Radical Anions of *syn*- and *anti*-[2.2](1,4)Anthracenophanes Studied by Electron–Nuclear Double Resonance Spectroscopy

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Abstract: Intramolecular electron exchange in radical anions of *syn*- and *anti*-[2.2](1,4)anthracenophanes has been studied by ENDOR spectroscopy and by Hückel molecular orbital theory, including resonance integrals between the π-electron systems. It is found that spin density in the radical anion tends to accumulate on the overlapping part of the molecule. In addition, the nonequivalent β-methylene splittings observed for these anions can be explained by a tightly rocking model of methylene chains.

Since Weissman[2] reported the delocalization of the unpaired electron between the two benzene rings in the [2.2]-paracyclophane anion, there have been a number of ESR studies applied to the radical anions and cations of cyclophane derivatives.[3-8] Williams et al.[4] reported ESR studies on the radical anions in a series of [2.2]paracyclophanes and α,ω-diarylalkanes and investigated the effects of changing the length of the methylene chains. Gerson et al.[5] investigated several [2.2]cyclophane radical anions and reported that the spin distribution between the two equivalent π systems is affected by both solvent and the extent of the π systems. Thus, transannular electronic interactions have been studied in detail for those anions of [2.2]cyclophanes in which the two π systems lie in parallel and are superimposed on each other. However, ESR studies have not been reported for [2.2]cyclophane anions in which the π systems are partially stacked, except for those of the anti isomer of [2.2](1,4)naphthalenophane.[5b,6]

In the present paper, we report ENDOR studies on the radical anions of 1,4-dimethylanthracene (I), the reference compound, and *syn*- and *anti*-[2.2](1,4)anthracenophanes (II and III), in which the two anthracene rings are wholly or partially stacked, respectively. These radical anions appear to be good systems for studying the effect of the extent of overlapping the transannular interaction.

In order to explain the observed ring hyperfine splittings, the simple HMO calculations, which include the resonance integrals between the π-electron systems as parameters, were carried out. Based on the experimentally determined unpaired spin distributions in these radical anions, the effect of partial stacking between two anthracenes on the transannular interaction is discussed. Furthermore, the nonequivalent β-methylene splittings observed for anions II and III are explained by the tightly rocking model of the methylene chains, using the Heller–McConnell relationship.[9] The conformations of the anions are discussed qualitatively in terms of the estimated dihedral angles of the β-methylene protons.

Experimental Section

anti- and *syn*-[2.2](1,4)anthracenophanes were synthesized and purified as reported elsewhere.[10,16] The radical anions were prepared by reduction with metallic sodium or potassium in several different solvents, such as 1,2-dimethoxyethane (DME), tetrahydrofuran (THF), and 2-methyltetrahydrofuran (2-MeTHF), in an acetone–dry ice bath. The radical anions II and III were stable only at temperature lower than −30 and −80 °C, respectively.

The ENDOR spectra were recorded by a JEOL Type ES-EDX-1 spectrometer, under operating conditions similar to those described elsewhere.[11]

Results and Discussion

The ENDOR spectrum of anion I, a reference compound for the [2.2](1,4)anthracenophanes, is shown in Figure 1. The spectrum can be easily analyzed with reference to the ESR spectrum. The observed hyperfine coupling constants are listed in Table I.

The ENDOR spectra of anions II and III are shown in Figure 2. The ESR spectra of these anions have been reported.[6] However, the hyperfine coupling constants were not determined because of the complicated hyperfine structures. The signals in these ENDOR spectra were assigned by reference to the hyperfine coupling constants for anion I and for the anion of [2.2](9,10)anthracenophane,[4-6] which is structually related to the anion II. The observed hyperfine coupling constants for these anions are listed in Table I.

The ENDOR spectra of the anions II and III were measured in several solvents (DME, THF, and 2-MeTHF). The observed hyperfine coupling constants are little affected by solvents and countercations. From Table I, one can see that the hyperfine coupling constants for the anions II and III are about one-half of the corresponding ones for the anion I. This indicates that the unpaired electron is completely delocalized over the two equivalent anthracene rings.

The following interesting results were obtained. The 9-proton hyperfine coupling constant, A_9^H, for the anion III is considerably smaller than that for anion II (2.68 G for II and 2.44 G for III). On the other hand, the other ring proton hyperfine coupling constants for both anions are nearly equal. Furthermore, the β-methylene protons of anions II and III give rise to two different hyperfine coupling constants (0.56 and 0.91 G for II and 0.15 and 1.68 G for III). These nonequivalent splittings of β-methylene protons can be accounted for by means of molecular distortion. Thus it can be considered that in these molecules a preferred rotation of anthracene rings occurs about the methylene bridge. In the anion of [2.2]-(9,10)anthracenophane, such a molecular distortion is not possible; the two anthracene rings are rigid and are parallel to each other, and the β-methylene protons give only one hyperfine coupling constant, as previously reported.[4-6]

Ring-Proton Splittings. In the previous ESR studies on the radical anions of cyclophane derivatives, MO calculations have not been carried out for explaining the hyperfine coupling constants, except in the study by Ishitani and Nagakura[7] of the anion of [2.2]paracyclophane by an SCF-CI method.

Recently, Yoshimi and Kuwata[12] accounted for the unpaired electron density in cation radicals of aromatic dimers by a simple HMO calculation which includes the resonance

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Table I. Observed Proton Coupling Constants (G) for the Radical Anions of 1,4-Dimethylanthracene and *syn*- and *anti*-[2.2](1,4)-Anthracenophanes

	solvent	A_2^H $(A_7^H)^a$	A_8^H	A_9^H	$A_1^{CH_2}$
1,4-dimethyl- (I)	DME	1.53	2.73	5.49	1.68
	THF	1.52	2.78	5.52	1.70
	2-MeTHF	1.53	2.76	5.53	1.60
syn- (II)	DME	0.70 0.77	1.13	2.68	0.56 0.90
	THF	0.72 0.79	1.13	2.67	0.57 0.91
	2-MeTHF	0.74	1.12	2.73	0.54 0.90
anti- (III)	DME	0.73 0.79	1.11	2.44	0.15 1.68
	THF	0.72 0.78	1.11	2.41	0.15 1.66
	2-MeTHF	0.72 0.78	1.10	2.35	0.15 1.67

[a] The ring 2 and 7 proton coupling constants of radical anions II and III are not clearly assigned.

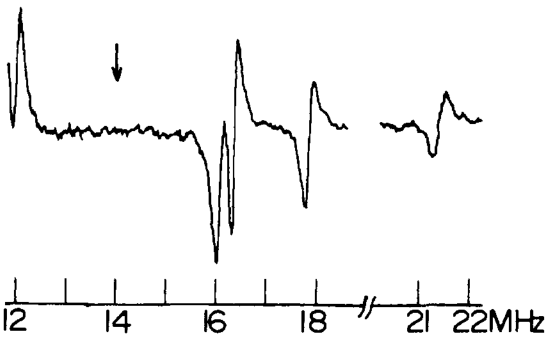

Figure 1. ENDOR spectrum of the anion of 1,4-dimethylanthracene obtained by reduction with sodium in THF solution at −100 °C.

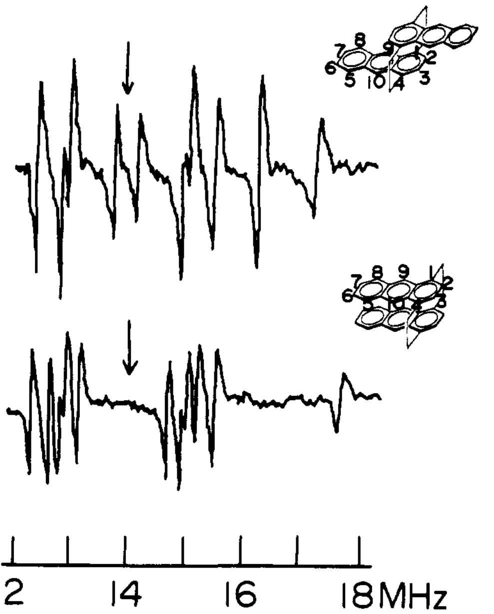

Figure 2. ENDOR spectra of anions of *syn*- and *anti*-[2.2](1,4)anthracenophanes obtained by reduction with sodium in THF solution at −100 °C: top, *anti*-; bottom, *syn*-.

integrals between the carbon atoms of the aromatic rings.

In the present study, we carried out similar HMO calculations, which include the ($2p\sigma$-$2p\sigma$) type resonance integral for pairs of carbon atoms between the two anthracene rings lying on top of each other. This type of resonance integral, $\beta(C^u\text{-}C^l)$, is assumed to be proportional to the overlap integrals, as follows:

$$\beta(C^u\text{-}C^l) = \frac{S(C^u\text{-}C^l)}{S_{\pi\pi}}\beta \qquad (1)$$

where the value of $S_{\pi\pi}$ is taken to be 0.25. The values of $\beta(C^u\text{-}C^l)$ were varied as semiempirical parameters from 0.05β to 0.4β. The overlap integral between the carbon atoms of the upper and lower ring is taken from the table of Mulliken et al.,[13] and the values of 0.4β and 0.05β correspond to about 2.65 and 3.70 Å for the distances between the two aromatic rings.

For the sake of simplicity, the two aromatic rings are assumed to be planar and parallel. The inductive parameter of the methylene group was taken into account to the same order as that of the methyl group; that is, the Coulomb integral of the 1 or 4 positions was estimated to be $\alpha_1 = \alpha_4 = \alpha - 0.2\beta$.[8]

For the anion II, the calculated values of unpaired electron spin densities are independent of the value of $\beta(C^u\text{-}C^l)$ and are just one-half of the values of the corresponding ones of the anion I, as expected.

In Figure 3, the unpaired electron densities of anion III are plotted against the values of $\beta(C^u\text{-}C^l)$. As the value of $\beta(C^u\text{-}C^l)$ increases, the spin densities at carbon atoms 1 and 2 increase, although the spin densities at the other positions decrease. That is, the spin population in anion III tends to accumulate on the overlapping part of the anthracene rings when the resonance integral $\beta(C^u\text{-}C^l)$ becomes larger. On the other hand, it is noteworthy that in the limiting case, $\beta(C^u\text{-}C^l) \rightarrow 0$, each spin density of anion III approximates the corresponding spin density of anion II.

The calculated spin densities match the experimental ones when the value of $\beta(C^u\text{-}C^l)$ is assumed to be 0.2, and this value corresponds to the distance (3.1 Å) between the stacked aromatic rings. The experimental spin densities (ρ_i^π) of the ring carbons were estimated by the McConnell relationship,[14] $A_i^H = Q\rho_i^\pi$, where the A_i^H is the ring proton hyperfine coupling constant and $Q = -27$ G. The distances between the stacked aromatic rings for the various paracyclophane molecules are known to be 2.8–3.7 Å.[16,17] The value, 3.1 Å, thus obtained can be considered to be qualitatively reasonable.

The experimental result that the hyperfine coupling constant, A_9^H, for anion III is small in comparison with A_9^H for anion II can now be understood as follows. In the anion III, where two anthracene rings are partially stacked, the transannular effect makes the spin population accumulate on the overlapping part of the molecule, and the conjugation between

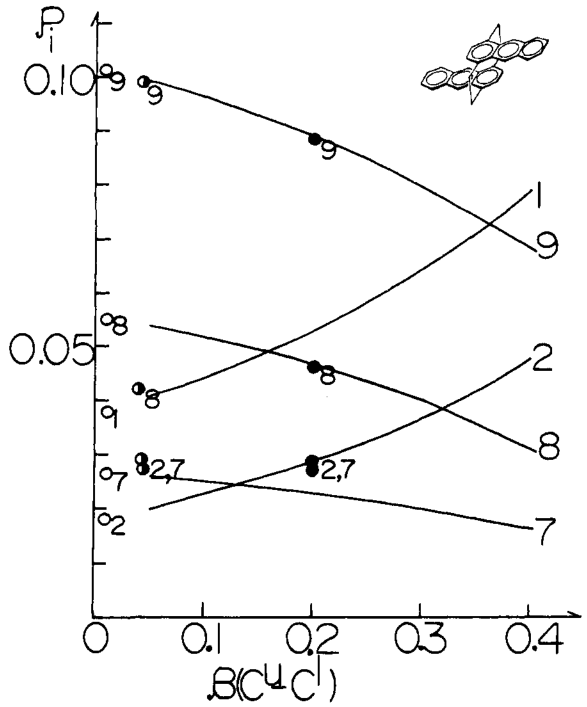

Figure 3. Calculated spin densities in the anion of *anti*-[2.2](1,4)anthracenophane as a function of the resonance integral $\beta(C^{u}-C^{1})$: calculated values, ○; experimental values, ◑$_i$, *syn*-; ●$_i$, *anti*-.

the two equivalent π systems is increased. Thus the π energy of the molecule is effectively stabilized.

Nonequivalent β-Methylene Proton Splittings. The β-methylene protons of anions II and III give two different hyperfine splittings, and the absolute value of the difference between two nonequivalent β-proton splittings of anion III, $|1.66 - 0.15|$ G, is very large in comparison with the value of anion II, $|0.91 - 0.57|$ G.

In previous ESR and ENDOR studies,[8] exceptional hindrance of internal rotation of the methylene chain was reported for 4,4′-, 3,4′-, and 3,3′-polymethylenediphenyl anions, where two methylene protons gave two different hyperfine splittings. The nonequivalent β-methylene proton splittings have been understood by assuming a tightly rocking model of the methylene chain, based on the Heller–McConnell relationship (eq 2).[9] In these cases, the sum of the two dihedral angles of the nonequivalent β protons is about $2\pi/3$.

A similar situation probably exists in the present case. Based on the HMO's spin density (ρ_1^{π}) at the 1 position and observed methylene proton splittings, the equilibrium dihedral angles, θ, were calculated using the following equation.[9]

$$A_1^{CH_2} = B\rho_1^{\pi}\cos^2\theta \tag{2}$$

Taking the value of B to be 54 G, the values of dihedral angles, θ, were calculated to be 48 and 59° for anion II and 41 and 77° for anion III. From the results of the X-ray analysis of the molecule II[16] and estimated dihedral angles, a preferable conformation of anion II was assumed as illustrated in Figure 4.

For the molecule III, the conformational analysis by the X-ray method has not yet been reported. Nevertheless, the structure of anion III is proposed on the basis of the estimated dihedral angles, as follows.

According to the investigation of hindered internal rotation of alkyl groups,[15] the motion of the methylene groups of anion III is thought to be strongly restrained by the steric repulsion due to the neighboring 9-CH (or 10-CH) groups, and the β-methylene protons therefore prefer to be away from the 9-ring proton (or 10-ring proton). Furthermore, the present HMO calculation suggests that the total π energy of anion III is progressively stabilized with increasing area of ring overlap in the molecule. From the above physical considerations and the estimated dihedral angles, the struction of anion III has been approximated as shown in Figure 4.

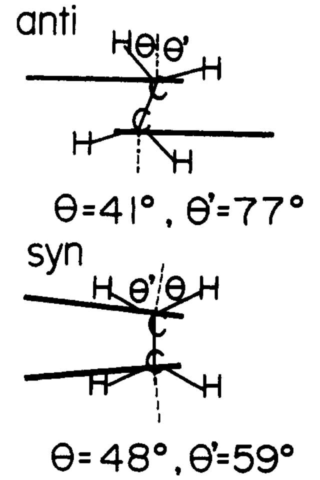

Figure 4. Geometrical structures assumed for anions of *syn*- and *anti*-[2.2](1,4)anthracenophanes. θ and θ' denote the calculated dihedral angles of the β-methylene protons.

The structure of anion III, thus obtained, is more or less qualitative. This conformation, however, not only satisfies the energy minimum conditions (π energy + steric repulsion) but also explains the experimental result that the absolute value of the difference between two distinct β-methylene proton splittings for anion III is larger than that for anion II.

In this section, we have discussed the stability of a molecular conformation based on the π energy calculated from the HMO method. We admit that the HMO method does not give a precise value of the π energy. Nevertheless, we believe that the conclusion obtained is qualitatively right and help us to understand the spin distribution of the paracyclophane anion and the transannular interaction.

References and Notes

(1) (a) Ehime University; (b) Osaka University.
(2) S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 6462 (1958).
(3) R. M. Dessau, *J. Chem. Phys.*, **54**, 5430 (1971); F. Tanaka and N. Mataga, *Bull. Chem. Soc. Jpn.*, **46**, 2591 (1973); F. Gerson, G. Kaupp, and H. Ohya-Nishiguchi, *Angew. Chem.*, **89**, 666 (1977).
(4) D. J. Williams, J. M. Pearson, and M. Levy, *J. Am. Chem. Soc.*, **93**, 5483 (1971).
(5) (a) F. Gerson and W. B. Martin, Jr., *J. Am. Chem. Soc.*, **91**, 1883 (1969); Ch. Elschenbroich, F. Gerson, and J. A. Reiss, *ibid.*, **99**, 60 (1977); (b) F. Gerson, W. B. Martin, Jr., and Ch. Wylder, *ibid.*, **98**, 1318 (1976).
(6) T. Hayashi, M. Mataga, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **48**, 416 (1975).
(7) A. Ishitani and S. Nagakura, *Mol. Phys.*, **12**, 1 (1967).
(8) K. Ishizu, F. Nemoto, H. Hasegawa, K. Yamamoto, and M. Nakazaki, *Bull. Chem. Soc. Jpn.*, **46**, 140 (1973); K. Ishizu, F. Nemoto, K. Yamamoto, and M. Nakazaki, *ibid.*, **48**, 2168 (1975).
(9) C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).
(10) T. Toyoda, I. Otsubo, T. Otsubo, Y. Sakata, and S. Misumi, *Tetrahedron Lett.*, 1731 (1972); A. Iwama, T. Toyoda, T. Otsubo, and S. Misumi, *ibid.*, 1725 (1973); *Chem. Lett.*, 587 (1973).
(11) T. Yamamoto, K. Sato, and Y. Miyamae, *Jpn. J. Appl. Phys.*, **11**, 1508 (1972).
(12) H. Yoshimi and K. Kuwata, *Mol. Phys.*, **23**, 297 (1972).
(13) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).
(14) H. M. McConnell, *J. Chem. Phys.*, **24**, 633, 764 (1956).
(15) F. Nemoto and K. Ishizu, *J. Phys. Chem.*, **79**, 1730 (1975); F. Nemoto, F. Shimoda, and K. Ishizu, *Bull. Chem. Soc. Jpn.*, **48**, 2627 (1975); F. Nemoto, *ibid.*, **49**, 1194 (1976).
(16) Recently, the molecular geometry of *syn*-[2.2](1,4)anthracenophane has been determined by X-ray crystallography, and the geometrical structure obtained indicates that the two anthracene rings slightly fan out and their distances lie between 2.79 and 3.79 Å: T. Toyoda and S. Misumi, *Tetrahedron Lett.*, 1479 (1978); A. Iwama, T. Toyoda, M. Yoshida, T. Otsubo, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **51**, 2988 (1978).
(17) C. J. Brown, *J. Chem. Soc.*, 3265 (1953).