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5,6,11,12-tetra-phenylnaphthacene anion and cation radicals**

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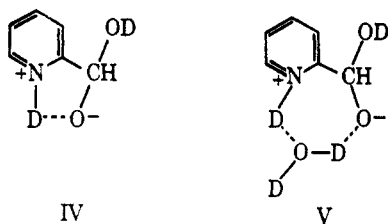
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pyridinecarboxaldehyde hydrate. However, the standard free energy changes for the hydration of 2- and 4-pyridinecarboxaldehyde are comparable, implying that structures IV and V which contain *cyclic* hydrogen bridging do not play dominant roles in stabilizing the ground state of the 2-pyridinecarboxaldehyde hydrate.

Electron Spin Resonance Spectra of 5,6,11,12-Tetraphenylnaphthacene

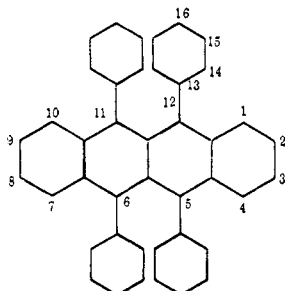
Anion and Cation Radicals

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The electron spin resonance (esr) spectra of 5,6,11,12-tetraphenylnaphthacene (rubrene) anion and cation radicals prepared by electrochemical generation are given. The assigned experimental coupling constants are compared to those calculated from simple Hückel molecular-orbital (HMO) theory. The possibility of bond formation between nonadjacent carbon atoms is discussed, and calculations are made to determine the effect this would have on the esr spectra. The angle between the phenyl substituents and the naphthacene nucleus obtained from the esr spectra agrees with that reported for an X-ray crystallographic study of a similar compound.

Recent interest in the chemiluminescent reactions²⁻⁴ of



5,6,11,12-tetraphenylnaphthacene (rubrene) prompted an investigation of the anion and cation radicals of this hydrocarbon. Additional interest centers on the nonplanarity of the molecule caused by interaction of two phenyl groups *peri* to each other. Jaffé and Chal-

vet⁵ in a study of phenyl-substituted naphthacenes postulated an interaction between the adjacent phenyl groups in rubrene which leads to a bathochromic effect in the ultraviolet spectrum.

In a previous paper,⁶ we reported a study of the esr spectra of 9-phenylanthracene and 9,10-diphenylanthracene anion radicals. Assignments of the cou-

(1) To whom all correspondence and request for reprints should be directed.

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pling constants for these radicals were presented, and these assignments were shown to be consistent with molecular-orbital calculations for a certain angle between the phenyl rings and the anthracene nucleus. The study of the esr spectra of rubrene ion radicals reported here was undertaken to further test the validity of this approach to structure determinations.

Results and Discussion

Anion Radical. The generation of rubrene anion radical was attempted by potassium metal reduction in dimethoxyethane (DME), using an apparatus that has been previously described.⁶ In this experiment, a purple solution, which gave no esr signal, was obtained. Upon continued reduction, this purple solution turned brown and yielded an esr spectrum, which was recognized as that of the biphenyl anion radical. Because rigorous purification techniques were employed, we think it unlikely that biphenyl was present as an impurity. Hence, the cleavage of one or more of the phenyl substituents with a subsequent recombination to form biphenyl probably occurs. If the purple solution is exposed to air, it immediately reacts to give the color of the original solution. These experiments lead us to believe that the purple solution corresponds to the dianion. The potassium treatment was repeated several times, but it was not possible to effect a one-electron reduction.

Since sodium is not as strong a reducing agent as potassium, the same experiment was performed with sodium metal. In this experiment a dark olive-green solution was obtained which gave a well-resolved esr spectrum. If the reduction was allowed to continue, however, the purple solution resulted which again gave no esr signal. Since the esr spectrum of the radical resulting from sodium metal reduction of rubrene was quite narrow, and since cleavage has been shown to occur upon potassium reduction, we felt that additional evidence was necessary to show that the radical formed by sodium metal reduction was indeed rubrene anion radical. We therefore carried out exhaustive controlled potential electrolysis at -1.2 v vs. a silver-silver iodide reference electrode in a dimethylformamide (DMF) solution. Vacuum transfer was made to 3-mm tubing, and the radical solution was examined at -50° . The esr spectrum thus obtained is shown in Figure 1a. This radical solution was dark olive-green, and the spectrum shown in Figure 1a is the same as the one obtained from sodium metal reduction. If electrolysis is carried out at a potential corresponding to the plateau of the second polarographic wave, a purple solution is obtained which gives no esr signal.

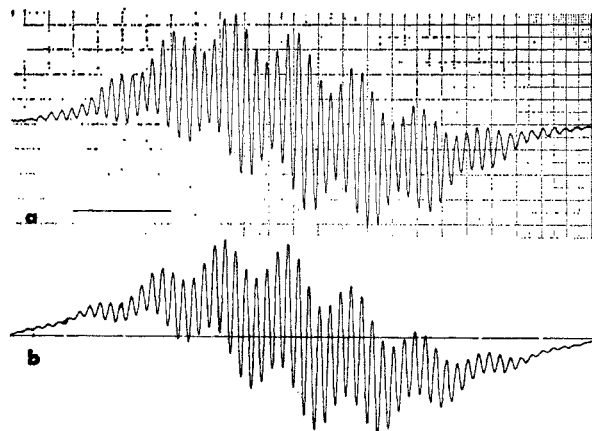


Figure 1. (a) Top: esr spectrum of 5,6,11,12-tetraphenylanthracene anion radical prepared by electrochemical reduction in DMF and examined at -50° ; (b) bottom: theoretical simulated esr spectrum using the coupling constants given in the last column of Table I and a line width of 0.12 gauss.

The experimental coupling constants for the rubrene anion radical were determined from the spectrum shown, and these are listed in the last column of Table I. A theoretical simulated spectrum using these coupling constants and a line width of 0.12 gauss is shown in Figure 1b.

Table I: Experimental and Theoretical Coupling Constants of 5,6,11,12-Tetraphenylanthracene Anion Radical Using Hückel Spin Densities

Carbon atom	Hückel/spin density	a_H , gauss ^d			Exptl
		Colpa-Bolton ^a	Giacometti-Nordio-Pavan ^b	McConnell ^c	
1	0.0493	1.30	1.46	1.48	1.54 ^e
2	0.0305	0.81	0.91	0.91	1.09 ^e
14	0.0068	0.18	0.20	0.20	0.21
15	0.0001	0.00	0.00	0.00	...
16	0.0073	0.20	0.21	0.22	0.21

^a $Q = 27$ and $K = 12$ gauss. ^b $Q_1 = 31.5$ and $Q_2 = 7.0$ gauss. ^c $Q = 30$ gauss. ^d All coupling constants are expressed with their absolute value. ^e Assigned to this position on the basis of MO theory. ^f Calculated for $\theta = 65^\circ$.

Hückel molecular orbital calculations were made as previously described,⁶ with the assumption that all steric strain is relieved by rotations of the phenyl rings out of the plane of the naphthalene nucleus. The resonance integral, β , for the bonds connecting the phenyl substituents to carbons 5, 6, 11, and 12 varies as $\cos \theta$, where θ is the angle of deflection of the phenyl

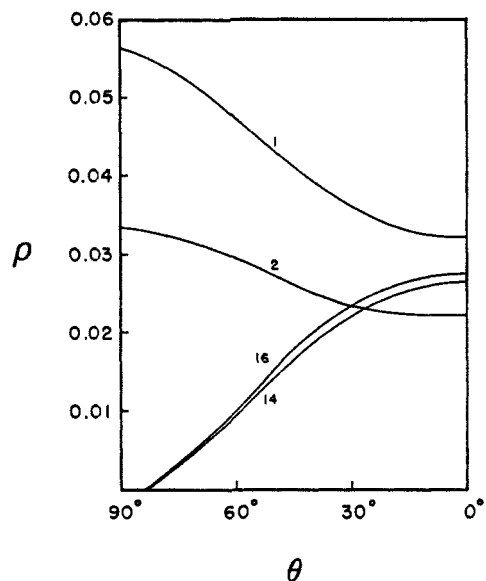


Figure 2. Plot of the Hückel spin densities as a function of θ for 5,6,11,12-tetraphenylnaphthacene. The numbers correspond to the positions of the carbon atoms.

substituents out of the plane of the naphthacene nucleus. A plot of the Hückel spin densities, ρ , as a function of θ is shown in Figure 2. It was assumed in these calculations that the value of θ is the same for all phenyl substituents. The possibility of the existence of two stereoisomers is recognized, but both would yield the same esr spectrum. By finding the value of θ at which best agreement is achieved between the "experimental" (McConnell equation) and theoretical spin densities, θ is found to be 65° . The Hückel spin densities at this value of θ are given in column two of Table I. The theoretical coupling constants were calculated using these spin densities and the equations of Colpa-Bolton,⁷ Giacometti-Nordio-Pavan,⁸ and McConnell.⁹ These values are given in columns three, four, and five of Table I.

Cation Radical. Malachuk, Marcoux, and Adams¹⁰ recently reported the preparation and esr observation of rubrene radical cation. The radical was prepared by oxidation employing the methanesulfonic acid-nitrobenzene system. They did not give an interpretation of this spectrum.

We attempted to prepare rubrene cation radical by oxidation with concentrated sulfuric acid. However, the hydrocarbon is so insoluble in sulfuric acid that no reaction occurs even when the solution is heated. Rather than try to find another chemical method of forming the cation radical, electrochemical oxidation was employed, using methylene chloride as a solvent. Controlled potential electrolysis was carried out at

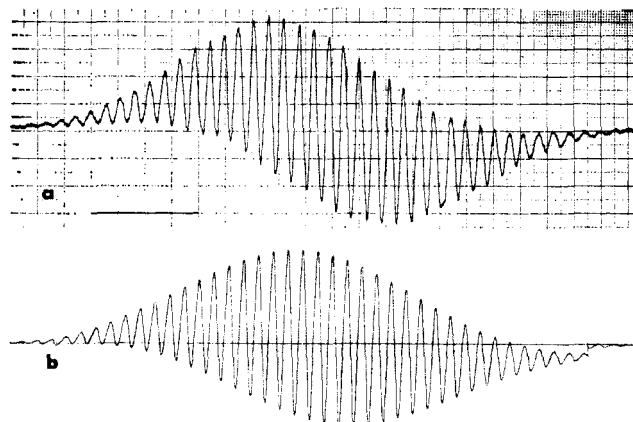


Figure 3. (a) Top: esr spectrum of 5,6,11,12-tetraphenylnaphthacene cation radical prepared by electrochemical oxidation in methylene chloride and examined at -80° ; (b) bottom: theoretical simulated esr spectrum using the coupling constants given in the text and a line width of 0.12 gauss.

+1.1 v vs. a silver-silver perchlorate reference electrode and using a platinum foil as the working electrode. The cation radical formed is the same olive-green color as the anion radical as would be expected for an alternant hydrocarbon from the pairing theorem.¹¹

The esr spectrum of rubrene cation radical is shown in Figure 3a. By amplifying the output, 45 lines, equally spaced 0.29 gauss apart, can be seen. This spectrum is the same as the one observed by Malachuk, Marcoux, and Adams.^{10,12} It is clear that more than one set of coupling constants will reproduce this spectrum. It can also be seen that all coupling constants will be near integral multiples of the spacing between the lines. By calculating several theoretical spectra, using $0.29n$ gauss where n is an integer for the o - and p -proton coupling constant, it was seen that n must equal 1. With this value of a_H for the o - and p -protons, there are four possible combinations of coupling constants that will reproduce the spectrum: $a_{H(2,3,8,9)}$ can be 0.87 or 1.18 gauss, and $a_{H(1,4,7,10)}$ can be 1.45 or 1.74 gauss. Any of the four possible combinations will fit the experimental spectrum equally well. A theoretical simulated spectrum using coupling con-

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(12) We wish to thank Dr. R. N. Adams for sending us a copy of his spectrum.

stants of 0.29, 0.87, and 1.74 gauss is shown in Figure 3b.

For the purpose of determining θ , it is not necessary to know the complete correct assignment, as long as the smallest coupling constant is known. By determining the value of θ at which best agreement is achieved between the theoretical and "experimental" spin densities for the *ortho* and *para* carbon atoms, θ is found to be 60° . The Hückel spin densities for this value of θ and the theoretical coupling constants predicted from the equations of Colpa-Bolton, Giacometti-Nordio-Pavan, and McConnell are shown in Table II. Although the lower values in the last column of Table II are in better agreement with theory, one could not with confidence predict which experimental values are correct.

Table II: Experimental and Theoretical Coupling Constants for the 5,6,11,12-Tetraphenylnaphthacene Cation Radical Using Hückel Spin Densities

Carbon atom	Hückel ^f spin density	a_H , gauss ^d			
		Colpa-Bolton ^a	Giacometti-Nordio-Pavan ^b	McConnell ^c	Exptl
1	0.0470	1.24	1.39	1.50	1.45 or 1.74 ^e
2	0.0294	0.79	0.87	0.94	0.87 or 1.18 ^e
14	0.0091	0.25	0.26	0.29	0.29
15	0.0002	0.01	0.01	0.01	...
16	0.0098	0.26	0.29	0.31	0.29

^a $Q = 27$ and $K = 12$ gauss. ^b $Q_1 = 31.5$ and $Q_2 = 7.0$ gauss. ^c $Q = 32$ gauss. ^d All coupling constants are expressed in their absolute value. ^e Assigned to this position on the basis of MO theory. ^f Calculated for $\theta = 60^\circ$.

Nonneighbor Effects. In the HMO calculations discussed, it has been assumed that all phenyl groups have the same orientation with respect to the naphthacene nucleus. No interactions were considered in these calculations for nonneighboring carbon atoms.

There are two possible ways in which phenyl substituents on polyaromatic hydrocarbons can interact with the aromatic nucleus to produce a bathochromic effect on the ultraviolet spectra. One is by an overlap interaction, assuming that the phenyl ring and the naphthacene nucleus are not completely perpendicular to one another. A second type of interaction was proposed by Jaffé and Chalvet,⁵ who assumed that the substitution of two phenyl groups *peri* to one another on naphthacene would lead to such severe steric strain that the phenyl groups must be perpendicular to the naphthacene nucleus. They invoked interaction of nonneighboring carbon atoms, such as interactions between 1 and 14, to couple the groups together. However, this

study has shown that a consistent explanation of the results can be obtained completely within the scope of simple HMO theory (*i.e.*, β for nonneighboring atoms taken as zero) by assuming only small deviations from perpendicularity of the groups. The fact that the *ortho* and *para* positions on the phenyl substituents are equivalent also supports this viewpoint, since interactions of nonneighboring carbon atoms would definitely make the *ortho* and *para* positions nonequivalent. Moreover, models of the molecule constructed with regard to proper atomic radii show that the steric effects are about the same for angles between 70° and 90° . Finally Avoyan, Kitaigorodskii, and Struchkov's X-ray studies¹³ on 5,6-dichloro-11,12-diphenylnaphthacene show that the naphthacene nucleus is planar, and that the phenyl groups were oriented at an angle of 70° to this nucleus. These results tend to support the results found here. It is, of course, recognized that the structure of a compound is not necessarily the same in the solid as it is in solution, and that the structure of a neutral compound is not necessarily the same as that of its ion radical.

Even when the *peri* phenyl substituents are parallel to each other in a plane perpendicular to the plane of the naphthacene nucleus, several unfavorably short nonbonded carbon-carbon distances occur. The distance between phenyl rings is 2.5 Å, when 3.8 Å is needed to avoid steric repulsion. Thus, Jaffé and Chalvet have suggested the possibility of an interaction between adjacent phenyl rings. Their basis for such an interaction arose from the observation that larger bathochromic shifts occur in the ultraviolet spectra of phenyl-substituted naphthalenes when the two phenyls are *peri* to one another (*i.e.*, 5,6) than when they are remote from one another (*i.e.*, 5,12). Calculations were made to study the effect of interactions between adjacent phenyl substituents on esr spectra. Such interactions have been introduced into the HMO calculations by allowing the resonance integrals β_j between corresponding atoms of the adjacent phenyl groups to have values of 0.1 and 0.2 β_0 , where β_0 is the usual Hückel resonance integral. The introduction of such bonds in rubrene has the effect of making the hydrocarbon nonalternant, and for such hydrocarbons HMO calculations are poor. It also has the effect of reducing the spin density on the *ortho* positions by 0.0008 and the *para* positions by 0.0014 for a β_j of 0.2 β_0 . For this same β_j value the spin densities on the 1,4,7,10 positions are increased by 0.002, and the spin densities on the 2,3,8,9 positions are increased by 0.001. Thus, if such an interaction did exist, and if the HMO

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calculations are approximately correct, it would have a small effect on the esr spectra.

Experimental Section

Rubrene was obtained from K & K Chemical Co. It was vacuum sublimed five times with the purest component being taken each time for resublimation until dark ruby red crystals were obtained. Its purity was then established by carbon-hydrogen analysis, melting point, mass spectrometry, polarography, and fluorescence spectrometry.

The methods of purification of DME⁶ and DMF¹⁴ have been previously described. Methylene chloride was obtained from Aldrich Chemical Co. and used as received as its purity was established by other electrochemical studies.¹⁵

A Varian Associates V-4502 spectrometer employing 100-kc field modulation was used. The field sweep was calibrated by using Fremy's salt in one side of a V-4532 dual-sample cavity, and the low field splitting of

this spectrum was taken to be 13.0 gauss. The spectra were recorded on a Moseley 7100B dual channel recorder.

The HMO calculations were done on a Control Data Corp. 6600 computer and were then plotted on the CDC 160 plotter.

The electrochemical cell has been described previously.⁶

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The Defect Structure of Cuprous Iodide and Its Catalytic Properties¹

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Changes in the defect structure of cuprous iodide have been generated by chemical means (exposure to iodine) and by ion migration in an applied electrical field (solid-state electrochemical cell). The hole density has been found to control the rate of catalytic decomposition of isopropyl iodide to propylene and propane. Low defect concentration seems to favor propylene formation. The kinetics of the reaction are measured. The mechanism leading to the observed product distribution is discussed.

Introduction

The relationship between the defect structure of a solid and the kinetics and mechanism of reaction occurring on its surface are of fundamental importance in heterogeneous catalysis. In principle, an electrochemical cell employing a solid ionic semiconductor allows control of the chemical potential of its con-

stituents by ion migration in an applied electrical field. In this way the activity ratio of cations to anions may be altered (within the limits of the homogeneity range of the solid) and the defect concentration (excess elec-

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