular structure is planar, the two protons in the methylene groups must be equivalent stereochemically and must have the same splitting constants. On the other hand, if the two aromatic rings twist about the bond joining the rings, the hyperfine splittings of the two methylene protons will become different, and the larger the amount of the twist becomes, the larger will the ratio of the axial and the equatorial proton splitting constants be. The observed ratio of the axial and the equatorial proton splittings in the 9,10-dihydrophenanthrene radical anion was 9.25. For the case of the 4,5,9,10-tetrahydropyrene radical anion, this ratio was 4.82. Furthermore, by assuming that $B_0=0$, the dihedral angle for the axial proton of the 9,10-dihydrophenanthrene radical anion is calculated to be 11°. This value is larger than the value, 3°, for the 4,5,9,10-tetrahydropyrene radical anion previously reported. These results indicate that the twist angle between the two benzene rings would be larger in the 9,10-dihydrophenanthrene radical anion than in the case of the 4,5,9,10-tetrahydropyrene radical anion, which is in agreement with the conclusion obtained from the studies by means of the NMR and UV spectra.[6)]

ESR of the 4,5-Dihydropyrene Radical Anion. In the case of the 4,5-dihydropyrene radical anion(III), the two methylene protons will probably be in different states stereochemically, *i.e.*, in the axial and equatorial states, as in the cases of the 9,10-dihydrophenanthrene or 4,5,9,10-tetrahydropyrene radical anion, although the distortion of the molecule from a planar structure is small because of the presence of the 9—10 π bond. We examined the ESR spectra of the 4,5-dihydropyrene radical anion in the hope of getting information on the structure of the molecule and the inversional motion.

The observed spectra are shown in Figs. 5 and 6. The spectrum in Fig. 5 is analyzed in terms of four sets of triplet splittings, which can reasonably be assigned to the hyperfine interaction with the ring protons on the basis of a comparison with the spin-density distribution estimated by the MO calculation (Table 2). When the anion is prepared by reduction with potassium in 1,2-dimethoxyethane, the hyperfine splitting due to the methylene protons is not resolved. On the other hand, when the radical is prepared by reduction with potassium in 2-methyltetrahydrofuran, the radical shows a spectrum with further splittings due to the interaction with the methylene protons and a potassium ion associated with the radical anion (Fig. 6). The appearance of the methylene proton splitting is attributed to the redistribution of the odd electron in the molecule by the cationic field of the associated potassium ion. Unfortunately, the spectra could not be analyzed unequivocally because of the low S/N ratio, the complicated hyperfine pattern, and imperfect resolution. In the spectrum obtained at 20°C, however, the additional hyperfine splittings due to the methylene protons and the associated potassium seem to consist of eight lines. If it is assumed that the four methylene protons show quintet splitting with a binomial intensity ratio, and that potassium show a splitting with a splitting constant of half of the four methylene protons, an eight-line pattern with roughly the same intensity ratio as the observed one can be expected for the methylene proton and the potassium hyperfine splittings. According to this analysis, the two types of methylene protons, axial and equatorial, will be in an averaged state as a result of the fast inversional motion. The inversion rate will

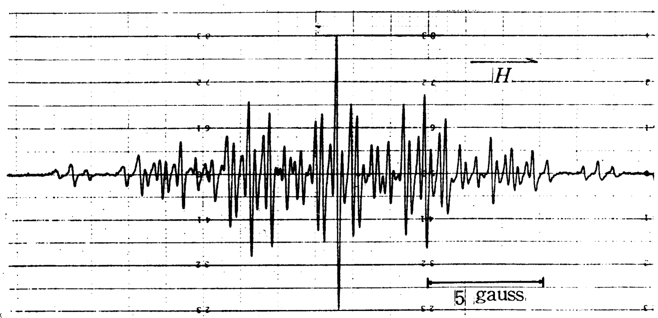

Fig. 5. ESR spectrum of the 4,5-dihydropyrene radical anion in 1,2-dimethoxyethane with potassium ion at 20°C.

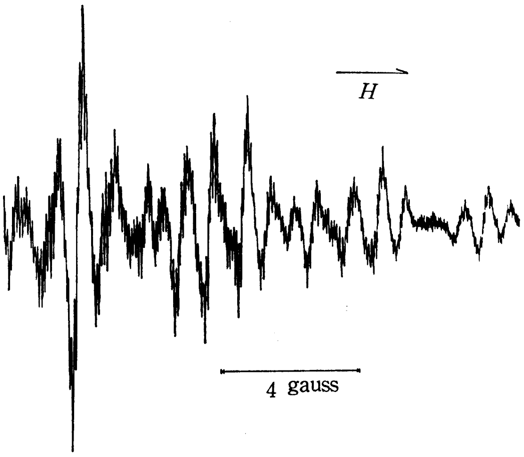

Fig. 6. ESR spectrum of the 4,5-dihydropyrene radical anion in 2-methyltetrahydrofuran with potassium ion at 20°C.

Table 2. Hyperfine splitting constants and spin densities for the 4,5-dihydropyrene radical anion[a)] (in gauss)

Position	1,8	2,7	3,6	9,10	CH_2
Hyperfine splitting constants at 20°C[b)]	3.782	0.632	2.887	4.677	<0.06
Spin densities[c)]	0.1469	−0.0348	0.1152	0.1969	—

a) The radical was prepared with potassium in 1,2-dimethoxyethane.
b) Absolute values.
c) The values were obtained by the McLachlan's calculation using the parameters shown in the footnote c of Table 1.

then be faster than approximately 10^8 Hz. The NMR spectrum of the neutral molecule of 9,10-dihydropyrene shows a single line for the methylene protons, with a δ value of 3.22. This means that the inversional motion of the neutral molecule is apparently a fast process on the NMR time scale. More reliable information on the methylene protons in ESR is desirable for the analysis of the inversion process of the 9,10-dihydropyrene anion.

The numerical calculations were carried out on the NEAC 2200 Model 700 computer at the Computer Center, Tohoku University.