Line-Width Alternation in the Electron Spin Resonance Spectra of the Anion Radicals of Hydropyrenes[1]

By Masamoto IWAIZUMI and Taro ISOBE

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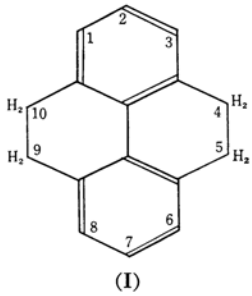
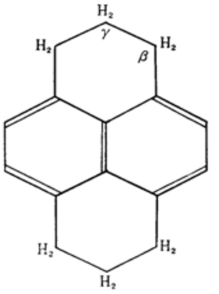
Recently, a number of ESR spectra have been reported in which the line width alternate in magnitude from one hyperfine component to another. This althernating line-width has been observed in the spectra of the durosemiquinone cation,[2] the naphthazarine semiquinone cation,[3] the dinitrodurene anion,[4] the *m*-dinitrobenzene anion,[5] the pyracene anion,[6] and several other radicals.[7] In the former two cases, the phenomenon has been attributed to the hindered rotation or rotational isomerization of the hydroxy groups, and in the dinitrodurene radical, to the hindered rotation of the nitro groups. On the other hand, in the case of the *m*-dinitrobenzene anion, the phenomenon has been ascribed to the effect of the collisions with solvent molecules or to the effect of formation of short-lived solvent complexes, and in the case of the pyracene anion, to the effect of the movement of the associated counter ions.

In this paper, we will report on the ESR of the anion radicals of 4, 5, 9, 10-tetrahydropyrene (I) and 1, 2, 3, 6, 7, 8-hexahydropyrene (II). The ESR spectra of these radicals vary with the temperature remarkably and exhibit a marked line-width alternation effect, which may be attributed to the conformational interconversion: the inversion in the tetrahydropyrene anion radical, and the isomerization between the chair-like conformation and the boat-like one in the hexahydropyrene anion radical. Recently, de Boer et al.[8] found the same phenomenon in the hexahydropyrene anion radical. We will indicate, furthermore, that the ESR spectrum of the hexahydropyrene anion radical, when the radical is prepared with sodium or with potassium in THF, shows one more additional line-width alternation effect, which may be attributed to the effect of the associated counter ions, as in the case of the alkali-pyracene radical ion.



(I)



(II)

Experimental

Commercial tetrahydropyrene and hexahydropyrene were purified by chromatography. The radicals were prepared by an alkali metal reduction method. The alkali metals used were lithium, sodium, and potassium, and the solvents used were 1, 2-dimethoxyethane (DME) and tetrahydrofuran (THF). The ESR spectra were measured with a Hitachi X-band ESR spectrometer, model MPU-3B, using field modulation at 100 kc./s. The temperature was controlled by letting dry and cooled nitrogen gas flow through a Dewar jacket passing through the sample cavity, and the temperature was varied by changing the flow rate of the gas. The temperature was measured with a copper-constantan thermocouple.

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[1] Presented at the symposium on Electron Spin Resonance, Tokyo, November, 1964.

[2] J. R. Bolton and A. Carrington, *Mol. Phys.*, **5**, 161 (1962); A. Carrington, ibid., **5**, 425 (1962).

[3] J. R. Bolton, A. Carrington and P. F. Todd, ibid., **6**, 169 (1963).

[4] J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 1156 (1962).

[5] J. H. Freed, P. H. Rieger and G. K. Fraenkel, ibid., **37**, 1881 (1962).

[6] E. de Boer and E. L. Mackor, *Proc. Chem. Soc.*, **1963**, 23; E. de Boer and E. L. Mackor, *J. Am. Chem. Soc.*, **86**, 1513 (1964).

[7] J. H. Freed, I. Bernal and G. K. Fraenkel, *Bull. Am. Phys. Soc.*, **7**, 44 (1962); R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); I. Bernal and G. K. Fraenkel, *J. Am. Chem. Soc.*, **86**, 1671 (1964); J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **41**, 699 (1964); S. H. Glarum and J. H. Marshall, ibid., **41**, 2182 (1964).

[8] E. de Boer and A. P. Praat, *Mol. Phys.*, **8**, 291 (1964).

Results and Discussion

The ESR Spectra of the Tetrahydropyrene Anion Radical.—All the anion radicals of the tetrahydropyrene prepared under the respective conditions mentioned above exhibit similar spectra, though the spectra are not strictly identical in respect to the broadening, probably because of the coupling with metal ions. Representative spectra are shown in Fig. 1. At elevated temperatures, +63°C, the spectrum is well resolved and can be interpreted as arising from a triplet splitting due to the two equivalent protons, a fairly small nonet splitting from eight equivalent protons, and a still smaller quintet splitting from four equivalent

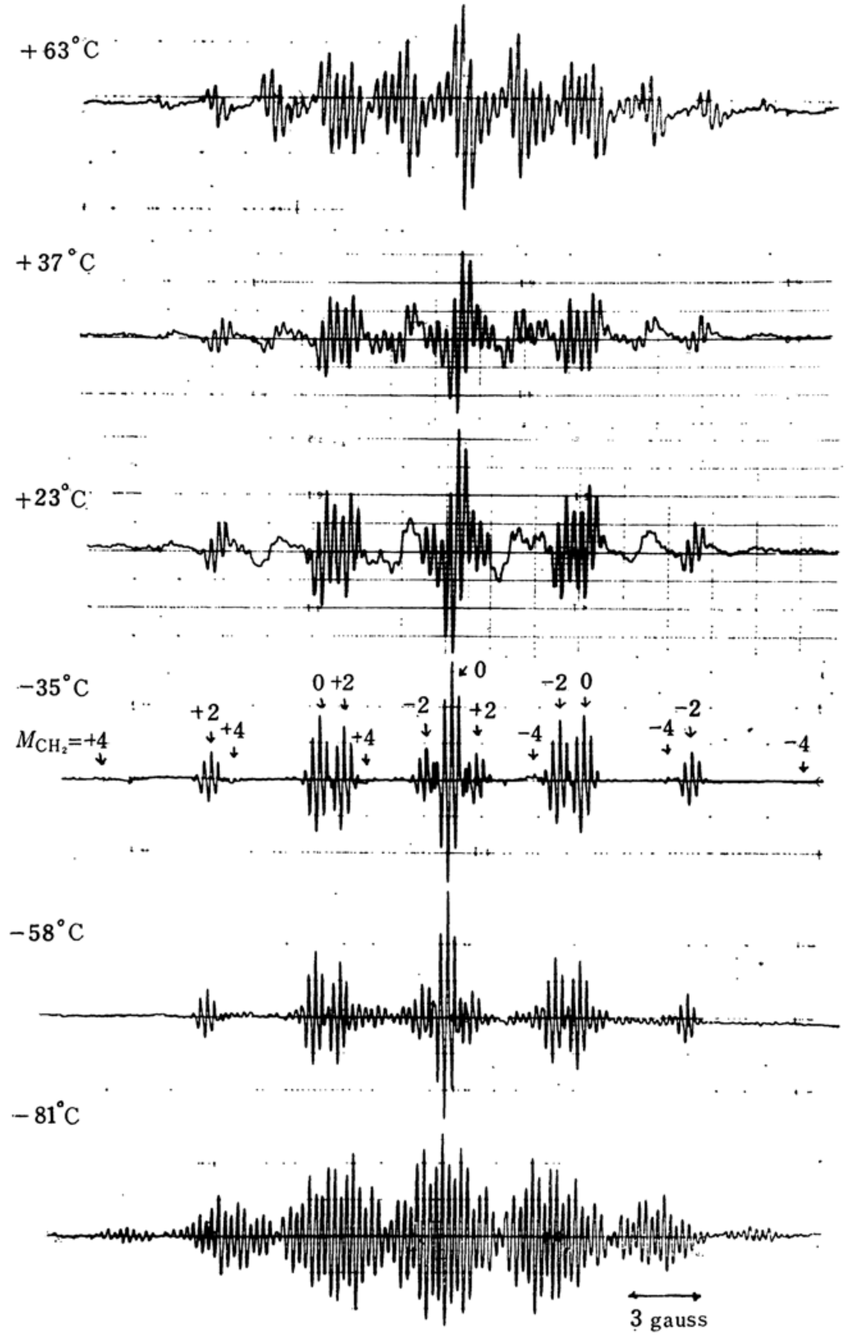
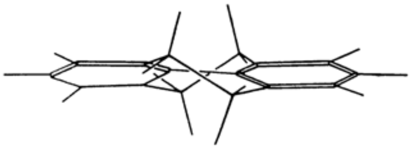


Fig. 1. ESR spectra of 4,5,9,10-tetrahydropyrene anion radical in DME at various temperatures with K$^+$ as counter ion.

protons. Based on the symmetry of the molecule, one can unambiguously attribute the triplet splitting to the coupling at position 2, the nonet splitting, to the coupling with aliphatic protons, and the quintet splitting, to the coupling at position 1. On the other hand, at room temperature or below, the spectrum exhibits a marked line-width alternation effect: let M_{CH_2} be the total z component of the nuclear spin angular momenta of the methylene protons; the hyperfine components with $M_{CH_2}=\pm 1$ and ± 3 are then broadened considerably, and at $-35°C$, they are not observed in a spectrum recorded at a low amplitude of the field modulation. At still lower temperatures, this alternation effect again disappears, and the splittings due to the methylene protons are divided into two quintet splittings, the hyperfine splitting constants being 3.78 and 0.79 gauss. The variation in the spectra with the temperature was completely reversible except that, about 50°C, a diminution in the signal intensity due to the decomposition of the radicals was observed. The observed hyperfine splitting constants are listed in Table I.

Here, one would like to consider the structure of the tetrahydropyrene anion radical. In view of the results obtained by Braude et al.,[9] it is likely that the tetrahydropyrene anion radical is in a non-planar conformation (III)



(III)

and that the two methylene protons are not in the same situation: one of them is placed in the axial conformation, while the other is in the equatorial. When the inversion of the molecular conformation occurs, the situations of the two methylene protons will be reversed. If the life time of the individual configuration, τ, is sufficiently short compared with $|\gamma(a_{\mathrm{equ.}}-a_{\mathrm{ax.}})|^{-1}$, where γ is the gyromagnetic ratio of the electron and where $a_{\mathrm{equ.}}$ and $a_{\mathrm{ax.}}$ are the respective hyperfine splitting constants for the equatorial and the axial protons, the hyperfine splitting due to the methylene protons will be an average of the axial and the equatorial proton splittings. If the life time of the individual configuration is sufficiently long, the respective splittings due to the equatorial and the axial protons will be observed. However, when the life time of the individual configuration is comparable with $|\gamma(a_{\mathrm{equ.}}-a_{\mathrm{ax.}})|^{-1}$, the line-width alternation effect will be observed. Experiments at various temperatures yield spectra corresponding to each of these situations. The spectrum observed at 63°C corresponds to $|\gamma(a_{\mathrm{equ.}}-a_{\mathrm{ax.}})|^{-1}\ll\tau$, that observed at $-81°C$, to $|\gamma(a_{\mathrm{equ.}}-a_{\mathrm{ax.}})|^{-1}\gg\tau$, and that observed at intermediate temperatures, to $|\gamma(a_{\mathrm{equ.}}-a_{\mathrm{ax.}})|^{-1}\approx\tau$. Therefore, it seems reasonable to conclude that the variation in the spectra with the temperature and the line-width alternation effect may be attributed to the dynamical motion of the inversion of the molecular conformation. The two hyperfine coupling constants for the methylene protons, observed at $-81°C$, are assigned to the couplings with the axial and the equatorial protons, the larger to the axial protons and the smaller to the equatorial, on the basis of theoretical considerations.[10] Recently, Ōki et al.[11] examined the rate of the inversion of *o, o'*-bridged biphenyls by the NMR technique. In their technique, the rate of the inversion of the tetrahydropyrene was found to be too fast for the two kinds of methylene protons to be observed separately.

Using the hyperfine coupling constants for the equatorial and the axial protons, the life time of the individual configuration can be calculated to be in the range of 10^{-7}—10^{-9} sec. From the temperatures of their upper and lower limits, the inversion barrier may be estimated to be 4—5 kcal./mol.

TABLE I. HYPERFINE SPLITTING CONSTANTS FOR THE TETRAHYDROPYRENE ANION RADICAL (in gauss)

	+23°C	−81°C
a_1	0.32	0.28
a_2	5.68	5.68
$a_{\mathrm{ax.}}$	—	3.81
$a_{\mathrm{equ.}}$	—	0.79
$a_{\mathrm{ax.}}+a_{\mathrm{equ.}}$	4.65	4.60

TABLE II. HYPERFINE SPLITTING CONSTANTS FOR THE HEXAHYDROPYRENE ANION RADICAL (in gauss)

	+23°C	−81°C
a_4	1.68	1.68
a_γ	0.41	0.51
$a_{\beta.\mathrm{ax.}}$	—	8.00
$a_{\beta.\mathrm{equ.}}$	—	2.02
$a_{\beta.\mathrm{ax.}}+a_{\beta.\mathrm{equ.}}$	9.87	10.02

The ESR Spectra of the Hexahydropyrene Anion Radical.—In the spectrum of the hexahydropyrene anion radical too, drastic changes in the hyperfine structure with the temperature were observed, as is shown in Fig. 2.

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[9] E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, **1955**, 3776.

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

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

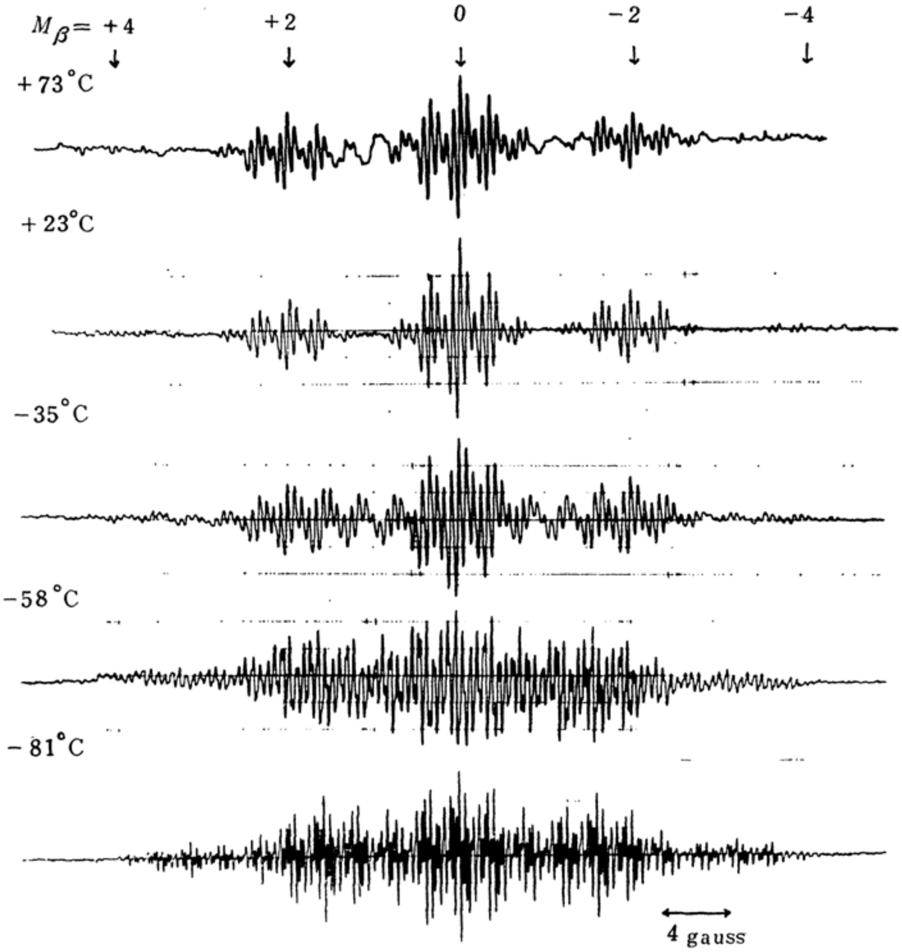
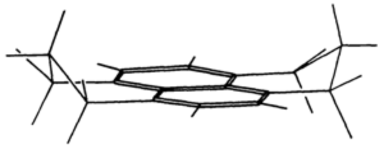
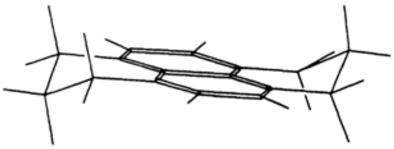


Fig. 2. ESR spectra of 1,2,3,6,7,8-hexahydropyrene anion radical in DME at various temperatures with K$^+$ as counter ion.

These changes in the spectrum with the temperature can be explained, as has recently been reported by de Boer et al.,[8)] in terms of the dynamical equilibrium between the boat-like (IV) and the chair-like (V) conformations of the radical ions. This causes modulations in the isotropic hyperfine splittings, giving rise to a pronounced line-width alternation effect. The spectrum at a lower temperature is well explained by the hyperfine splittings coming from the fixed conformations of the radical. The hyperfin splitting constants are listed in Table II. However, when the temperature of the solution is raised, a marked alternation in the widths of the hyperfine components of the β proton multiplet is observed. At room temperature, only the five components with M_β = 0, ±2 and ±4 and with statistical weights of 18 : 8 : 1 are observed, where M_β is the total z component of the nuclear spin angular momenta of the methylene protons at the β position. The other components are broadened and unobservable at a low field amplitude of the field modulation, and the mean life time of the individual configuration may be comparable with the hyperfine separation between two β protons, $\sim 10^{-8}$ sec.



(IV)



(V)

As compared with the spectra in Fig. 2,

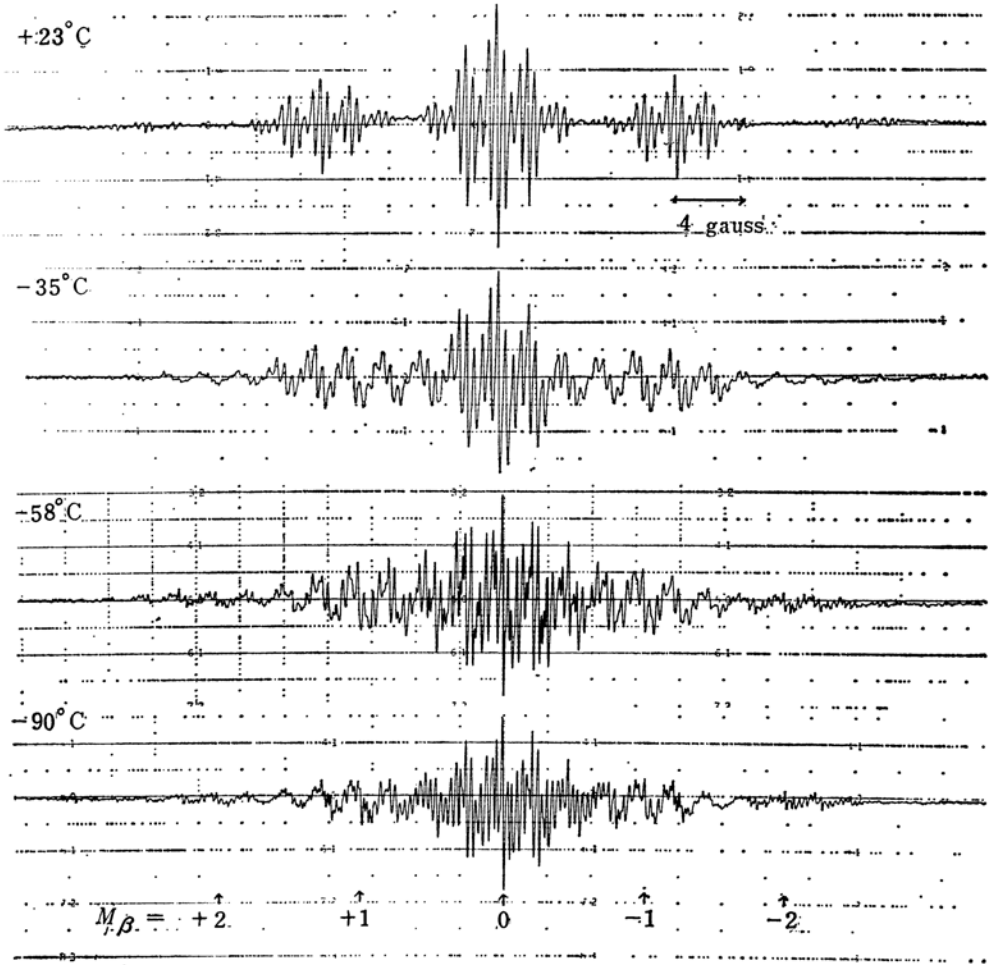
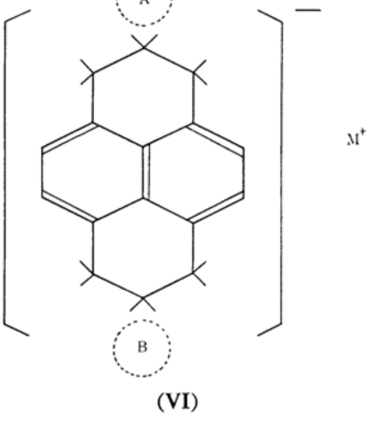


Fig. 3. ESR spectra of 1,2,3,6,7,8-hexahydropyrene anion radical in THF at various temperatures with K^+ as counter ion.

however, the spectra coming from the radicals prepared by the reduction with potassium or sodium in THF show somewhat different features, at lower temperatures, from those in Fig. 2, as is shown in Fig. 3. In these spectra, a marked alternation in the widths of the hyperfine components of the axial protons at the β position is observed; the hyperfine components with $M_{\beta.\text{ax.}}=\pm1$ are broader than those with $M_{\beta.\text{ax.}}=0$ and ±2, where $M_{\beta.\text{ax.}}$ is the total z component of the nuclear spin angular momenta of the axial protons at the β position.

Recently, de Boer et al.[6] observed a line width alternation effect in the ESR spectrum of the alkali-pyracene radical ion. In this case the phenomenon was ascribed to the effect of the motion of the associated alkali metal ion between two equivalent positions in the anion radical. In the present case the situation seems similar to that of the pyracene anion radical. Therefore, the following may be considered. In DME the alkali metal-hexahydropyrene radical is completely dissociated into ions, whereas in THF an ion pair (VI)



(VI)

occurs, and a dynamic equilibrium exists between the two possible conformations of the ion pair. Considering it analogously to the alkali-pyracene radical ion, the alkali metal may be placed on two symmetrical positions, A and B.

The Hyperfine Splitting Constants of the Aliphatic Protons. — The isotropic hyperfine splitting constants of aliphatic protons in a variety of hydrocarbon-free radicals have been determined by ESR studies. Heller and McConnell[10] have suggested that the hyperfine splitting constants for protons at the β position* can be described by the relation:

$$a_{\beta}^{\mathrm{H}} = (A + B\cos^2\theta)\,\rho_{\mathrm{C}}^{\pi}$$

where ρ_{C}^{π} is the spin density in the p orbital of the contiguous carbon atom, θ is the angle between the axis of the p orbital and the C–H bond, both projected on a plane perpendicular to the C–Ar bond, and A and B are constants. This equation has been justified by the studies of a variety of irradiated single crystals of alkyl carboxylic acids and others.[12] In these crystals the protons are frequently considered to be in fixed orientations.

In our experiments, at a sufficiently low temperature, the radicals reveal the hyperfine splitting constants in a fixed orientation, although the radicals are in solutions. If it is assumed that $A=0$, $B=46$ gauss and $\theta_{\mathrm{ax.}}=\theta_{\mathrm{equ.}}-120°$, where $\theta_{\mathrm{ax.}}$ and $\theta_{\mathrm{equ.}}$ are the θ values for the axial and the equatorial protons, from the above relation one may calculate that $\theta_{\mathrm{ax.}}=3°$ and $\rho_{\mathrm{C}}^{\pi}=0.08$ for the tetrahydropyrene anion radical, and $\theta_{\mathrm{ax.}}=0°$ and $\rho_{\mathrm{C}}^{\pi}=0.17$ for the hexahydropyrene anion radical. These angles are approximately that found in models of these molecules. The values of ρ_{C}^{π} are comparable to the spin densities, 0.11 and 0.20, at the corresponding positions in the naphthalene and the biphenyl anion radicals,[13] which have conjugation systems similar to those of the tetrahydropyrene and the hexahydropyrene anion radicals respectively. For the γ protons of the hexahydropyrene anion radical, one would expect two different splitting constants. However, only a single γ splitting constant was observed. Theoretical calculations of the spin distribution in these radicals are in progress.

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Chemical Research Institute of
Non-Aqueous Solutions
Tohoku University
Katahira-cho, Sendai

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* The proton positions are defined by the notation: $\text{Ar-}\underset{\beta}{\text{CH}_2}\text{-}\underset{\gamma}{\text{CH}_2}\text{-}$.

[12] D. Pooley and D. H. Whiffen, *Mol. Phys.*, **4**, 81 (1961); A. Horsfield, J. R. Molton and D. H. Whiffen, ibid., **4**, 425 (1961), **5**, 115 (1962), N. M. Atherton and D. H. Whiffen, ibid., **3**, 103 (1960); D. Pooley and D. H. Whiffen, *Trans. Faraday Soc.*, **57**, 1445 (1961); I. Miyagawa and K. Itoh, *J. Chem. Phys.*, **36**, 2157 (1962).

[13] A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).