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Electron Spin Resonance Spectra of 9-Phenylanthracene

and 9,10-Diphenylanthracene Anion Radicals

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The electron spin resonance (esr) spectra of 9-phenylanthracene and 9,10-diphenylanthracene anion radicals prepared by electroreduction in N,N-dimethylformamide and potassium metal reduction in dimethoxyethane are given. The assigned experimental coupling constants are shown to be in good agreement with those calculated using molecular orbital theory. A brief study of how different factors in radical ion preparation affect esr spectrum resolution is described.

In a previous paper[2] we reported a study of the esr spectrum of 9,10-diphenylanthracene (DPA) anion radical. An assignment for the coupling constants for this radical was presented and this assignment was shown to be consistent with a molecular orbital calculation for a certain angle between the phenyl rings and the anthracene nucleus. The study of the esr spectrum of 9-phenylanthracene (PA) anion radical reported here was undertaken to test whether the
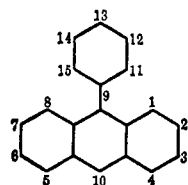
calculated angle in DPA and its spectrum assignment was consistent with that for PA. The esr spectrum of PA is more difficult to interpret than that of DPA because exchange of the phenyl ring in the 10 position for a hydrogen makes the 1 and 4 and the 2 and 3 hydrogens no longer equivalent. This additional complexity required a more highly resolved spectrum to obtain a satisfactory interpretation. A study was therefore undertaken to examine how different methods of radical preparation affected the resolution in esr spectra. In the course of this study a more highly resolved spectrum of DPA anion radical was obtained and the improved assignment of coupling constants for this radical is also given.

Results and Discussion

Resolution of Spectra. Of the two principal methods of producing aromatic hydrocarbon anion radicals, alkali metal reduction and electrochemical reduction, the former method has been used in all but a few cases. There are two different techniques using electrochemical reduction: generation of the radical at an electrode inside the cavity (the *intra muros* technique)[3] and external generation with some form of transfer to an esr cell.[4,5] The advantages and disadvantages of both of these methods have been reviewed by Adams.[6]

A comparison of the alkali metal and electrochemical generation methods of anion radical production involves the use of different solvents and counterions. It has been shown that both solvent and counterion affect resolution and coupling constants in an esr spectra.[7-9]

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

(2) L. O. Wheeler, K. S. V. Santhanam, and A. J. Bard, *J. Phys. Chem.*, **70**, 404 (1966).

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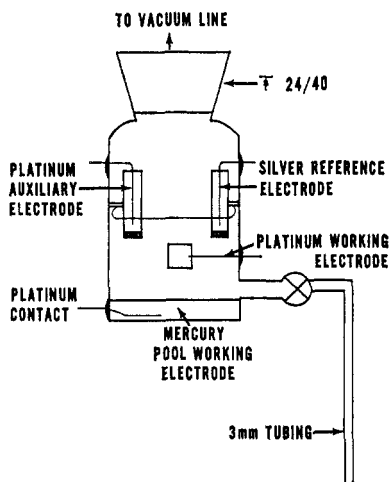(9) A. H. Reddoch, *J. Chem. Phys.*, **43**, 225 (1965).

Figure 1. Vacuum cell for controlled-potential electrolysis.

Figure 2. Vacuum apparatus for alkali metal reduction.

In an attempt to determine the conditions which yield optimum resolution, experiments were performed varying solvent, counterion, and temperature. The solvents were dimethylformamide (DMF), acetonitrile (ACN), and dimethoxyethane (DME); the counterions were potassium and the tetra-n-butylammonium cation. The temperature was varied from −80° to room temperature.

A new electrolytic cell was designed in which oxidations and reductions could be carried out and solution transfer to 3-mm tubing made under an inert atmosphere (see Figure 1). This is very important because the anion radicals react with traces of oxygen and other substances. This cell is simpler and more convenient than the one previously described.[5] We at first thought that the flat Varian aqueous solution sample cell would have to be employed in studies involving DMF as a solvent to avoid difficulties in tuning the esr spectrometer. The use of this cell is inconvenient because it is not vacuum tight and it does not fit into the variable-temperature apparatus dewar flask. We found, however, that the esr spectrometer could be tuned with some difficulty, using 3-mm tubing containing DMF.

The apparatus used for alkali metal reductions[10] (Figure 2) differs from the one usually employed.[11] The five side arms make it possible to observe the resolution of the spectrum as a function of the concentration of the radical in a single experiment by allowing the reaction to proceed to different extents in the reaction bulb and transferring the solution to the esr side-arm tubes at various times. Actually two factors that affect resolution are changed simultaneously in this kind of experiment—the concentration of the radical and the rate of electron exchange between parent com-
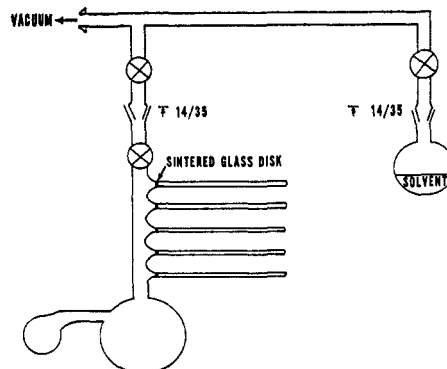
pound and radical. However, this latter effect is probably negligible at the temperatures employed, −60 to −80°. The frits filter the potassium metal from the solution and thus prevent the reaction from continuing in the esr sample tube.

The effect of different factors on resolution was examined by observing the spectrum of DPA anion radical prepared by different methods. The spectrum for DPA anion radical prepared by internal generation has been described by Sioda and Koski,[12] who observed a rather poorly resolved 13-line spectrum. We have found similar lack of resolution in several studies using a room-temperature *intra muros* technique. Somewhat better resolution is obtained when exhaustive external electrochemical reduction is used and the spectrum examined in a flat sample cell at room temperature.[2] Even higher resolution is obtained when the radical is prepared by exhaustive external controlled-potential electrolysis in DMF under vacuum and examined at −50° (Figure 3 (top)) and when it is obtained by potassium reduction in DME and examined at −80° (Figure 3 (bottom)).

In this study we found that the resolution improves according to the following sequence: the *intra muros* generation technique at room temperature yields the poorest resolution followed by exhaustive external controlled-potential electrolytic generation examined at room temperature and external electrolytic generation examined at −50°. Potassium metal reduction examined at −80° produces the most highly resolved spectrum. The reason external electrolytic generation gives a better spectrum than that obtained with internal generation at room temperature is probably

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(11) D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Am. Chem. Soc.,* **78,** 116 (1956).

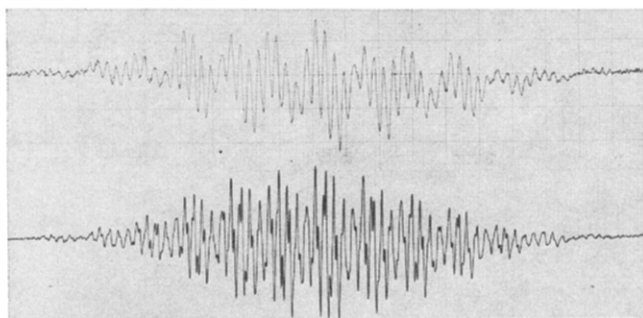(12) R. E. Sioda and W. S. Koski, *ibid.,* **87,** 5573 (1965).

Figure 3. Top: derivative esr spectrum of DPA anion radical produced by electroreduction of 10^{-3} M DPA solution containing 0.1 M tetra-n-butylammonium iodide in DMF. Temperature, $-50°$. Bottom: derivative esr spectrum of DPA anion radical produced by potassium reduction in DME. Temperature, $-80°$.

Figure 4. Top: derivative esr spectrum of PA anion radical produced by electroreduction of 10^{-3} M PA solution containing 0.1 M tetra-n-butylammonium iodide in DMF. Temperature, 25°. Middle: derivative esr spectrum of PA anion radical produced by potassium metal reduction in DME. Temperature, $-80°$. Bottom: calculated spectrum using constants in last column of Table I with a line width of 0.12 gauss.

because the exchange rate between parent compound and radical[13] is much lower in the external case. It is very difficult to achieve quantitative conversion of parent to radical using the internal generation technique. The difference between electrolytic generation and potassium reduction at low temperatures is probably caused by differences in solvent and counterions. We conclude that in the case of hydrocarbon anion radicals optimum resolution is achieved by alkali metal reduction and observation of the spectra at low temperatures. The anion radicals of benzene, naphthalene, anthracene, and biphenyl produced by alkali metal reduction have been examined. The optimum resolution was achieved by examination of their esr spectra at $-60°$ or lower, which would appear to further verify this conclusion, although we have not prepared these anion radicals by electrolytic methods. It is not possible from our data to state whether the increased resolution is caused by the change in solvent or counterion or both.

DPA Anion Radical. The improved resolution in the spectrum of DPA anion radical when prepared by potassium metal reduction (Figure 3 (bottom)) allows the following assignment of coupling constants (in gauss): $a_H(1, 4, 5, 8) = 2.60$, $a_H(2, 3, 6, 7) = 1.47$, $a_H(p) = 0.30$, and $a_H(o) = 0.24$. These values are slightly different from those previously reported[2] and separate coupling constants of the o- and p-hydrogens of the phenyl rings are observed. The calculated angle between the phenyl rings and the anthracene nucleus, θ (68°), is unaltered.

PA Anion Radical. The esr spectrum of PA has been reported by Fu, Sheng, and P'an.[14] Their spectrum was very poorly resolved and consisted of 17 major lines with a very slight indication of further splitting. They postulated the following coupling con-
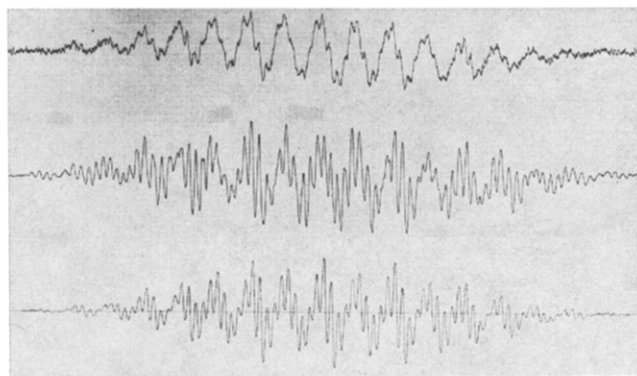
stants (in gauss): $a_H(10) = 5.36$, $a_H(1, 4, 5, 8, 13) = 2.68$, $a_H(11, 15) = 1.34$, and $a_H(2, 3, 6, 7) = 0.27$.

The spectrum of PA anion radical obtained by exhaustive, external controlled-potential electrolysis and examined at room temperature is shown in Figure 4 (top), while that obtained by potassium metal reduction and examined at $-80°$ is shown in Figure 4 (middle). A theoretically computed spectrum using the coupling constants in the last column of Table I

Table I: Experimental and Theoretical Coupling Constants for the Anion Radical of 9-Phenylanthracene

| Carbon atom | Spin density | | a_H, gauss | | |
	Hückel[a]	McLachlan[b]	Theory[c]	Theory[d]	Experimental
1	0.091	0.110	2.83	2.54	2.52[e]
2	0.048	0.034	0.91	1.34	1.66[e]
3	0.045	0.027	0.72	1.26	1.34[e]
4	0.093	0.117	3.00	2.60	2.76[e]
10	0.193	0.263	6.28	5.40	5.60
11	0.009	0.012	0.32	0.25	0.28
12	0.000	-0.004	0.11	0.00	
13	0.010	0.014	0.38	0.28	0.28

[a] Calculated using $\theta = 68°$. [b] Calculated using $\theta = 68°$ and $\lambda = 1.2$. [c] Calculated using the Colpa–Bolton equation where $Q = 27$ and $K = 12$ and using the McLachlan spin density. [d] Calculated using the McConnell equation where $Q = 28$ and using the HMO spin density. [e] Assigned to this position on the basis of analogy with HMO theory.

(13) R. L. Ward and S. I. Weissman, *J. Am. Chem. Soc.*, **79**, 2086 (1957).

(14) K-H. Fu, H-Y. Sheng, and C-L. P'an, *K'o Hsueh T'ung Pao*, 540 (1956).

and assuming 100% Lorentzian line shape is shown in Figure 4 (bottom). Using the internal generation technique, a spectrum of PA anion radical in DMF was obtained which was comparable in resolution to that obtained by external controlled-potential electrolysis. When the internal generation technique was tried using ACN as a solvent, the esr spectrum of anthraquinone anion radical was obtained. This same type of reaction has been observed with anthracene anion radical. Studies are currently in progress to determine the mechanism of this reaction.

Molecular Orbital Calculations. It has been shown that the resonance integral, β, for the bond between the phenyl ring and the anthracene nucleus can be represented by $\beta = \beta_0 \cos \theta$ where β_0 is the resonance integral for a carbon–carbon bond in a planar system.[15] β_0 is defined for a bond length of 1.397 A. Streitwieser[16] has described procedures that can be used to correct for deviations from this standard bond length, but they have a negligible effect on the calculated value of θ, if θ is greater than 60°. Simple Hückel molecular orbital[16] and McLachlan[17] calculations were made for PA assuming values of θ between 0 and 90°. A plot of the spin density, ρ, as a function of θ based on HMO calculation is given in Figure 5.

From an examination of the spectrum of PA anion radical, a quartet of splitting 0.28 gauss is evident in the extreme wing lines. This splitting can only be attributed to the *o*- and *p*-hydrogens on the phenyl substituent. From this fact and from Figure 5, a value of $\theta = 68°$ is found. After complete determination of all the coupling constants, it is seen that the predicted values from simple HMO theory are in very good agreement with the experimental values. The value of θ is also in good agreement with those previously reported for this type of compound.[2,18] It has not been possible despite repeated attempts to observe separate coupling constants for the *o*- and *p*-protons of PA anion radicals. It can be seen that our assignment differs from that given by Fu, *et al.,*[14] which they made on the basis of a very poorly resolved spectrum. We have found that their coupling constants and the line widths found in this study give a poor reproduction of our spectra. This illustrates an important point seldom mentioned in esr literature. The ability of a given set of coupling constants to reproduce a spectrum does not guarantee that they are the correct assignment. This point becomes particularly important in the case of poor resolution.

Experimental Section

DPA and PA were obtained from Aldrich Chemical Co. DPA was used as received since its high purity
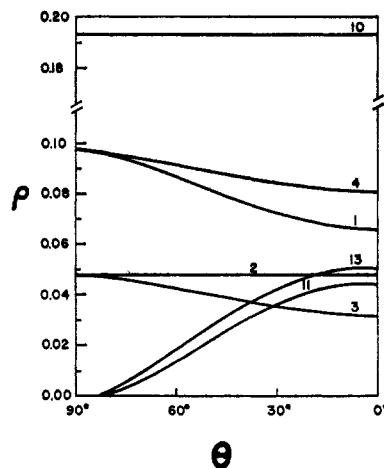

Figure 5. Variation of the spin density (ρ) as a function of the angle between the phenyl ring and the anthracene nucleus (θ) as calculated by HMO theory. The numbers represent the appropriate carbon atom.

was established by electrochemical studies[5] and melting point. PA was purified by vacuum sublimation with the purest component being taken from the first sublimation and subjected to a second purification. Its purity was then established by polarography and melting point. DME obtained from Ansul Co. was dehydrated by the addition of calcium hydride and lithium aluminum hydride, refluxed for 16 hr over lithium aluminum hydride, and vacuum distilled. The method of purification of the DMF has been described previously.[5]

Preparation of the radical by reduction with potassium was as follows. The potassium was stored under mineral oil and prior to use it was washed with purified solvent before being cut and placed in the reaction vessel (Figure 2). The hydrocarbon was placed in a capillary tube and put in the reaction vessel along with a stirrer. The system was evacuated and the potassium metal was distilled from the side bulb into the main flask to form a mirror. The solvent was then distilled over by cooling the reaction flask with liquid nitrogen. By activating the stirrer the capillary tube was broken and the speed of the reaction between potassium and hydrocarbon was controlled by adjusting the temperature.

External electrolysis was carried out in the cell shown in Figure 1. This cell has the advantage of not requiring separate inlets for auxiliary and reference

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(17) A. D. McLachlan, *Mol. Phys.*, 3, 233 (1960).

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electrode. The cell was attached to the vacuum line and the sample tube and vacuum stopcock were evacuated. The stopcock was then closed and the cell removed from the vacuum line. Mercury was added first and then a solution containing the hydrocarbon and the supporting electrolyte. The cell was reattached to the vacuum line and again evacuated. After electrolysis the cell was brought to atmospheric pressure by bleeding in helium. The stopcock was then opened only to the bulb portion of the vacuum stopcock and a few milliliters of solution was drained. Then the stopcock was opened to the sample cell. The solution was frozen in the tube while the tube was removed with a torch. Transfer was then made to the spectrometer.

A Varian Associates V-4502 spectrometer empolying 100-kc field modulation was used. A Varian V-153c klystron (output 300 mw) was used.

The HMO and McLachlan calculations were done on a Control Data Corp. 6600 computer. The theoretical simulated spectra were calculated on the CDC 1604 computer and were then plotted on the CDC 160 plotter.

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.