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Stabilization Energy and Spin Distribution in Pyrenophane Cation Radicals

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The cation radicals of three [2.2]pyrenophanes in which two pyrene moieties are twisted each other by 0°, 35°, and 60° were investigated by ESR, ENDOR, and cyclic voltammetry. Considerable variations of the spin density distribution and the stabilization energy with the twisting angle have been observed. The obtained results are discussed in terms of modified Hückel-McLachlan type calculation.

A number of dimer cation radicals of aromatic hydrocarbons have been observed by electron spin resonance (ESR).[1–3] From the analysis of the hyperfine coupling constants (hfcc) it was confirmed that the unpaired electrons in the dimer cation radicals are distributed equally over the two aromatic moieties. Based on the ESR results and theoretical calculations it has been postulated that these dimer cations have eclipsed configurations in which one moiety lies upon the top of the other symmetrically.

On the other hand, X-ray studies indicate that the aromatic cation radical salts $(\mathrm{Ar})_2{}^{+}\cdot\mathrm{X}^{-}$ ($\mathrm{X}=\mathrm{PF}_6$) have twisted configurations with the twisting angles of 90° and 180°.[4] These observations show that the dimer configuration is very sensitive to the environment. Thus it is of interest to examine how the orbital energy and spin distribution vary with configuration.

In this work, we have measured the ESR, ENDOR (electron nuclear double resonance) spectra and the oxidation potentials of three [2.2]pyrenophanes, **1** to **3**, shown in Fig. 1. From their molecular models the twisting angles between the upper and lower pyrene moieties (θ) are estimated to be 0°, 35°, and 60° in **1**, **2**, and **3**, respectively. The obtained results are discussed based on a simple molecular orbital calculation of the spin density distributions and the orbital energies of the highest occupied molecular orbitals (HOMO) as a function of θ.

Experimental

Synthetic methods of the compounds **1** to **3** were reported elsewhere.[5] The cation radicals were generated by oxidation with $\mathrm{CF_3COOH}$ or $\mathrm{CF_3COOD}$ in $\mathrm{CH_2Cl_2}$, or by electrochemical oxidation. The oxidation potentials ($E^{\circ}_{1/2}$) were measured by cyclic voltammetry (CV). Further experimental details were similar to those described previously.[3,6]

Results and Discussion

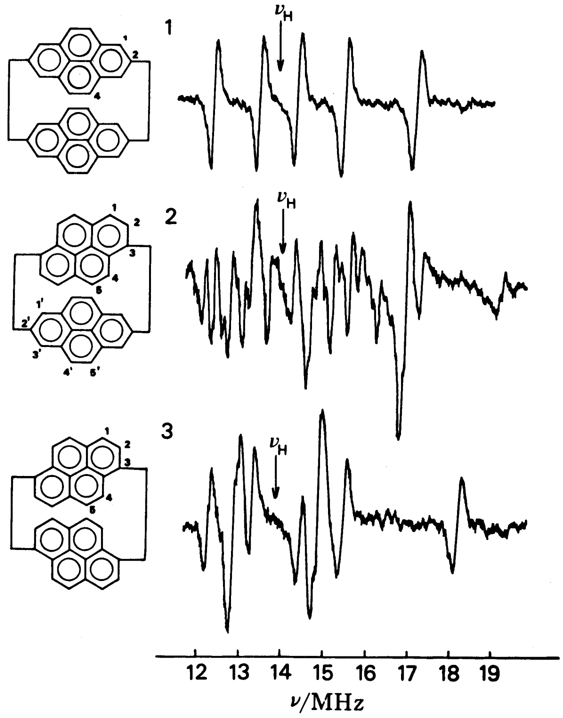

Fig. 1. Molecular structures and ENDOR spectra of three [2.2]pyrenophanes, **1** to **3**.

In Fig. 1 are shown the ENDOR spectra of $\mathbf{1}^{+\cdot}$, $\mathbf{2}^{+\cdot}$, and $\mathbf{3}^{+\cdot}$ observed at −85 °C. The obtained hfcc are given in Table 1 with those of pyrene dimer cation radical ($\mathbf{P}_2{}^{+\cdot}$).[1] The ESR spectra of $\mathbf{1}^{+\cdot}$ and $\mathbf{3}^{+\cdot}$ measured at −65 °C were well resolved but that of $\mathbf{2}^{+\cdot}$ was only partially resolved. These ESR spectra were all reconstructed well by the computer simulation using the hfcc obtained from the ENDOR spectra. The observed and simulated ESR spectra of $\mathbf{3}^{+\cdot}$, for example, are shown in Fig. 2. For the help of assignment, we also measured the ESR spectra of $\mathbf{1}^{+\cdot}$, $\mathbf{2}^{+\cdot}$, and $\mathbf{3}^{+\cdot}$ which were oxidized by excess amounts of $\mathrm{CF_3COOD}$ instead of $\mathrm{CF_3COOH}$. Their ESR spectra clearly showed the hyperfine splittings due to deuterons exchanged with the ring protons with the hfcc larger than about 2.0 G.** It is known that no H–D exchange takes place for the protons of the alkyl groups by $\mathrm{CF_3COOD}$.[7] The hfcc of protons exchanged by deuterons are indicated in Table 1.

The hfcc of $\mathbf{1}^{+\cdot}$ are similar to those of $\mathbf{P}_2{}^{+\cdot}$ and can be assigned easily. Therefore, $\mathbf{1}^{+\cdot}$ can be regarded as a good model for $\mathbf{P}_2{}^{+\cdot}$. The hfcc of $\mathbf{2}^{+\cdot}$ and $\mathbf{3}^{+\cdot}$, however, are different from those of $\mathbf{1}^{+\cdot}$ and $\mathbf{P}_2{}^{+\cdot}$ and cannot be assigned uniquely because of the presence of a large

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** 1 G=10^{-4} T.

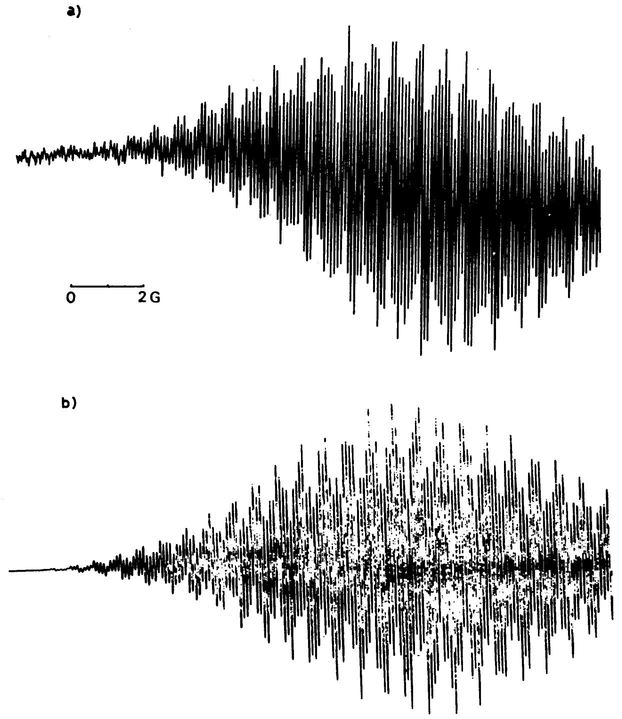

Fig. 2. The observed (a) and simulated (b) ESR spectra of $\mathbf{3}^{+\cdot}$.

Table 1. The hyperfine coupling constants and the oxidation potentials ($E^\circ_{1/2}$) of three pyrenophanes (**1**—**3**) compared with those calculated

	Obsd		Calcd	
	$E^\circ_{1/2}$[a)]/V	hfcc/G	Energy/β	hfcc/G
$\mathbf{P}_2^{+\cdot}$ (**P**)	(1.22)	(8H)2.659	(0.445)	(1)−2.318
		(8H)1.096		(4)−1.194
		(4H)0.575		(2) 0.705
$\mathbf{1}^{+\cdot}$	0.81	(8H)2.342[b)]	0.338	(1)−2.318
		(8H)1.107		(4)−1.195
		(8H)0.316		(2) 0.316[c)]
$\mathbf{2}^{+\cdot}$	0.94	(2H)3.702[b)]	0.382	(1)−3.904
		(2H)2.390[b)]		(4)−2.533
		(2H)2.090[b)]		(5)−2.294
		(2H)2.090		(3) 2.057[c)]
		(2H)1.653		
		(2H)1.290	d)	(2)−0.815
		(2H)1.155		(3′)−0.406
		(2H)0.840		(5′) 0.218
		(2H)0.720		(2′)−0.158[c)]
		(2H)0.450		
		(2H)0.130		(4′) 0.153
		— —		(1′) 0.137
$\mathbf{3}^{+\cdot}$	0.80	(4H)3.080[b)]	0.314	(1)−2.443
		(4H)1.144		(4)−1.259
		(4H)0.704	d)	(3) 0.992[c)]
		(4H)0.625		
		(4H)0.616		(5)−0.979
		(4H)0.440		(2) 0.711

a) Measured at room temperature. Solvent: CH_2Cl_2. Supporting eletrolyte: $(C_4H_9)_4NPF_6$. b) Protons exchanged to deuterons by using CF_3COOD. c) Bridge protons calculated with Q=11 G. d) Assignments of these hfcc are not unique.

number of hfcc. It should be noted here that the largest hfcc of $\mathbf{2}^{+\cdot}$ and $\mathbf{3}^{+\cdot}$, 3.702 G and 3.080 G, respectively, are much larger than that of $\mathbf{1}^{+\cdot}$, 2.342 G. This fact indicated that a considerable redistribution of the spin density takes place in $\mathbf{2}^{+\cdot}$ and $\mathbf{3}^{+\cdot}$.

We also measured the oxidation potentials ($E^\circ_{1/2}$) of these compounds by the CV technique to investigate the energy changes due to the twisting. $E^\circ_{1/2}$ of pyrene and **1** to **3** are also shown in Table 1. $E^\circ_{1/2}$ of **1** is 0.81 V, being lower than that of **P** by 0.41 V because of the transannular interaction, as we reported previously in the case of multilayered compounds.[3)] On the other hand, $E^\circ_{1/2}$ of **2** was appreciably higher than that of **1**. This increase is likely to be caused by the reduction of the resonance integral due to the twisted structure of **2**. Such a reduction of the stabilization energy has also been observed in the photoelectron spectra of several twisted naphthalenophanes.[8)] However, $E^\circ_{1/2}$ of **3** becomes comparable to that of **1** (0.80 V) in spite of its twisted structure.

In order to clarify the effects of the twisting angle in the dimer structure we calculated the spin density and the orbital energy by modified Hückel-McLachlan's method. We carried out the calculation with the assumption that the resonance integrals between the upper and lower atoms of pyrene moieties (β_{1-u}) are proportional to the 2pσ-2pσ type overlap integral between the upper and lower carbon atoms (S_{1-u}) and are given by[9)]

$$\beta'_{1-u} = A\cdot S_{1-u}\cdot \beta_{C-C}, \qquad (1)$$

where A is the proportionality constant. Two pyrene moieties were assumed to be 3.5 Å apart with the molecular planes parallel to each other. The effects of the bridging ethylene groups were taken into account by changing the Coulomb integrals of the carbon atoms ($\alpha_{C'}$) attached by the ethylene groups to $\alpha_{C'}=\alpha_C-0.1\beta$. In the first place, we calculated S_{1-u} in Eq. 1 and estimated β'_{1-u} using the parameter A. Subsequently we calculated the spin density by the McLachlan's method. Hfcc were calculated by using $Q=-25$ G for the ring protons and $Q=11$ G for the bridge protons. The latter value was estimated from the calculated spin density on the bridged carbon atoms and the hfcc of the ethylene protons obtained experimentally for $\mathbf{1}^{+\cdot}$. The bridge protons of $\mathbf{2}^{+\cdot}$ and $\mathbf{3}^{+\cdot}$ are not equivalent with those of $\mathbf{1}^{+\cdot}$ because of the torsion of the ethylene groups, but the deviations from the equivalent positions are not so large. Therefore, this value was used for the bridge protons of $\mathbf{2}^{+\cdot}$ and $\mathbf{3}^{+\cdot}$ in order to make a rough estimate of their hfcc. The calculated hfcc for A=4.0 are given in Table 1.

The agreement between the calculated and observed hfcc in $\mathbf{P}_2^{+\cdot}$ and $\mathbf{1}^{+\cdot}$ is very good. The spin density distribution in $\mathbf{1}^{+\cdot}$ and $\mathbf{3}^{+\cdot}$ does not depend much on the choice of A and the unpaired electron is equally distributed over the two pyrene moieties, whereas the unpaired electron in $\mathbf{2}^{+\cdot}$ is almost localized on one moiety (upper moiety in Fig. 1). This is due to the fact

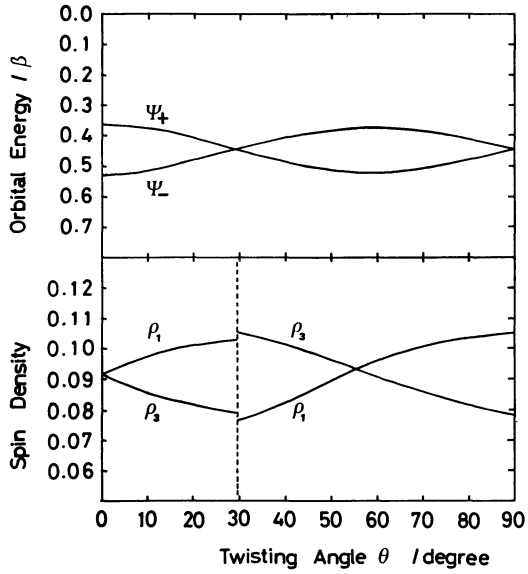

Fig. 3. Twisting angle (θ) dependences of the Hückel orbital energies and the spin densities at positions 1 and 3 in the pyrene dimer cation radical ($\mathbf{P}_2^{+\cdot}$).

that the positions attached by the bridging ethylene groups in the two pyrene moieties of **2** are not equivalent. At $A=4.0$ a fairly good agreement between the observed hfcc of $\mathbf{2}^{+\cdot}$ and the calculated one was obtained in spite of the simple calculation. Comparing the observed hfcc of $\mathbf{2}^{+\cdot}$ and $\mathbf{3}^{+\cdot}$ with those calculated, the largest hfcc of $\mathbf{2}^{+\cdot}$ and $\mathbf{3}^{+\cdot}$, 3.702 G and 3.080 G, respectively, can be assigned both to the protons attached to the position 1 shown in Fig. 1. However, there remains some ambiguities in the assignment of smaller hfcc of $\mathbf{2}^{+\cdot}$ and $\mathbf{3}^{+\cdot}$.

The variation of $E^\circ_{1/2}$ and the increase of the spin density on position 1 can be caused by the effect of the twisting and the difference in the position attached by the ethylene groups. It is necessary to decide which is the main cause. In Fig. 3 are shown the dependences of the orbital energies in unit of β and the spin densities on the twisting angle θ, which were obtained by Hückel-McLachlan's method without the effects of the ethylene groups. At $\theta=0°$ the energies of the bonding orbital ψ_- and antibonding orbital ψ_+ constructed by the combination of HOMO of the two pyrene moieties are split into two due to the transannular interaction. As θ increases, the energies of these two orbitals approach each other because of the reduction of the resonance stabilization. At $\theta=30°$ the two orbitals invert their energies and the energy of ψ_- reaches a maximum at $\theta=60°$. The energy of ψ_- at $\theta=60°$ is almost equal to that of ψ_+ at $\theta=0°$. The orbital energies of HOMO at 0°, 35°, and 60° calculated including the effects of the ethylene groups are indicated in Table 1 for the sake of comparison. These values are about 0.04β higher than those with the corresponding angles given in Fig. 3. This means that the effect of the ethylene groups to the HOMO only lifts the orbital energies by 0.04β. This behavior corresponds well to the variation of the $E^\circ_{1/2}$ of **1** to **3**.

The spin densities on the position 1 and 3, ρ_1 and ρ_3, respectively, also vary with θ as shown in Fig. 3. The spin densities change discontinuously at $\theta=30°$, corresponding to the inversion of the energies of ψ_+ and ψ_-. ρ_1 at $\theta=35°$ can be converted to the hfcc of 2.0 G, which is much smaller than 3.702 G obtained experimentally in $\mathbf{2}^{+\cdot}$. On the other hand, the calculated hfcc at position 1 with the bridge effects (Table 1) are close to the experimental values. It is then concluded that the effect of the bridging ethylene groups is the main cause of the large hfcc at position 1 in **2**. ρ_1 at $\theta=60°$ is close to ρ_1 at $\theta=0°$ irrespective of the effects of ethylene groups. However, the largest hfcc obtained experimentally in $\mathbf{3}^{+\cdot}$ (3.080 G) does not agree so well with that calculated (2.443 G).

In conclusion, as the twisting angle θ between the two moieties increases, the spin redistribution occurs because of the change in the resonance integral β'_{1-u} accompanying the loss of the resonance stabilization. As the angle increases further, ψ_+ and ψ_- invert their energies and gradually regain the resonance stabilization.

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