BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (10), 2801—2802 (1977)

The ESR and ENDOR Spectra of the [2.2](2,7)Pyrenophane Anion Radical

Kazuhiko Ishizu, Yoshinori Sugimoto, Teruo Umemoto,* Yoshiteru Sakata,* and Soichi Misumi*

Department of Chemistry, Faculty of Science, Ehime University, Matsuyama, Ehime 790

**The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565*

(Received April 4, 1977)

Synopsis. The ESR and ENDOR spectra of the [2.2](2,7)-pyrenophane anion, which was prepared by reduction with alkali metal in ethereal solvents, were observed. From a comparison of the spin densities for the anion with those for the pyrene anion, the delocalization of the unpaired electron between the stacked aromatic rings was demonstrated.

Since ESR was successfully used in studies of the intramolecular electron exchange in the [2.2]paracyclophane anion by Weissman,[1] the transannular interaction between the aromatic nuclei has been reported for several cyclophanes, such as [2.2](1,4)naphthalenophane[2] and [2.2](9,10)anthracenophane,[3] where the cyclophane derivative has been regarded as an artificial dimer of the alkyl-substituted aromatics, and the proton hyperfine splitting showed nearly half the value of that for the corresponding monomer anion. In the present note, we wish to report our ESR and ENDOR studies of the [2.2](2,7)pyrenophane anion. Studies of [2.2]-(2,7)pyrenophane have been interesting since, because the pyrenophane MO occupied by the unpaired electron has a node at the bridging positions (2,7) of the pyrene ring, the delocalization of the unpaired electron due to σ-π exchange or the hyperconjugative interaction between the methylene and aromatic groups can be ignored. Therefore, one may expect to elucidate the pure transannular effect on the spin density regardless of either the hyperconjugative or the inductive effect of the bridged ethylene groups in the present case.

Experimental

The synthesis of materials has been described elsewhere.[4] The anion radical was prepared by reduction with sodium in 1,2-dimethoxyethane (DME) and tetrahydrofuran (THF). The ENDOR spectra were recorded with a JEOL-type EX-EDX-1 spectrometer under the operating conditions similar to those described previously.[5]

Results and Discussion

Figure 1 shows the ESR spectrum of the pyrenophane anion, which was prepared by reduction with sodium in DME. The ESR spectrum is composed of 25 hyperfine lines equally spaced, with a line width of 150 mG. The ESR hyperfine structure can be adequately analyzed in terms of the splittings (2.18 G) due to the 8 equivalent protons; the structure is split further into 9 lines attributable to the other equivalent protons with a splitting constant of nearly half. No important changes were detected in the ESR hyperfine structure obtained with THF, and the extra splittings of the alkali metal cation have never been observed anywhere.

The ENDOR spectra of pyrene and pyrenophane anions are shown in Fig. 2. The pyrene anion gives the three ENDOR signals (15.33, 16.88, and 20.71 MHz) above the free proton frequency (13.89 MHz). The splittings were assigned with reference to the previous ESR studies;[6] $a_2^H=a_7^H=1.02$, $a_4^H=a_5^H=a_9^H=a_{10}^H=2.13$, and $a_1^H=a_3^H=a_6^H=a_8^H=4.87$ G. On the other hand, the ENDOR signals of the pyrenophane anion were recorded at 15.40 and 17.05 MHz above the free proton frequency. No ENDOR absorption

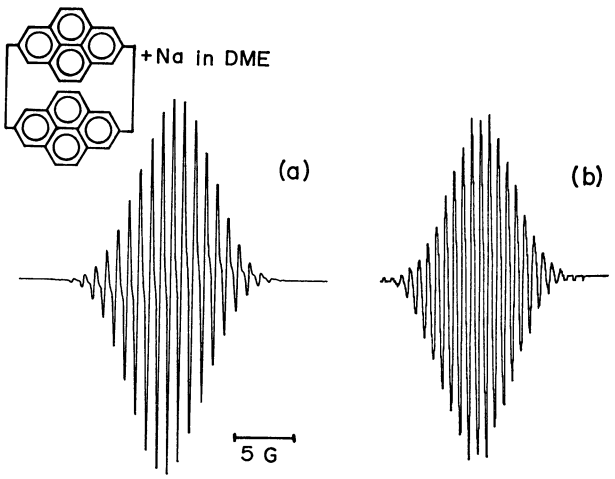

Fig. 1. (a) ESR spectrum of [2.2](2,7)pyrenophane anion recorded at room temperature. (b) A computer simulation of the ESR spectrum.

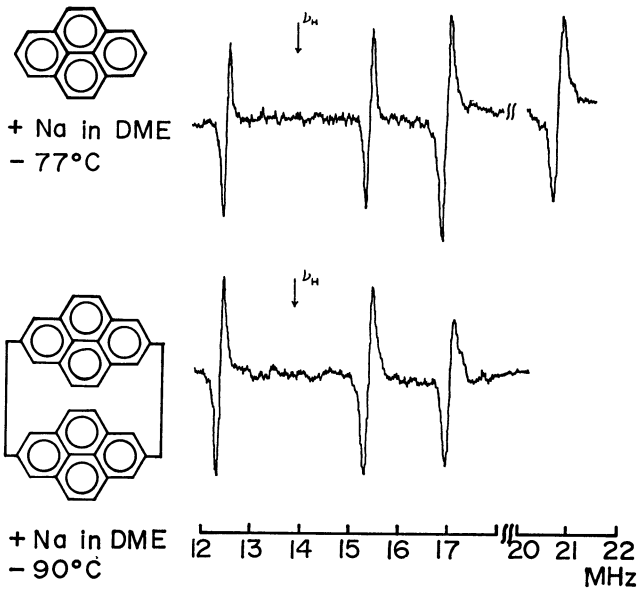

Fig. 2. Higher frequency halves of ENDOR spectra of pyrene and [2.2](2,7)pyrenophane anions. ν_H: free proton frequency.

attributable to the bridging methylene groups can be detected. The splittings of each pyrene group were determined to be 1.08 G for a_4^H, a_5^H, a_9^H, and a_{10}^H and 2.25 G for a_1^H, a_3^H, a_6^H, and a_8^H. Based on the present assumption, computer calculations of the ESR line intensities showed an excellent agreement with the observed spectrum, as is shown in Fig. 1.

The splittings of the pyrene and pyrenophane anions thus determined are summarized in Table 1.

In the previous ESR works on the cyclophane anions, it was pointed out that the spin-density distrubution showed a large dependence on the degree of the transspatial exchange of the unpaired electron in the cyclophane. In [2.2]paracyclophane, however, the doubly degenerated antibonding orbital of the benzene anion causes much difficulty.[7] The importance of the inductive effect of the methylene groups was recently proposed, and the unpaired electron is believed to occupy the orbital which can be expressed by a linear combination of the antisymmetric orbital relative to a plane passing through the two opposite centers and perpendicular to the benzene ring.[8] For [2.2](9,10)anthracenophane, the largest spin densities were assigned to the bridging positions, 9 and 10. Therefore, the possibility of the hyperconjugative interaction of the methylene, which also causes a perturbation on the spin densities, in particular, for the positions with small spin densities, can not safely be ruled out.

Table 1. Proton hyperfine splittings of pyrene and the [2.2](2,7)pyrenophane anion
(absolute value in G)

Position	2, 7	4, 5, 9, 10	1, 3, 6, 8
Pyrene	1.02	2.13	4.87
Pyrenophane	$<$150 mG	1.08	2.25

As may be seen in Table 1, the observed ring-proton splittings of the pyrenophane anion are very close to the half-values of those of the pyrene anion radicals, and the methylene proton splitting is very small. This means that the unpaired orbital of the pyrenophane is antisymmetric with respect to the plane passing through the bridging position and perpendicular to the aromatic plane, indicating a negative spin density at the bridging position.

A perturbation of the spin densities due to the hyperconjugative interaction of the methylene group can thus be ignored. A tentative calculation of the methylene proton was performed under the assumptions that the spin densities at the bridging positions, ρ^π, are not affected much by the methylene substitution and that the magnitude of the spin density is reduced to the half-value from that of the pyrene anion.[9] If the methylene protons are tightly fixed in the positions taking the dihedral angle to be $\theta=60°$, the methylene proton splitting can be estimated to be 0.220 G, based on McConnell and Heller's equation, $a^R=B\rho^\pi \cos^2\theta$, $|B|=50$ G.[10] The calculated value is indeed small, and it would be diminished to the order of the ESR linewidth in the real molecule.

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