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ESR Spectra of Radical Ions Generated from 5,10-Dihydroindeno[2,1-*a*]indene

Keiichiro Ogawa,* Hiroshi Suzuki,† Jiro Higuchi,†† Kunihiko Tajima,††† and Kazuhiko Ishizu†††,*
Department of Chemistry, The College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153
†Department of Chemistry, Faculty of Science, Kanagawa University, Tsuchiya, Hiratsuka 259-12
††Department of Physical Chemistry, Faculty of Engineering, Yokohama National University,
Tokiwadai, Hodogaya-ku, Yokohama 240
†††Department of Chemistry, Faculty of Science, Ehime University, Bunkyo-cho, Matsuyama 790

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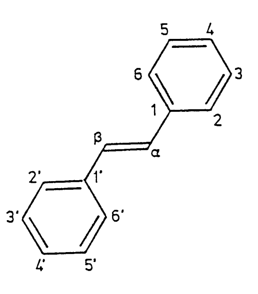
Synopsis. While each the ESR hyperfine coupling constants (hfc's) for the aromatic protons of the anion radical derived from 5,10-dihydroindeno[2,1-*a*]indene ($\mathbf{2}^{-\cdot}$) is similar to that of the corresponding protons of the cation radical of the same compound ($\mathbf{2}^{+\cdot}$) as well as of the radical ions of (*E*)-stilbene ($\mathbf{1}^{-\cdot}$ and $\mathbf{1}^{+\cdot}$), the methylene protons of $\mathbf{2}^{-\cdot}$ shows an unusually large hfc value, which is much larger than that of $\mathbf{2}^{+\cdot}$. This is interpreted in terms of the so-called "Whiffen Effect."

ESR studies of the (*E*)-stilbene anion radical ($\mathbf{1}^{-\cdot}$) have been repeatedly carried out.[1–4] In the previous paper we reported unambiguous assignment of the ESR hyperfine coupling constants (hfc's: *a*) of the (*E*)-stilbene anion radical ($\mathbf{1}^{-\cdot}$), of which spectrum exhibits hyperfine coupling from two nonequivalent pairs of *ortho* and *meta* protons because of the slow internal rotation of the C-Ph bonds.[4] Recently Courtneidge et al. reported the ESR spectrum of the (*E*)-stilbene radical cation ($\mathbf{1}^{+\cdot}$), which exhibits only one hyperfine coupling constant for the *ortho* protons and one for the *meta* protons, showing that the internal rotation of the C-Ph bonds of the cation radical is fast on the ESR time scale.[5] We report here ESR spectra of the anion radical and the cation radical derived from the title compound 5,10-dihydroindeno[2,1-*a*]indene (**2**), so called a "stiff stilbene," a model compound of the planar (*E*)-stilbene in which the internal rotation of the C-Ph bonds in the (*E*)-stilbene moiety is severely restricted by the methylene chains.[6–7]



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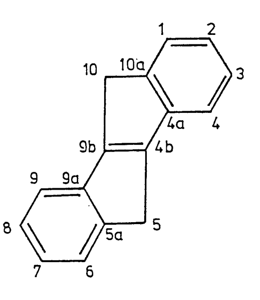

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Experimental

Preparation of the parent compound **2** was described in a previous paper.[6] The anion radical was prepared by reduction of **2** with sodium metal in 1,2-dimethoxyethane at the temperature of dry ice and acetone. The cation radical was prepared by oxidation of **2** with $CF_3COOH/(CF_3CO)_2O$ in dichloromethane.

The ESR spectra were recorded on a JEOL FE2-XG X band spectrometer operating with a 100 KHz field modulation. An aqueous solution of $(KSO_3)_2NO$ was used for the magnetic field calibration.

Results and Discussion

Figures 1 and 2 show the ESR spectra of $\mathbf{2}^{-\cdot}$ and $\mathbf{2}^{+\cdot}$, respectively, and Table 1 gives *a* values for $\mathbf{2}^{-\cdot}$ and $\mathbf{2}^{+\cdot}$ together with those for $\mathbf{1}^{-\cdot}$ and $\mathbf{1}^{+\cdot}$. The ESR spectrum of the anion radical $\mathbf{2}^{-\cdot}$ shows an unusually large quintet splitting (a=1.420 mT) assigned to four equivalent protons of the two methylene groups and four sets of triplet splitting (a=0.391, 0.264, 0.070, and 0.017 mT) assigned to the aromatic ring protons. The *a* values of 0.391 and 0.264 mT are undoutedly assigned to the *para* protons (the protons attached to C2 and C7) and the *ortho* protons (the protons attached to C4 and C9), respectively. The *a* values of 0.070 and 0.017 mT are assigned to the *meta* protons attached to C1 and C6 and to those to C3 and C8, respectively, since in the case of $\mathbf{1}^{-\cdot}$ the *a* value for the protons of positions 5 and 5′, which correspond to positions 1 and 6 in $\mathbf{2}^{-\cdot}$, respectively, is larger than that of positions 3 and 3′, which correspond to positions 3 and 8 in $\mathbf{2}^{-\cdot}$, respectively.

The ESR spectrum of the cation radical $\mathbf{2}^{+\cdot}$ is apparently much different from that of the anion radical $\mathbf{2}^{-\cdot}$. It shows a septet splitting (a=0.053 mT) and three sets of triplet splitting (a=0.487, 0.277 and 0.107 mT). The *a* values of 0.487 and 0.277 mT are safely assigned to the *para* protons (the protons attached to C2 and C7) and the *ortho* protons (the protons attached to C4 and C9), respectively.

The septet splitting (a=0.053 mT) is interpreted by an accidental degeneracy of the *a* for the four equiva-

Table 1. ESR Hyperfine Coupling Constants (*a*/mT) for the Protons of (*E*)-Stilbene (**1**) and 5,10-Dihydroindeno[2,1-*a*]indene (**2**) Radical Ions

Position	$\mathbf{1}^{-\cdot\,a)}$	$\mathbf{1}^{+\cdot\,b)}$	Position	$\mathbf{2}^{-\cdot\,c)}$	$\mathbf{2}^{+\cdot\,c)}$
2,2′	0.193	0.278	4,9	0.264	0.277
6,6′	0.303	0.278	10a,5a		
ortho (average)	0.248	0.278			
3,3′	0.031	0.072	3,8	0.017	0.053
5,5′	0.084	0.072	1,6	0.070	0.107
meta (average)	0.058	0.072	*meta* (average)	0.044	0.080
4,4′	0.402	0.453	2,7	0.391	0.487
α,β	0.450	0.453	4b,9b		
			5,10	1.420	0.053

a) In dimethoxyethane at 183 K, conterion K^+.[4] b) In trifluoroacetic acid at 265 K.[5] c) This work.

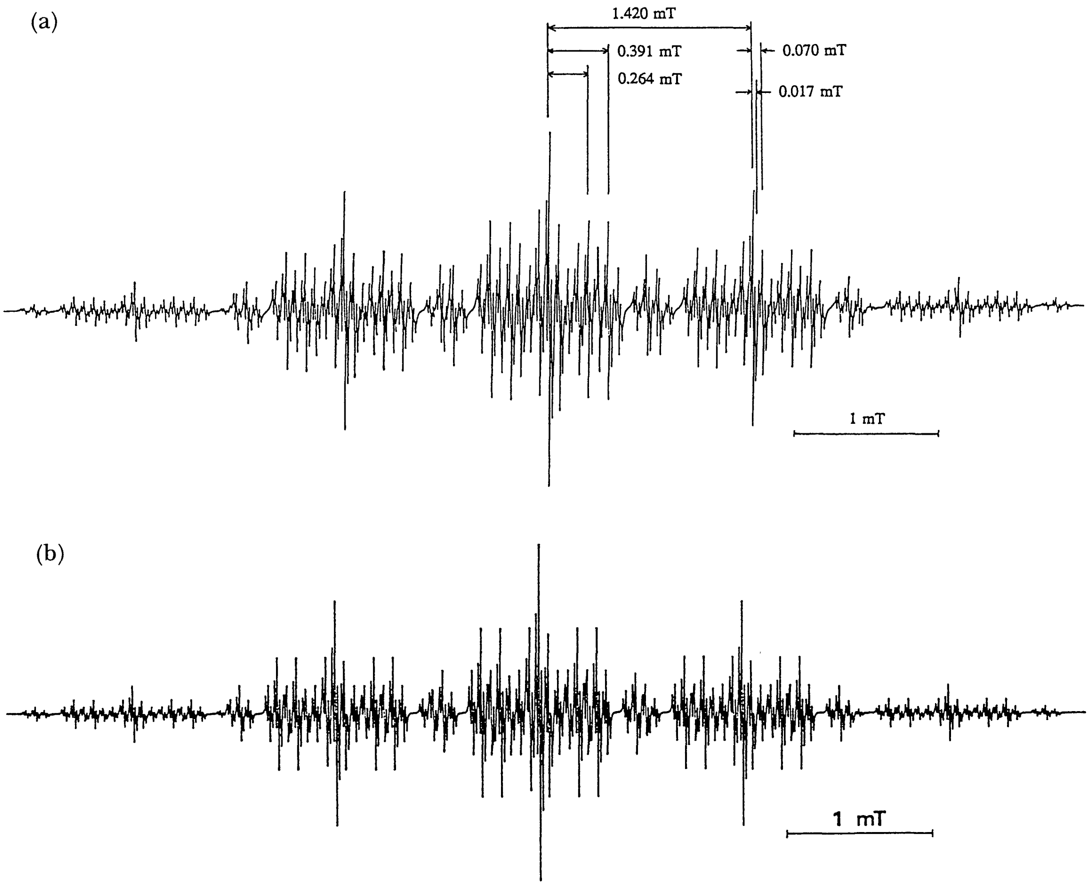

Fig. 1. (a) The observed ESR spectrum recorded at 193 K of the anion radical of 5,10-dihydroindeno[2,1-*a*]indene ($2^{-\cdot}$) in dimethoxyethane and (b) the simulated spectrum.

lent methylene protons with that for one pair (i.e., two protons) of the two nonequivalent pairs of *meta* protons. The *a* value of 0.107 mT is assigned to the other equivalent pair of *meta* protons. The former (a=0.053 mT) is assigned to the protons attached to C3 and C8, and the latter (a=0.107 mT) to the protons attached to C1 and C6, since the order in the magnitude of *a* values for these protons is expected to be the same in $2^{-\cdot}$ and $2^{+\cdot}$.

The results show that the *a* values for the aromatic ring protons of the radical ions of **2** are similar to those for the corresponding protons of the corresponding radical ions of **1**. In addition, they show that the *a* values of the cation radicals are slightly larger than the corresponding *a* values of the anion radicals derived from the same parent compound in accordance with a general feature for the ESR spectra of the cation and the anion radicals of alternant hydrocarbons.[8-10] In contrast, the *a* value for the methylene protons of $2^{-\cdot}$ (1.420 mT) is much larger than that of $2^{+\cdot}$ (0.053 mT). This finding, which is the most notable feature of the results, shows that there is a great difference in the magnitude of the interaction of the methylene protons with the singly occupied π molecular orbital (SOMO) by hyperconjugation between the anion and the cation radical. This is explained in terms of the so-called "Whiffen Effect"[11] as follows.

According to Whiffen, the *a* value of protons of a methylene group which is connected at two points with a π system having odd π electrons is expressed by the following equation:

$$a=Q(C_1+C_2)^2 \qquad (1)$$

where Q is the constant in the McConnell equation, and C_1 and C_2 are the coefficients of the π atomic orbitals at the two points of connection in the SOMO. This equation shows that the *a* value is large when C_1 and C_2 are of the same sign ("Whiffen Effect") and it is small when they are of opposite sign ("Anti-Whiffen Effect"). That is, according as C_1 and C_2 are of the same sign or of opposite sign, the hyperconjugation through the methylene group acts constructively or destructively with respect to the spin density on the methylene protons.

The SOMO's of $2^{-\cdot}$ and $2^{+\cdot}$ are shown in Fig. 3. Use of equation (1), a value of 3.50 mT for Q,[11] and the Hückel coefficients for stilbene (**1**)[5] (+0.274 for ortho positions and ±0.438 for α and β positions) gives

$$\text{for } 2^{-\cdot}\ a(\mathrm{CH_2})=3.50(0.274+0.438)^2=1.770\ \mathrm{mT}$$

and

$$\text{for } 2^{+\cdot}\ a(\mathrm{CH_2})=3.50(0.274-0.438)^2=0.094\ \mathrm{mT}$$

The calculated figures qualitatively compare well with the observed figures. This is an interesting example in which one of the two radical ions gener-

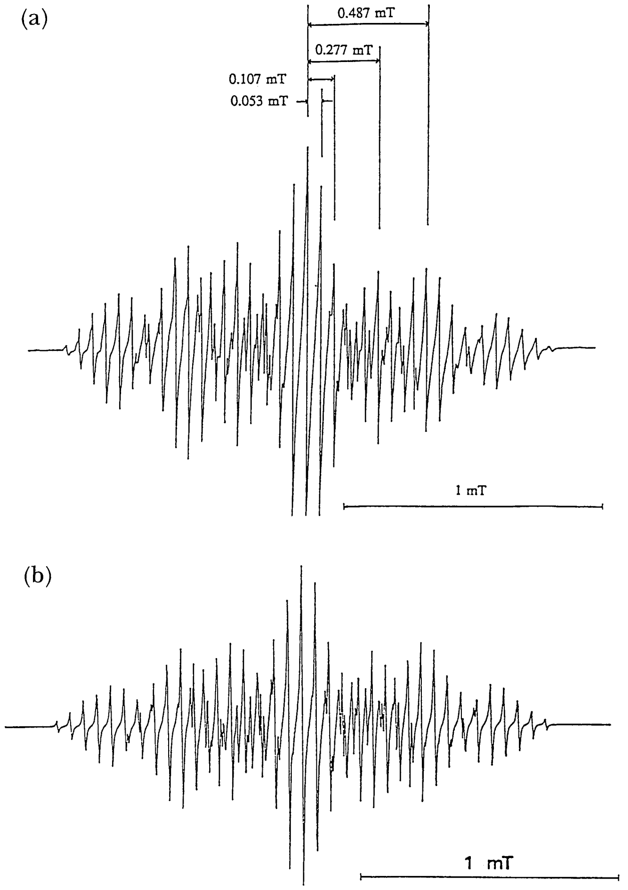

Fig. 2. (a) The observed ESR spectrum recorded at 253 K of the cation radical of 5,10-dihydroindeno[2,1-*a*]indene ($2^{+\cdot}$) in dichloromethane and (b) the simulated spectrum.

ated from an alternant hydrocarbon shows the Whiffen effect and the other the anti-Whiffen effect.

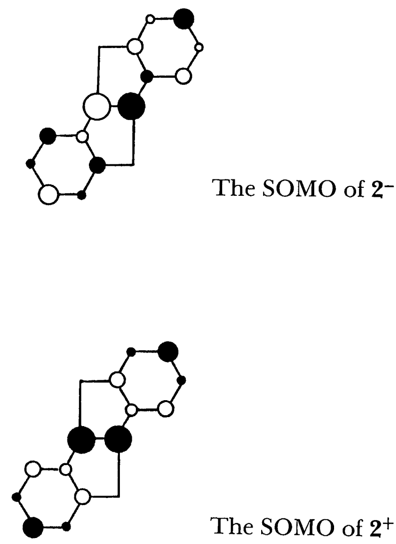

Fig. 3. Schematic representation of the SOMO's of $2^{-\cdot}$ and $2^{+\cdot}$.

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