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ESR Studies on the Anion Radicals of Some Triptycene and [2.2]Paracyclophane Derivatives

Toyoharu Hayashi, Noboru Mataga, Yoshiteru Sakata,* and Soichi Misumi*
Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560
**Institute of Sciencific and Industrial Research, Osaka University, Suita, Osaka* 565

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ESR spectra of anion radicals of some triptycene and [2.2]paracyclophane derivatives were observed and analyzed in order to study the delocalization interactions between composite aromatic rings.

It is important to study the delocalization interactions between the groups when a molecule contains two or more π-electronic groups separated by saturated chemical bonds. The mechanisms of charge transfer complex formation and of electron transfer reaction are closely connected with this problem. One can investigate electron transfer between the composite aromatic rings in anion radicals of [2.2]paracyclophane and triptycene derivatives by means of ESR measurements.

Weissman[1] reported the fast exchange or delocalization of the unpaired electron between the two benzene rings of the [2.2]paracyclophane anion. Furthermore, Gerson and Martin[2] observed that the unpaired electron in the anion radical of [2.2]paracyclophane in DME(dimethoxyethane) is completely delocalized between the two benzene rings, while it is only partially delocalized in the case of the THF (tetrahydrofuran) solution. In the latter solution, the interaction of the unpaired electron with the counter ion seems to suppress the complete delocalization.

Recently, Williams *et al.*[3] made ESR studies on anion radicals of some paracyclophane derivatives, [2.2](9,10)anthracenophane and [2.2](1,4)naphthalenophane. On the basis of their experimental results, they indicated that the unpaired electron is completely delocalized in the case of [2.2](1,4)naphthalenophane. However, they failed to determine its constants. On the other hand, Dessau[4] reported the complete delocalization of aromatic cationic site in the study of triptycene cation radical.

We have made also some ESR and optical studies on triptycene 1,4-quinone anion and 1,4-dimethoxytriptycene cation radicals, and have found out that there are no significant intramolecular delocalizations of the excess electron or the positive hole in the case of these ion radicals.[5] These results may be of some interest from the viewpoint of the electronic structures of ions and molecular complexes in solution. In the present paper, we discuss the results of ESR studies on anion radicals of related compounds, including benzotriptycene (abbreviated as I–1), dibenzotriptycene (I–2), naphthobenzotriptycene (I–3), [2.2](9,10)anthracenophane (II–1), and others.

Experimental

Triptycene and paracyclophane derivatives were synthesized and purified as reported elsewhere.[6] Commercially available THF and DME were dried over sodium sulphate, refluxed over metallic sodium wire for a day, and fractionally distilled. These solvents were degassed completely in the presence of metallic sodium flakes, distilled several times, and finally stored over the sodium-potassium alloy in a vacuum.

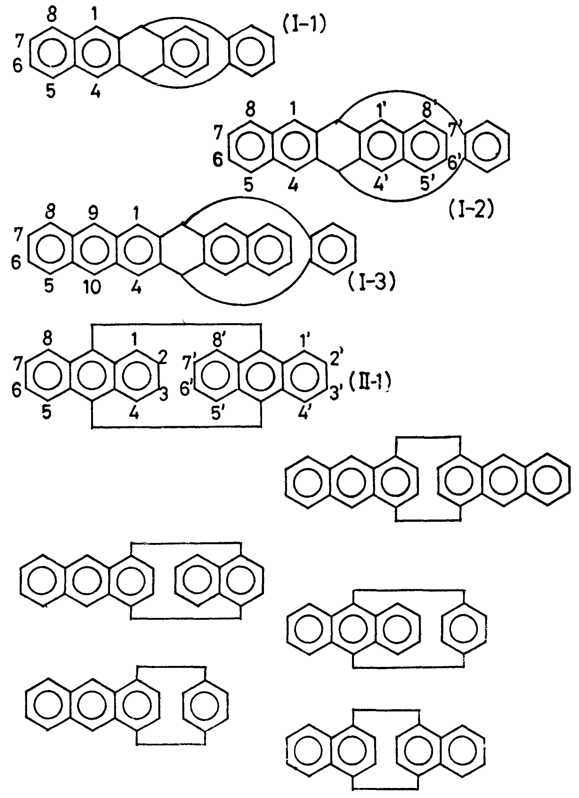

Fig. 1.

The purified solvent was distilled into the sample tube containing the compound. The solution was stirred with a magnetic stirrer and deaerated completely. Alkali metal mirror was formed inside the glass tube after distilling the alkali metal several times. The sample tube containing the alkali metal mirror and the sample solution (separated by a breakable seal from the mirror) was sealed off the evacuating system and immersed in a dry ice–ethanol bath. Then, the solution was put in contact with the metal mirror.

A tube containing anion radical solution prepared by the method as described above was placed in the microwave cavity cooled below −80 °C by the cold nitrogen gas flow. Temperature was then raised near to −50 °C carefully in order to attain the best condition for detecting the ESR signal. When the temperature was raised further, the anion radical was converted to some diamagnetic species and the ESR signal intensity was not recovered when the temperature was lowered again.

Some compounds were examined also by the method of electrochemical reduction in order to exclude the effect of the counter ion. These studies were conducted at room temperature with dimethylformamide(DMF) solutions, and halfwave potentials were also determined. The electrochemical measurements were kindly performed by Drs. T. Kubota and H. Miyazaki of Shionogi Research Laboratory.

The ESR spectra were recorded with a JES-ME-2X or 3BX spectrometer using X-band. The simulation of the spectra, assuming the Lorentzian line shape and appropriate line widths, were made by using the HITAC-700.

Results and Discussion

Benzotriptycene Anion Radical. The anion radical was prepared by the electrochemical reduction in DMF at room temperature. The halfwave potential, $E_{1/2}=-2.58$ V *vs.* SCE, is nearly the same as that of naphthalene. The spectrum in Fig. 2 shows a hfs due to a set of four equivalent protons and a set of two equivalent protons. Their hfs constants are $A_1=3.43$ gauss(G) and $A_2=1.24$ G, respectively. In conformity with the case of 2,3-dimethylnaphthalene anion radical, we assume that the constant A_1 is due to the protons in positions 5, 6, 7, 8, namely H_5, H_6, H_7, H_8, and A_2 to protons H_1, H_4. The contribution from the two bridgehead protons are not very clear being masked by the relatively large line widths (about 0.5 G). It is suggested that four equivalent protons are further separated to two sets of two equivalent protons because of the fact that the line widths of outer lines are a little larger than those of inner ones. In any way, since we cannot observe any hfs due to the delocalization of the unpaired electron on two benzene rings, the odd electron seems to be well localized on the naphthalene ring.

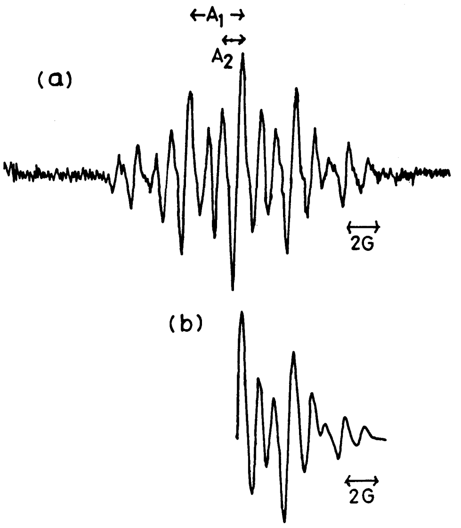

Fig. 2. (a) ESR spectrum of benzotriptycene (I-1) anion radical generated by electrolytic reduction; solvent DMF room temperature, (b) Computer simulated spectrum.

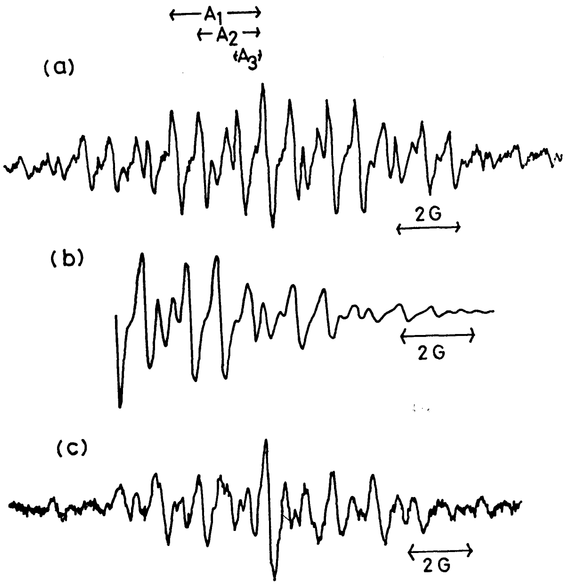

Fig. 3. (a) ESR spectrum of dibenzotriptycene (I-2) anion radical generated by sodium metal reduction; solvent dimethoxyethane (DME), temperature −50 °C. (b) Computer simulated spectrum. (c) Generated by electrolytic reduction at second reduction potential, solvent DMF, room temperature.

Table 1. Assignment of the hfs constants of dibenzotriptycene anion radical (I-2) in comparison with those of 2,3-dimethylnaphthalene anion radical (DMN) (in units of G)

	DMN	I-2
a_1, a_4 (a_1', a_4')	4.09	2.02
a_5, a_8 (a_5', a_8')	5.20	2.83
a_6, a_7 (a_6', a_7')	1.73	0.81
a (CH_3)	1.73	

Dibenzotriptycene Anion Radical. The spectrum obtained by either electrochemical reduction in DMF at the first reduction potential or reduction with sodium metal in DME at −78 °C is exactly the same. Therefore, the spectrum obtained by reduction with sodium metal does not seem to be affected significantly by the counter ion. The first and second half-wave reduction potentials were $E_{1/2}=-2.65$ V and −2.85 V *vs.*, SCE respectively. We have not yet completed the analysis of the spectrum at the second reduction potential. The spectrum obtained by the reduction with sodium metal in DME is shown in Fig. 3. Its hfs seems to be ascribed to three sets of four equivalent protons, their hfs constants being $A_1=2.93$ G, $A_2=2.09$ G, and $A_3=0.89$ G, respectively. The assignment of hfs constants was made as indicated in Table 1. One can see from the table that the hfs constants of (I-2) are about one-half of the corresponding ones of the 2,3-dimethylnaphthalene anion radical. Thus, it may be concluded that the unpaired electron is completely delocalized over the two naphthalene rings. However, it is not delocalized on the benzene ring.

Naphthobenzotriptycene Anion Radical. The ESR spectrum of (I-3) obtained by reduction of the neutral molecule with sodium metal in DME is shown in Fig. 4a. Its hfs can be ascribed to a set of two equivalent protons ($A_1=5.44$ G), a set of four equivalent protons ($A_2=2.88$ G), a set of two equivalent protons ($A_3=1.52$ G), and a set of two equivalent protons ($A_4=0.25$ G). The assignment of these hfs constants was made as indicated in Table 2, where they are

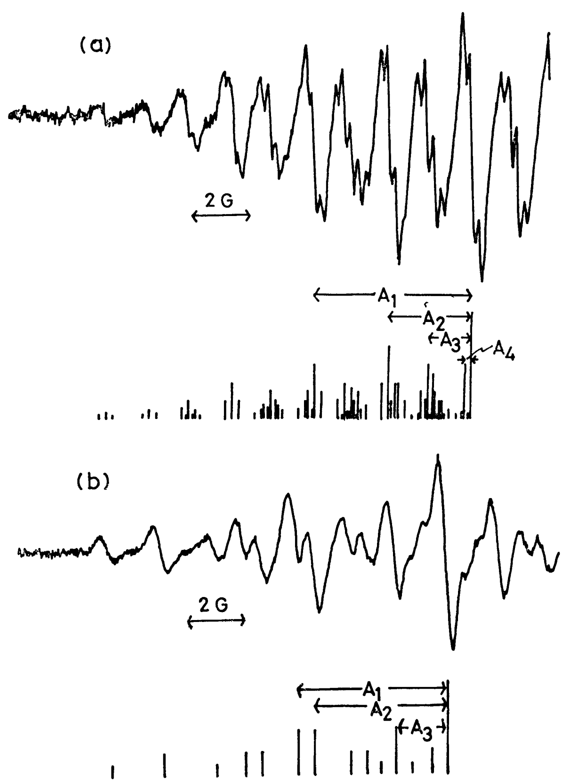

Fig. 4. ESR spectrum of naphthobenzotriptycene (I-3) anion radical; (a) solvent DME, temperature −50 °C, sodium metal reduction, (b) solvent THF, temperature −50 °C, sodium metal reduction.

TABLE 2. ASSIGNMENT OF THE hfs CONSTANTS OF NAPHTHOBENZOTRIPTYCENE ANION RADICAL (I-3) IN COMPARISON WITH THOSE OF ANTHRACENE ANION RADICAL (A). (in units of G)

	A	I-3
a_1, a_4, a_5, a_8	2.66	2.88
a_6, a_7	1.53	1.52
a_9, a_{10}	5.28	5.44

compared with those of anthracene anion radical. The assignment of A_4 to the bridgehead protons seems to be quite reasonable. As far as we know, there has been no clear-cut observation of hfs due to the bridgehead protons of triptycene. For example, Stock and Suzuki[7] investigated the semiquinone anion radicals of 1,4-dihydroxytriptycene and 9-methyl-1,4-dihydroxytriptycene, and Dessau[4] studied the cation radical of triptycene. However, the hfs due to the bridgehead protons was not observed clearly in both cases being covered with rather large line widths. In any way, the present result clearly show that the unpaired electron in (I-3) is well localized on anthracene ring.

In contrast to other compounds investigated here, (I-3) gave a quite different spectrum when the reduction was conducted in THF as indicated in Fig. 4b. Its hfs can be analyzed, but its origin is not yet elucidated. The hfs of the spectrum can be ascribed to three sets of two equivalent protons, their hfs constants being A_1=5.4 G, A_2=4.8 G, and A_3=1.8 G, respectively. It appears that we can ascribe formally this ESR spectrum to an unpaired electron being on the naphthalene composite ring. However, that the unpaired electron is on the naphthalene ring in (I-3) is highly improbable.

On reduction in THF, the solution becomes purple at first, which is also the characteristic color of the anion formed in DME solution, and then the color of solution changes drastically to blue on further reduction by sodium or potassium metal in Dry Ice-ethanol bath. We have confirmed that this phenomenon does not occur even in mixed solvents of DME and THF, the volume ratio of DME to THF being changed from 1 to 0.1.

This remarkable solvent effect might be explained as follows. It seems to be more easy to make anion-metal cation ion-pair in THF than in DME, since the solvation of ions is stronger in DME than in THF, leading to dissociation of the pairs in DME. Therefore, the ion-pair is formed in THF, and two anion radicals may be linked together, assisted by the positive counter ions, at the position of anthracene composite ring to become diamagnetic, since the unpaired electron is located on this ring. On further reduction, the naphthalene ring may react with alkali metal, and the ESR spectrum of naphthalene anion radical may be obtained. Some other explanations than this might be possible including the mechanism assuming the decomposition of the compound on reduction. Further studies on the problem is now going on in our laboratory.

[2.2](9,10)Anthracenophane Anion Radical. The anion radical prepared in DME at −78 °C gave too complicated ESR spectra to be analyzed completely. However, when the temperature was carefully raised near to but a little below 0 °C and again lowered to −50 °C, quite neat spectrum was obtained. The spectrum indicated in Fig. 5 shows hfs due to three sets of eight equivalent protons, and their hfs con-

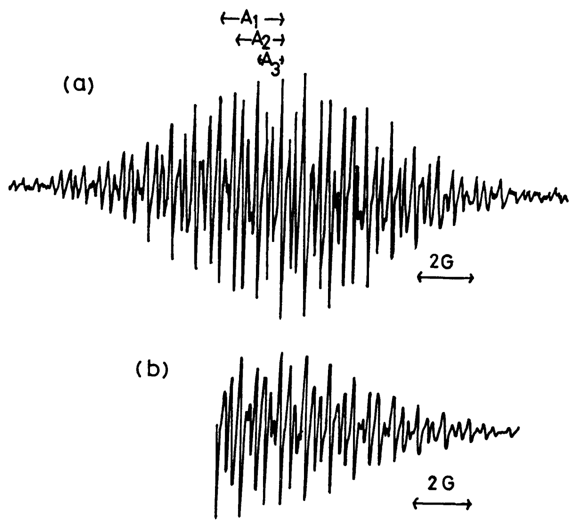

Fig. 5. (a) ESR specturm of [2.2](9,10)anthracenophane anion radical; solvent THF, temperature −50 °C, sodium metal reduction, (b) Computer simulated spectrum.

stants are $A_1=2.14$ G, $A_2=1.63$ G, and $A_3=0.82$ G, respectively. Computer simulated spectrum is in a good agreement with the observed.

Williams *et al.*[3] also reported the ESR spectra of (II-1). However, they failed to analyze the complicated spectra. Their spectra were similar to those we have obtained just after the preparation of the anion radicals at −78 °C in DME. Only the hfs constant of the methylene protons was determined by them to be 1.63 G, using the deuteration technique. This value of the hfs constant is exactly the same as our A_2 value. The complicated spectrum obtained immediately after the preparation of radicals at −78° C seems to be a superposition of the spectra of several species probably including some paramagnetic decomposition products. When the temperature was raised up to near 0 °C the decomposition products were presumably converted to some diamagnetic species, and finally some portion of (II-1) remained. Our assignment was performed by taking into consideration the ESR spectra of 9,10-dimethylanthracene and also the results of Williams *et al.* The hfs constants of (II-1) are compared with those of 9,10-dimethylanthracene in Table 3. These results seem to indicate that the unpaired electron is completely delocalized over the two anthracene rings.

We have measured also ESR spectra of anion radicals of other paracyclophane derivatives. Among them are [2.2]paracycloanthracenophanes, [2.2](1,4)-naphthaleno(1,4)anthracenophane, and anti-[2.2](1,4)-anthracenophane.[6] Their ESR spectra are very complicated, and we have not yet attained to any complete agreement between the experimental and computer simulated spectra. Only can it be said that the unpaired electron is fairly well delocalized over the different composite aromatic rings in the case of these paracyclophane derivatives in contrast to the case of triptycene derivatives where the localization of the unpaired electron on the aromatic ring with the largest electron affinity prevails. This result seems to be reasonable in view of the stronger interaction between the composite aromatic rings in the paracyclophane derivatives than in the triptycene derivatives.

Table 3. Assignment of the hfs constants of [2.2]-(9,10)anthracenophane anion radical (II-1) in comparison with those of 9,10-dimethylanthracene anion radical (DMA) (in units of G)

	DMA	II-1
a_1, a_4, a_5, a_8 (a_1', a_4', a_5', a_8')	2.90	2.14
a_2, a_3, a_6, a_7 (a_2', a_3', a_6', a_7')	1.52	0.82
$a(CH_3)$ or $a(CH_2)$	3.88	1.63

From the results of the present investigation, one may conclude that, in the case of the triptycene derivatives, the unpaired electron is localized on a aromatic ring of the largest electron affinity, and when the triptycene derivative contains the same two aromatic rings, it is completely delocalized over them. In the case of paracyclophane derivatives, the unpaired electron is delocalized over two groups even if they are different from each other.

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