or

$$n_2FD^{1/2}\bar{C}_B(0, s) = \bar{g}(s, \rho) - \exp(-\tau_1 s)\bar{g}(s, \rho) + (1 - R)\exp(-\tau_1 s)\bar{g}(s, \rho') \quad (44a)$$

The inverse transform of (44a) is

$$n_2FD^{1/2}C_B(0, t) = g(t, \rho) - S_{\tau_1}(t)g(t - \tau_1, \rho) + (1 - R)S_{\tau_1}(t)g(t - \tau_1, \rho') \quad (45a)$$

where $g(t, \rho)$ is as given in eq 13 in the text. For $\tau_2 < t < \tau_1$, $S_{\tau_1}(t) = 1$, and eq 12 in the text results.

Electron Spin Resonance Spectra of 9,10-Diphenylanthracene Anion and Cation Radicals

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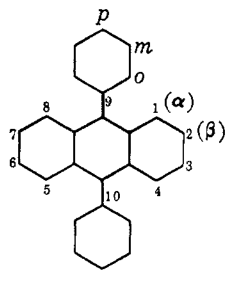
The electron spin resonance (esr) spectra of the 9,10-diphenylanthracene radical anion, prepared by electroreduction in N,N-dimethylformamide, and of the cation, prepared by treatment with concentrated sulfuric acid, are given. The experimental coupling constants are compared with those calculated using Hückel molecular orbital theory assuming different angles between the phenyl rings and the anthracene nucleus.

Recent interest in chemiluminescent[2] and electrochemical[3] reactions of 9,10-diphenylanthracene (DPA) prompted an investigation of anion and cation radicals of DPA. Additional interest in DPA radicals centers on the nonplanarity of the parent molecule caused by interactions of the *o*-hydrogens on the phenyls in the 9 and 10 positions and hydrogens on the anthracene nucleus at positions 1, 4, 5, and 8. By comparing the coupling constants obtained from experimental spectra with those calculated by molecular orbital methods, an estimation of the angle between the phenyl rings and the anthracene nucleus can be obtained.



Brunner and Dörr[4] reported the esr spectrum of DPA anion radical in liquid ammonia at −40°, produced by reaction of DPA with alkali metal. They obtained a 17-line spectrum with a total width of 5.3 gauss and concluded that no conjugation with the phenyl rings occurred and that a very large spin density was present on the 9 and 10 positions. An abstract of a paper mentioning an esr spectrum of DPA radicals has appeared,[5] but details of this work are unavailable.

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[1] To whom all correspondence and requests for reprints should be directed.

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[3] K. S. V. Santhanam and A. J. Bard, to be submitted for publication.

[4] V. E. Brunner and F. Dörr, *Ber. Bunsenges. Physik. Chem.*, **68**, 468 (1964).

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We report here the spectra of the anion radical of DPA produced by controlled-potential electroreduction in N,N-dimethylformamide and the cation radical produced in concentrated sulfuric acid.

Results and Discussion

Anion Radical. The esr spectrum of DPA anion is shown in Figure 1. A computer-simulated spectrum is shown based on the following coupling constants (in gauss): $a_H(\alpha) = 2.76 \pm 0.05$, $a_H(\beta) = 1.38 \pm 0.03$, $a_H(o) = a_H(p) = 0.28 \pm 0.01$; a line width (between the maxima and minima of the first derivative presentation) of 0.1 gauss (Lorentzian line shape) is also shown. Of the 67 theoretical lines 63 are observed experimentally. The total width of the spectrum is 17.2 gauss.

Cation Radical. The esr spectrum of DPA cation radical produced by dissolving DPA in hexane and treating with concentrated sulfuric acid is shown in Figure 2. A computer-simulated spectrum is shown based on the following coupling constants (in gauss): $a_H(\alpha) = 2.46 \pm 0.03$, $a_H(\beta) = 1.23 \pm 0.02$, $a_H(o) = a_H(p) = 0.41 \pm 0.01$; a line width of 0.16 gauss is also shown. All 41 theoretical lines can be seen experimentally. On continually decreasing the concentration of the radical ion by dilution with concentrated sulfuric acid and operating at power levels of about 20 db, a more highly resolved spectrum can be obtained (Figure 3). This corresponds to coupling constants of $a_H(\alpha) = 2.45 \pm 0.03$, $a_H(\beta) = 1.22 \pm 0.02$, and $a_H(o) = a_H(p) = 0.45 \pm 0.01$ gauss.

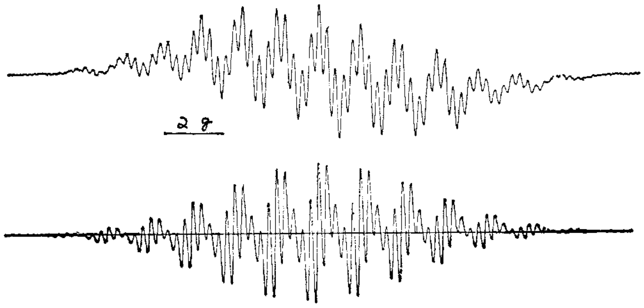

Figure 1. Top: derivative esr spectrum of DPA anion radical produced by electroreduction of 10^{-3} *M* DPA solution containing 0.1 *M* tetra-*n*-butylammonium iodide in N,N-dimethylformamide. Spectrometer conditions: modulation amplitude, 0.1 gauss; power, 10 db; sweep time, 25 min. Bottom: calculated spectrum using constants in text.

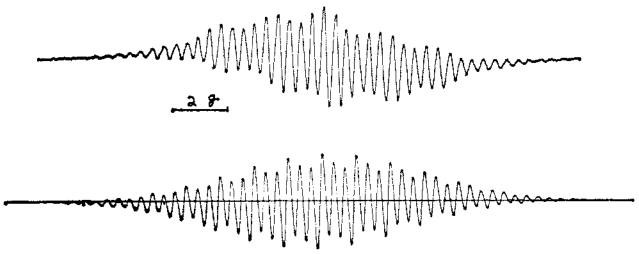

Figure 2. Top: derivative esr spectrum of DPA cation radical produced by treating a 5×10^{-3} *M* DPA solution in hexane with concentrated sulfuric acid. Spectrometer conditions: modulation amplitude, 0.07 gauss; power, 20 db; sweep time, 25 min. Bottom: calculated spectrum using constants in text.

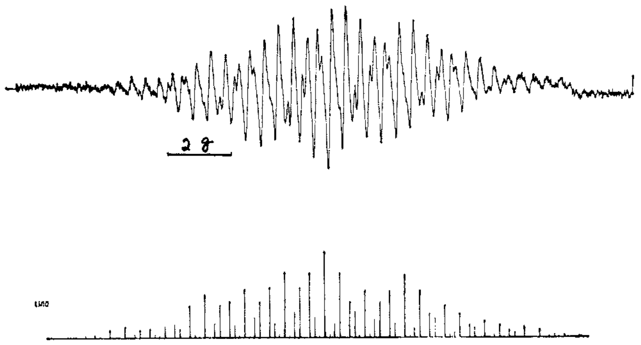

Figure 3. Top: derivative esr spectrum resulting from dilution of solution of DPA cation radical with concentrated sulfuric acid. Spectrometer conditions: modulation amplitude, 0.04 gauss; power, 20 db; sweep time, 25 min. Bottom: calculated spectrum.

HMO Calculations. Simple Hückel molecular orbital (HMO) calculations[6] were performed, assuming different angles (θ) between the phenyl rings and the anthracene nucleus and assuming that the resonance integral, β, varied as the cosine of θ.[7] The resulting spin densities (ρ) are shown as a function of θ in Figure 4. The ratios of the coupling constants for the anion radical correspond most closely to calculated spin densities for θ near 68°. The cation radical shows a larger coupling constant for the *o*- and *p*-phenyl hydrogens, indicating a larger amount of conjugation with the phenyl rings and thus a smaller θ (61°). Jones[8] estimated a θ of at least 57°, based on molecular models.

Bolten[9] has given the following equation for relating

$$A_H = -[Q \pm K\rho]\rho$$

spin densities to proton coupling constants for HMO calculated spin densities where Q and K are empirically determined constants based on measurements of a number of aromatic hydrocarbons and are taken to have the values of 27 and 12 gauss, respectively. The

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[7] M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3345 (1952).

[8] R. N. Jones, *ibid.*, **67**, 2127 (1945).

[9] J. R. Bolton, *J. Chem. Phys.*, **43**, 309 (1965).

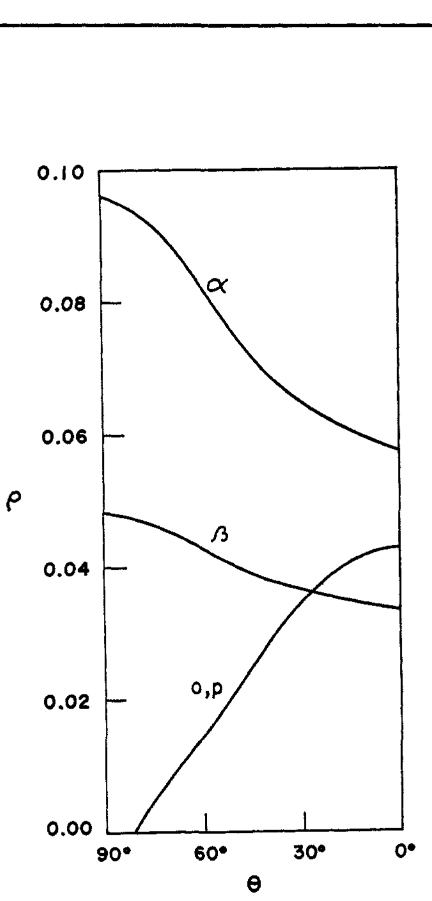

Figure 4. Variation of the spin density (ρ) with angle between phenyl rings and anthracene nucleus (θ) as calculated by HMO theory.

sign in the equation corresponds to the charge on the radical. The calculated coupling constants for the anion radicals using $\theta = 68°$ for calculation of ρ and based on this equation are $a_H(\alpha) = 2.27$, $a_H(\beta) = 1.17$, and $a_H(o) = a_H(p) = 0.26$ gauss. For the cation radical using $\theta = 61°$, they are $a_H(\alpha) = 2.15$, $a_H(\beta) = 1.13$, and $a_H(o) = a_H(p) = 0.45$ gauss. Coupling constants based on a single Q for each radical or the original equation given by Colpa and Bolton,[10] in which $Q = 31.2$ and $K = 17$, are in better agreement with experimental results. Although the usual results for hydrocarbon radicals indicate that larger proton coupling constants are found with cation radicals, this is not the case here for the α and β protons. This may be caused by a difference in angle in the anion and cation radicals.

The results obtained in this study differ from those obtained by Brunner and Dörr[4] in liquid ammonia. Specific solvent effects for hydrocarbon radicals are probably small since the esr spectra of 9,10-dimethylanthracene anion radical are very similar in both liquid ammonia[4] and dimethoxyethane.[11] Even for the phenyl rings rotated perpendicular to the anthracene nucleus ($\theta = 90°$), a wider spectrum would be expected, assuming no extreme dependence of Q on temperature. Since some commercial samples of DPA have been known to contain anthraquinone,[12] Brunner and Dörr may have been observing the radical anion of this substance which has appreciable spin density on the oxygens and which produces a narrow esr spectrum.[13]

Experimental Section

A Varian Associates V-4502 spectrometer employing 100-kc field modulation was used. A Varian V-153C klystron (output 300 mw) was used; attenuation levels represent attenuation of the output of this klystron in a standard Varian bridge. Samples were contained in the flat Varian aqueous sample cell.

The anion radical was prepared by controlled-potential electroreduction of DPA at a mercury cathode in a solution of N,N-dimethylformamide containing 0.1 *M* tetra-*n*-butylammonium iodide. The solution was degassed, and the reduction and transfer to the esr cell were carried out on a vacuum line.[3] The solution of the anion radical produced under these conditions was stable for at least 4 hr. The radical anion is very unstable in the presence of traces of oxygen or impurities, however.

The cation radical was prepared by dissolving DPA in 2–3 ml of hexane and treating this solution with about 10 ml of concentrated sulfuric acid. Similar results were obtained by dissolving the DPA in acetonitrile and N,N-dimethylformamide before treating with sulfuric acid. Spectra of samples treated by this procedure were always better than those obtained by dissolving the DPA directly in concentrated sulfuric acid.

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

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[11] (a) J. R. Bolton, A. Carrington, and A. D. McLachlan, *ibid.*, **5**, 31 (1962); (b) D. Bachmann, *Z. Physik. Chem.* (Frankfurt), **43**, 198 (1964).

[12] R. N. Adams, University of Kansas, private communication.

[13] (a) M. Adams, M. S. Blois, and R. H. Sands, *J. Chem. Phys.*, **28**, 774 (1958); (b) G. Vincow and G. K. Fraenkel, *ibid.*, **34**, 1333 (1961).