

Electrochemistry and electron spin resonance spectroscopy of 9,10-di(.alpha.-naphthyl)anthracene

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need not necessarily mean that this number of electrons is actually added simultaneously, but, most probably, that there are two successive steps too nearly simultaneous to be distinguished.⁶⁴ These results are in accord with the shift of $E_{1/2}$ with pH and with the controlling processes in the electrochemical reduction of pyrimidine itself^{65,66} (the pyrimidine ring is the site of reduction in the adenine series).

Current-Time Curves. The variation of current with time during the life of a single drop ($i-t$ curves) was recorded for sequential drops from a vertical capillary. Due to depletion of the solution surrounding the drop,⁶⁷ $i-t$ curves so obtained produce $\log i$ vs. $\log t$ plots, which are curves convex to the time axis, so that the choice of the slope is ambiguous. Although such plots cannot be used to calculate the amount of diffusion control, they can show the depression of the instantaneous current expected for a strongly adsorbed depolarizer;^{40,67} $i-t$ curves recorded on the limiting portion of the normal wave for 0.25 mM solutions of adenine, adenosine, and AMP at pH 2.5 do not show any such depression.

Ac Polarography. The general pattern for an ac polarogram for a 0.25 mM solution of an adenine nucleoside or nucleotide in pH 2.5 McIlvaine buffer (0.5 M ionic strength) at 25° consists of a

depression of the base current with a minimum at *ca.* -0.6 V, a broad peak at -0.85 to -1.09 V, and a narrow main peak at -1.25 to -1.29 V (Figure 3 and Table II). The summit potential, E_s , of the latter, which is the ac faradaic peak, is 40-45 mV more negative than $E_{1/2}$ of the corresponding dc polarographic wave. The broad peak and the foot of the main peak at less negative potential are above the background base current for adenosine, AMP, and ATP, and below for deoxyadenosine and dAMP. No depression of the base current is observed at potentials more negative than that of the main peak.

This pattern is essentially unchanged for 0.50 mM dAMP solution with increasing pH up to *ca.* pH 4.5, where the main peak begins to decrease sharply and disappears by pH 6 (Figure 4 and Table III). With increasing pH, E_s becomes more negative ($E_s = -1.120 - 0.064\text{pH}$), ($E_{1/2} - E_s$) decreases linearly (*ca.* 15 mV/pH), the background discharge shifts to more positive potential, and the magnitude of the base current depression at *ca.* -0.6 V increases. The broad peak at *ca.* -1.0 V is above background base current over the whole pH range. No depression of the base current below that of the background electrolyte is observed on either side of the main peak except for a very small depression on the positive side at pH 2.0.

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(66) J. E. O'Reilly and P. J. Elving, *J. Electroanal. Chem.*, **21**, 169 (1969).

(67) J. Kùta and I. Smoler in "Progress in Polarography," Vol. 1, P. Zuman and I. M. Kolthoff, Ed., John Wiley and Sons, Inc., New York, N. Y., 1962, p 43.

The Electrochemistry and Electron Spin Resonance Spectroscopy of 9,10-Di(α -naphthyl)anthracene

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Abstract: Both the anodic and cathodic electrochemistry of 9,10-di(α -naphthyl)anthracene were studied. It was found to be oxidized in methylene chloride to a cation radical which slowly decomposed to another electroactive species. The reduction proceeded through two one-electron steps, the first reversible, the second irreversible. The esr spectra of both the cation and anion radicals were obtained and interpreted. The angle between the anthracene and naphthalene nuclei was found to be 75° by both electrochemical and esr techniques. This latter result is discussed in the context of previously determined angles for other molecules.

The relief of steric strain by twisting about essential single bonds is a chemical phenomenon that has been studied for many years in many ways. The goal of these studies is normally to determine the extent of the departure from coplanarity exhibited by the parts of the molecule in question, and the techniques directed to this end are most often spectroscopic. A frequently cited and studied example is provided by biphenyl.¹ Aryl-substituted polycyclic aromatic hydrocarbons have also received a great deal of attention. These latter-named molecules are of special interest because the magnitude of the steric repulsion energy is very much a function of the position in which the aryl substitution occurs. Compare for example the different amounts of steric interaction encountered in the three isomeric phenylanthracenes.

The structures of 9,10-diphenylanthracene (9,10-DPA), 9,10-di(α -naphthyl)anthracene (9,10-DNA), and 9,9'-bianthryl have been discussed on the basis of their

ultraviolet absorption spectra.² The ultraviolet spectra of several di- and polyphenyl anthracenes have also been reported.³ Molecules such as rubrene and 1,8-diphenylanthracene have been the subject of several studies because of the possible existence of a spiroconjugative interaction.⁴⁻⁶ The advent of sophisticated SCF techniques has made the quantitative interpretation of electronic spectra possible. Tinland has applied calculations of this type to naphthyl- and phenyl-substituted naphthalenes, anthracenes, and phenanthrenes.^{7,8} A similar approach has also been followed for 2-phenylanthracene and some of its derivatives.^{9,10}

(2) R. N. Jones, *J. Am. Chem. Soc.*, **63**, 658 (1941).

(3) S. D. Dickerman, D. deSouza, and P. Wolf, *J. Org. Chem.*, **30**, 1981 (1960).

(4) H. H. Jaffé and O. Chalvet, *J. Am. Chem. Soc.*, **85**, 1561 (1963).

(5) H. O. House, R. W. Magin, and H. W. Thompson, *J. Org. Chem.*, **28**, 2403 (1963).

(6) A. Zweig and J. B. Gallivan, *J. Am. Chem. Soc.*, **91**, 260 (1969).

(7) B. Tinland, *Theoret. Chim. Acta*, **11**, 385 (1968).

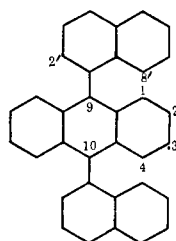
(8) B. Tinland, *J. Mol. Struct.*, **2**, 391 (1968).

(9) H. E. Holloway, R. V. Nauman, and J. H. Wharton, *J. Phys. Chem.*, **72**, 4468 (1968).

(1) C. Casalone, C. Mariani, A. Mugnoli, and M. Simonetta, *Mol. Phys.*, **15**, 339 (1968), and references therein.

Although these latter studies⁷⁻¹⁰ produced detailed structural information from electronic absorption spectra, magnetic resonance spectroscopy is probably capable of producing even greater amounts of structural information.

Although nmr has been applied to problems of this type,^{5,11} esr, when applicable, has been the source of more structural data. The most obvious application of esr is to species which exist as free radicals, such as 9-phenylxanthyl;¹² however, if the species of interest can be converted to an ion radical, measurements are also possible. In this latter case, however, it must be remembered that the structural properties determined are those of the ion radical and not necessarily those of the parent molecule. The anion and cation radicals of 9-phenyl- and 9,10-diphenylanthracene have been the subject of extensive esr studies in which the twist angle between the phenyl group and the anthracene nucleus was determined.^{13,14} The cation and anion radicals of rubrene have been treated similarly.¹⁵ Electrochemical techniques were important in these latter studies;¹³⁻¹⁵ consequently, it seemed obvious to attempt to relate quantitative electrochemical parameters to geometries. This was done qualitatively by Hoijtink¹⁶ and more recently in a quantitative fashion for 9,10-DPA.¹⁷ The electrochemical approach has probably been best described in a recent publication dealing with phenyl-substituted anthracenes.¹⁸ The combination of esr and electrochemistry is ideally suited to studies of this sort, since esr provides an experimental measure of the eigenvectors and electrochemical data provides a determination of the eigenvalues for the molecule in question.



The molecule 9,10-DNA was chosen for study because it would in theory present one of the most highly hindered molecules studied so far. In addition to being structurally interesting, it would test our ability to predict its behavior based on our general knowledge of the behavior of aromatic hydrocarbons.¹⁹

Results and Discussion

Electrochemistry of DNA. The anodic electrochemistry of 9,10-DNA was studied in methylene chloride

(10) H. E. Holloway, R. V. Nauman, and J. H. Wharton, *J. Phys. Chem.*, **72**, 4474 (1968).

(11) M. Rabinovitz, I. Agramat, and E. D. Bergmann, *Tetrahedron Lett.*, 4133 (1965).

(12) M. D. Sevilla and G. Vincow, *J. Phys. Chem.*, **72**, 3641 (1968).

(13) L. O. Wheeler, K. S. V. Santhanam, and A. J. Bard, *ibid.*, **70**, 404 (1966).

(14) L. O. Wheeler, K. S. V. Santhanam, and A. J. Bard, *ibid.*, **71**, 2223 (1967).

(15) L. O. Wheeler and A. J. Bard, *ibid.*, **71**, 4513 (1967).

(16) G. J. Hoijtink, *Rec. Trav. Chim.*, **74**, 1525 (1955).

(17) K. S. V. Santhanam and A. J. Bard, *J. Am. Chem. Soc.*, **88**, 2669 (1966).

(18) A. J. Bard, K. S. V. Santhanam, J. T. Maloy, J. Phelps, and L. O. Wheeler, *Discussions Faraday Soc.*, **45**, 167 (1968).

(19) M. E. Peover, "Electroanalytical Chemistry—A Series of Advances," Vol. 2, A. J. Bard, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, Chapter 1.

using cyclic, single sweep, and rotating disk voltammetry and controlled potential coulometry. Methylene chloride was chosen as solvent because hydrocarbon cation radicals have been shown to be more stable in this solvent²⁰ than in acetonitrile¹⁹ and because 9,10-DNA was more easily soluble in methylene chloride than in nitrobenzene.²¹ The polarogram obtained at 400 rpm from the rotating disk electrode (RDE) indicated two waves of equal magnitudes with $E_{1/2}$'s of +1.32 V and +1.76 V, respectively. The height of these waves was consistent with that expected for one-electron transfers. The value of the limiting current of the first wave was studied as a function of rotation rate in the region from 2000 to 9000 rpm and found to be in agreement with the Levich equation.²² These data are shown in Table I. The slight departure from constancy noted below 2000 rpm is indicative of an ece reaction,²³⁻²⁵ which is in agreement with previous voltammetric studies of aromatic hydrocarbon oxidations.¹⁹⁻²¹ The value of $E_{3/4} - E_{1/4}$ (ΔE , criterion of reversibility)²⁶ was 70 mV for the first wave at 500 rpm. The slope of a plot of $\log(i_d - i)/i$ vs. E was 79 mV for this wave. These results are those expected for a slightly irreversible one-electron transfer.

Table I. Limiting Current for Oxidation of 9,10-DNA at Rotating Disk Electrode^a

$\omega^{1/2}$, rad/sec ^{1/2}	i_1 , μA	$i_1/\omega^{1/2}$
7.32	2.75	0.37
10.7	3.88	0.36
12.5	4.37	0.35
14.8	4.88	0.33
16.4	5.38	0.33
17.9	5.90	0.33
20.7	6.83	0.33
22.9	7.48	0.33
25.5	8.30	0.33
27.2	8.95	0.33
29.3	9.28	0.32
30.7	9.89	0.32

^a The solution was 0.1 M TBAP in CH_2Cl_2 and contained 0.65 mM DNA. i_1 was measured at 1.58 V. Electrode area = 0.0217 cm^2 .

Cyclic voltammetry of this solution over a wide range of scan rates indicated a single anodic wave with a conjugate cathodic wave of equal magnitude. The value of the current function, $i_p/\nu^{1/2}C$,²⁷ was essentially constant and equal to that expected for a one-electron transfer. The current function did seem to show a very slight increase with scan rate which could be attributed to adsorption phenomena.²⁸ Because the noted increase was small, no further investigation into the possibility of reactant adsorption was made. The value of i_{pa}/i_{pc}

(20) J. Phelps, K. S. V. Santhanam, and A. J. Bard, *J. Am. Chem. Soc.*, **89**, 1752 (1967).

(21) L. S. Marcoux, J. M. Fritsch, and R. N. Adams, *ibid.*, **89**, 5766 (1967).

(22) V. G. Levich, "Physicochemical Hydrodynamics," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962.

(23) P. A. Malachuk, L. S. Marcoux, and R. N. Adams, *J. Phys. Chem.*, **70**, 4068 (1966).

(24) S. Karp, *ibid.*, **72**, 1082 (1968).

(25) L. S. Marcoux, S. W. Feldberg, and R. N. Adams, *ibid.*, **73**, 2611 (1969).

(26) J. Tômes, *Collection Czech. Chem. Commun.*, **9**, 12 (1937).

(27) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

(28) R. H. Wopschall and I. Shain, *ibid.*, **39**, 1514 (1967).

was determined and found to be equal to unity, within experimental limits, throughout the range of scan rates. The accurate measurement of this function was difficult however, because of the proximity of the background process. At a scan rate of 0.121 V/sec, $E_{p/2}$ (anodic) was +1.27 V, and the separation between anodic and cathodic peaks was 70 mV. These results are indicative of a slightly irreversible one-electron transfer, the product of which is stable in the time range of cyclic voltammetry.²⁷ The second wave which was detected at the RDE was nearly lost in the background process. It is not surprising that the ece decomposition of the radical cation, which was implied by the RDE results, was not reflected in the $i_p/v^{1/2}$ behavior,^{29,30} since it is not possible to make meaningful linear diffusion measurements at long times in methylene chloride because of its low viscosity. The presence of a slow reaction following charge transfer with a subsequent electron-transfer step could best be demonstrated by a technique whose kinetic window overlooks a slower region of chemical rate processes. Controlled potential coulometry is a technique which is ideally suited for this task.³¹

A solution of 7.12 mg of 9,10-DNA in methylene chloride with tetra-*n*-butylammonium perchlorate (TBAP) supporting electrolyte was electrolyzed at +1.5 V. The total electrolysis current was integrated using a voltage-to-frequency converter and electronic counter,^{32,33} and a current-time curve was obtained from a strip-chart recorder. The current-time curve initially showed exponential decay, but after about 7 min this curve began to level off and decrease at a much slower rate. A plot of $\log i$ vs. t is shown in Figure 1. The initial linear portion was followed by a concave upward section which gave way to a nearly linear decreasing portion. This is characteristic of an electron transfer followed by a slow chemical reaction, the product of which is also electroactive (ece scheme).³¹⁻³⁵ The current passed under the extrapolated linear portion of the $\log i$ vs. t wave (dotted line in Figure 1) corresponds to an n value of 0.94 electron/molecule. The electrolysis was discontinued before a total n value could be determined, as the exact nature of the follow-up reaction was not of immediate interest. These results confirm the conclusions drawn from the voltammetric studies. The oxidation of 9,10-DNA proceeds through a one-electron step to the cation radical, and this radical slowly decomposes to a product which is also oxidized at the same potential as the parent molecule. This is the anodic pathway that has been previously determined for other aromatic hydrocarbons.¹⁹⁻²¹

It is interesting to compare the reactivity of the 9,10-DNA cation to that of other hydrocarbon cations. Previous studies¹⁹⁻²¹ have suggested that the cation reactivity is determined by the extent of unpaired electron density on the various positions of the aromatic nucleus and that when the highly reactive positions are made unavailable for reaction, a stable cation will be observed. This has been shown to be the case with

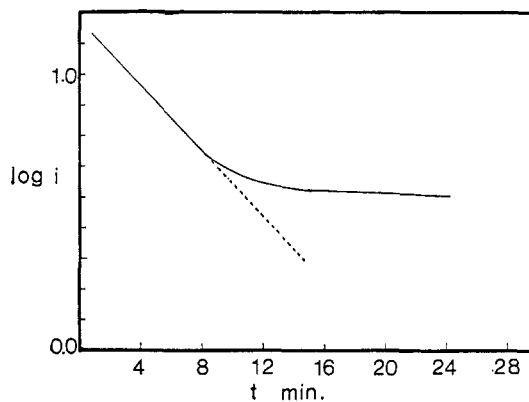


Figure 1. Log current vs. time behavior for the oxidation of 9,10-DNA in methylene chloride with TBAP supporting electrolyte. The current is in milliamperes.

9,10-DPA, and it was startling when 9,10-DNA⁺ was found to be less stable than 9,10-DPA⁺. Examination of the unpaired spin densities as determined by HMO calculations for the two cation radicals revealed that the position *para* to the point of attachment to the anthracene nucleus is the most reactive position on the substituent ring. This electron density is much larger in the case of 9,10-DNA⁺ than for 9,10-DPA⁺ at all angles of twist between the two rings. The decreased lifetime of the 9,10-DNA⁺ cation is thus in agreement with previous ideas about cation radical stability.

The electrochemical reduction was not studied in as great detail as was the oxidation, since it seemed nearly identical with that observed in the case of 9,10-DPA.¹⁷ Polarograms of this compound obtained in DMF indicated two one-electron waves at $E_{1/2}$'s of -1.82 and -2.40 V. Similar values were found when the experiment was carried out in carefully purified hexamethylphosphoramide (HMPA).

The determination of twist angles from electrochemical $E_{1/2}$ values depends upon the relationship between $E_{1/2}$ and the energy of the highest filled molecular orbital (homo), in the case of oxidation, and that of the lowest unfilled molecular orbital (lumo), in the case of reduction. This relationship was first noted by Maccoll³⁶ and Lyons,³⁷ and later carefully explicated by Hoijtink.³⁸ The value of m_{m+1} , the root of the HMO secular equation corresponding to the lumo, is found empirically from $E_{1/2}$ by comparison with the regression of the $E_{1/2}$'s of several similar molecules, obtained under similar conditions, upon the value of m_{m+1} for these molecules. This is shown in Figure 2 where the comparison values are those reported in ref 18. This value is then related to the twist angle θ by comparing it to a plot of m_{m+1} for 9,10-DNA vs. the twist angle θ , the values of m_{m+1} being calculated using the assumption $\beta = \beta_0 \cos \theta$, where β_0 is the standard carbon-carbon resonance integral of Hückel notation. The origin and validity of this latter approximation have recently been discussed.¹² The calculated variation of m_{m+1} with θ is shown in Figure 3. It may be seen that the value of -1.82 V for the $E_{1/2}$ of 9,10-DNA corresponds to a theoretical twist angle of 75°.

(29) R. S. Nicholson and I. Shain, *Anal. Chem.*, **37**, 178 (1965).

(30) R. S. Nicholson and I. Shain, *ibid.*, **37**, 190 (1965).

(31) A. J. Bard and J. S. V. Santhanam in "Electroanalytical Chemistry—A Series of Advances," Vol. 4, A. J. Bard, Ed., Marcel Dekker, Inc., New York, N. Y., in press.

(32) A. J. Bard and E. Solon, *Anal. Chem.*, **34**, 1181 (1962).

(33) A. J. Bard, *ibid.*, **35**, 1125 (1963).

(34) A. J. Bard and J. S. Mayell, *J. Phys. Chem.*, **66**, 2173 (1962).

(35) S. Karp and L. Meites, *J. Electronol. Chem.*, **17**, 253 (1968).

(36) A. Maccoll, *Nature*, **163**, 178 (1949).

(37) L. E. Lyons, *Research*, **2**, 587 (1949).

(38) G. J. Hoijtink and J. VanSchooten, *Rec. Trav. Chim.*, **71**, 1089 (1952).

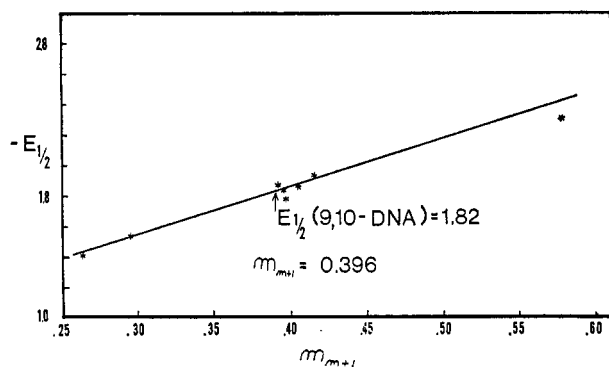


Figure 2. $E_{1/2}$ vs. m_{m+1} for the reduction of several aromatic hydrocarbons in DMF. The compounds are listed in order of increasing $E_{1/2}$: rubrene, tetracene, 1,10-diphenylanthracene, 9,10-diphenylanthracene, 1,9-diphenylanthracene, 9-phenylanthracene, and anthracene. These data taken from ref 18.

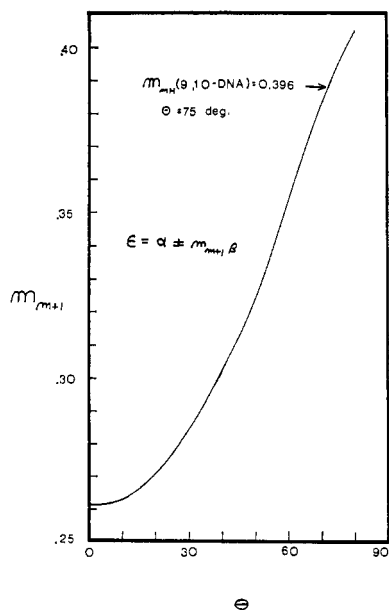


Figure 3. Plot of m_{m+1} for various degrees of twist angle θ for 9,10-DNA as determined by HMO calculations.

It is theoretically possible to use polarographic oxidation potentials in the same way as reduction potentials, and if this is done for 9,10-DNA using the oxidation data reported in reference 18, a value of θ of about 80° is obtained. It should be emphasized, however, that the values obtained from anodic data are probably subject to more error than those arising from reduction data because of the nature of the electrode process. In order for the correlation between $E_{1/2}$ and m_{m+1} to be valid, it is necessary that the electrode reactions be reversible and unperturbed. Because so many hydrocarbon oxidations involve chemical complications, it is very difficult to obtain a valid regression line by which to determine m_{m+1} .

Esr of Ion Radicals. Solutions of 9,10-DNA⁺ were prepared for esr study using both chemical and electrochemical techniques. The best spectra obtained from chemically prepared solutions were those prepared with a mixture of methanesulfonic acid and nitrobenzene.³⁹ These spectra were not as well resolved,

(39) P. A. Malachuk, L. S. Marcoux, and R. N. Adams, *J. Phys. Chem.*, **70**, 2064 (1966).

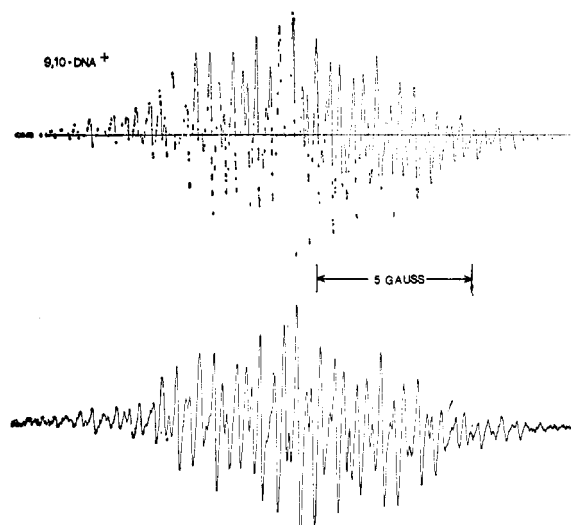


Figure 4. Esr spectrum for 9,10-DNA⁺ in methylene chloride. Top, computer simulation using parameters given in text; bottom, experimental.

however, as those obtained in methylene chloride using electrolytic generation. Because of the electrochemical follow-up reaction, the electrolytic generation was not totally straightforward; however, it was possible to prepare satisfactory solutions if the sample was taken rapidly and examined at low temperatures. The advantages of low temperature have been previously noted.⁴⁰ The spectrum obtained under these conditions is shown in Figure 4. This spectrum was interpreted using the computer simulation approach; the simulated spectrum of Figure 4 is obtained using the coupling constants shown in Table II with the assumption of a completely Lorentzian line shape and a line width of 0.120

Table II. Coupling Constants for 9,10-DNA Cation and Anion Radicals

No. of H	a_H , gauss		Position
	Cation	Anion	
4	2.70	2.55	1
4	1.21	1.38	2
2	0.47	0.40	4'
2	0.43	0.30	2'
2	0.29	0.17	5'

G. As can be seen, the agreement between the experimental and simulated spectra is quite satisfactory. The assignment of the couplings was done on the basis of Hückel calculations. The line width of 0.120 G is admittedly large and is probably caused in part by the very small unresolved splittings from protons in the 3', 6', 7', and 8' positions. The simulation approach can be misleading since a unique solution is not guaranteed; consequently, several alternative coupling schemes were considered and found to lead to simulated spectra whose appearance differed drastically from that observed.

Unpaired electron densities calculated at several values of the twist angle θ using the Hückel method and the assumption $\beta = \beta_0 \cos \theta$, for the essential single bond

(40) A. Reymond and G. K. Fraenkel, *ibid.*, **71**, 4570 (1967).

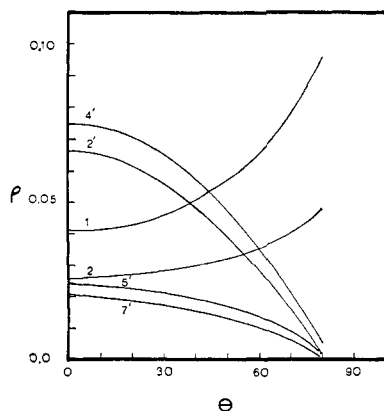


Figure 5. Variation of unpaired electron density for various positions of 9,10-DNA with twist angle θ .

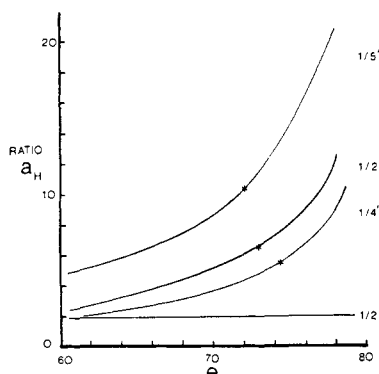


Figure 6. Variation of the ratio of unpaired electron densities with twist angle θ . The asterisks indicate experimental values for these ratios.

resonance integral, are shown in Figure 5. As expected, the unpaired electron density on the substituent naphthyl groups decreases rapidly as θ increases. Because the two sets of coupling constants vary in different directions, the ratios of the electron densities on the naphthyl to those on the anthracene nucleus are very sensitive functions of θ , as may be seen in Figure 6. By comparing the ratios of the appropriate coupling constants to those theoretical ratios shown in Figure 6, the experimental twist angle θ may be obtained without recourse to the perfidious constant Q of the McConnell⁴¹ equation. The values of θ determined from the ratios of coupling constants $a_H(1)/a_H(4')$, $a_H(1)/a_H(2)$, and $a_H(1)/a_H(5')$ were 74, 73, and 72°, respectively. The experimental values are indicated by asterisks in Figure 6. Calculations of theoretical coupling constants using the McConnell⁴¹ equation and some of the variations^{42,43} upon it and the Hückel densities at a twist angle of 73° gave coupling constants which agreed satisfactorily with the experimental values. These calculations also indicated that under the present conditions of resolution a splitting from the 7' position would not be expected.

Attempts to obtain the 9,10-DNA⁻ esr spectrum in a high degree of resolution were only partially successful. Controlled potential electrolysis at -2.0 V in DMF and HMPA proceeded with textbook simplicity.

(41) H. M. McConnell, *J. Chem. Phys.*, **24**, 632 (1956).

(42) J. P. Colpa and J. R. Bolton, *Mol. Phys.*, **6**, 273 (1963).

(43) G. Giacometti, P. L. Nordio, and M. V. Pavan, *Theoret. Chim. Acta*, **1**, 404 (1963).

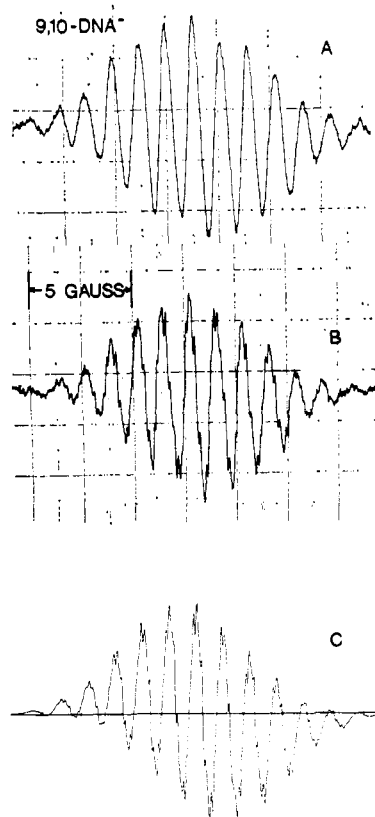


Figure 7. ESR spectra of 9,10-DNA⁻: (A) spectrum obtained from solution electrolyzed in DMF, (B) spectrum obtained by potassium reduction in HMPA, (C) computer simulation of B.

The resulting spectra, however, were only poorly-resolved thirteen-line spectra such as that shown in Figure 7. Both sodium and potassium reductions in dimethoxyethane and HMPA were only slightly more successful. The best resolution was obtained in the case of a potassium reduction of HMPA. This spectrum is also shown in Figure 7.

This latter spectrum could be simulated using the coupling constants shown in Table II, a line width of 0.175 gauss, and the assumption of totally Lorentzian line shape. Using the ratio technique discussed above, twist angles of 72, 74, and 75° for the coupling constant ratios $a_H(1)/a_H(4')$, $a_H(1)/a_H(2')$, and $a_H(1)/a_H(5')$ were obtained. It would, of course, be foolish to place any amount of confidence in coupling constants obtained from such a poorly-resolved spectrum, and conclusions drawn from these coupling constants are likewise suspect; however, the agreement found between these data and those for the cation radical is most satisfying.

Because much of the revival of interest in the electrochemistry of aromatic hydrocarbons was caused by the observation of electrogenerated chemiluminescence (ECL), resulting from the electrolysis of some of these compounds in aprotic media,⁴⁴ it seemed only natural to determine whether the 9,10-DNA system exhibited this behavior. The ac electrolysis of a 9,10-DNA solution in DMF with TBAP was carried out using techniques previously described.⁴⁵ ECL was observed un-

(44) A. J. Bard, K. S. V. Santhanam, S. A. Cruser, and L. R. Faulkner, "Fluorescence," G. Guilbault, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, Chapter 14, and references therein.

(45) L. R. Faulkner and A. J. Bard, *J. Am. Chem. Soc.*, **90**, 6284 (1968).

Table III. Twist Angles of Phenyl- and Naphthyl-Substituted Aromatic Hydrocarbons

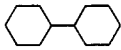
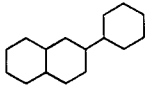
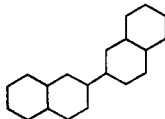
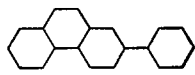
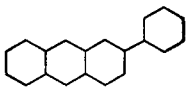
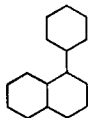
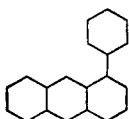
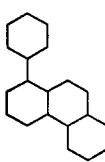
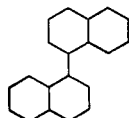
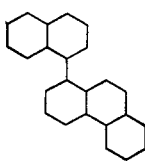
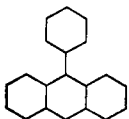
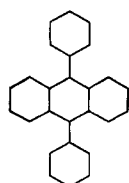
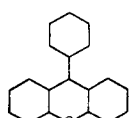
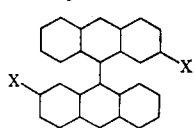
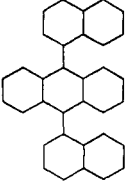
No.	Molecule	Twist angle, deg	Type	Technique	Ref
I		20-25	Neut	Uv	47
II		46 30	Neut Neut	Uv Uv	7 10
III		<10	Neut	Uv	7
IV		45	Neut	Uv	8
V		25	Neut	$E_{1/2}$	18
VI		34	Neut	Uv	7
VII		53	Neut	$E_{1/2}$	18
VIII		60	Neut	Uv	8
IX		<10	Neut	Uv	7
X		60-70	Neut	Uv	8
XI		68 60	Anion Cation	Esr Esr	14 54
XII		68 60 61	Anion Neut Cation	Esr Uv Esr	14 7 13
XIII		60	Neut	Esr	12
XIV		X = F 76 X = Cl 62 X = Br 85	Neut Neut Neut	Dipole moment Dipole moment Dipole moment	48 48 48

Table III (Continued)

No.	Molecule	Twist angle, deg	Type	Technique	Ref
XV		70-75	Anion	Esr	Present work
		70-75	Cation	Esr	Present work
		70-75	Neut	$E^{1/2}$	Present work

der these conditions, and the ECL emission spectrum was found to be identical with the 9,10-DNA fluorescence spectrum. No additional ECL bands appeared with prolonged electrolysis. This sort of behavior is the simplest sort of ECL and has been classified as Type I ECL in a recent review.⁴⁴ Interestingly enough, the compound chosen to illustrate Type I behavior, 9,10-DPA, bears many obvious similarities to 9,10-DNA.

Conclusions

From the above data two points become clear. The first, the fact that 9,10-DNA adheres to the previously described electrochemical behavior of aromatic hydrocarbons, is not as interesting as the second, *i.e.*, the determination of a twist angle of 70-75° for 9,10-DNA. This latter point requires more discussion because of the large number of assumptions which were made in order to reach this conclusion. The assumptions basic to the HMO method are well known and need not be reiterated; however, it should be pointed out that only a π interaction between the two aromatic nuclei has been assumed and that σ contributions have been ignored. This approach has recently been questioned.⁴⁶ The theoretical justification of the relationship $\beta = \beta_0 \cos \theta^{12}$ also neglected this breakdown of σ - π separability and pointed out that these effects would be smallest at positions far away from the essential single bond. We have also assumed all steric strain to be relieved by twisting as opposed to stretching; consequently, no correction for bond length was built into β for the essential bond. Examination of the molecule indicates that *cis-trans* isomers about the anthracene plane should be possible, and this cannot be taken into account in the HMO calculations. One would not, however, expect the difference in coupling constants to be detectable, and furthermore the existence of these isomeric forms has not been demonstrated. Finally it should be noted that the twist angle would not be expected to be static; hence the angles calculated are in reality time-averaged twist angles. Radical reactivity prohibited temperature variation experiments which could have perhaps revealed more about the dynamic aspect of the twist angle.

In order to compare the results from 9,10-DNA with those for other molecules, Table III was prepared. This table includes an angle for biphenyl in solution⁴⁷ in order that comparison can be made with similar molecules. Also included are angles for some substituted bianthryls which were determined from dipole moment measurements.⁴⁸ This table only includes

species for which a specific angle has been determined, and those species with more complicated interactions, such as rubrene, have been omitted. In very general terms, four different classes may be distinguished. The first class (A), comprised of molecules I-V, in which rotation is the least hindered, has an average twist angle of about 30°. The second class (B), represented by molecules VI-VIII, is obviously more hindered and appears to be more highly twisted; however, more measurements on molecules of this type would be necessary in order to state an average angle. The third class (C), molecules IX-XIII, seems to have a twist angle of about 60°. The drastic departure of 1,1'-binaphthyl from the anticipated behavior would suggest that a second look at this molecule is in order. The last class (D), molecules XIV and XV, is sparsely represented, but a twist angle of 75° seems representative. Although the similarity between 9,10-DNA and bianthryl is not as close as that between members of the other classes, the number and type of steric interactions are nearly the same. Classes C and D include anion radicals as well as neutral species. The great similarity in twist angles for the anion and cation radicals and the neutral species of the same structure would lead one to conclude that the major considerations are steric, and π interactions play a less important role in the case of these larger highly hindered molecules. The similarity between 9-phenylanthracene and 9-phenylxanthyl is in agreement with this idea. In those cases where the steric repulsion energy is only moderate, this may or may not be the case, as evidenced by biphenyl and some of its *para*-substituted derivatives.⁴⁹⁻⁵² The above discussion is clearly in qualitative order; however, it would be useful to have some way to assign numerical values to our chemical intuition. Moderate success in this direction has been achieved using calculations of the type described by Adrian.^{53,54}

This type of calculation combines the steric energy as set forth by Eyring⁵⁵ with the resonance energy obtained by π -electron calculations, in order to obtain the total energy as a function of twist angle. The resonance energy considered is only that for the essential bond and is obtained by subtracting the energy at 90° from that calculated at the angle of interest. The steric interaction between nonbonded carbon and hydrogen atoms was taken into account using Adrian's empirical

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

(50) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2795 (1962).

(51) P. H. Rieger and G. K. Fraenkel, *ibid.*, **39**, 604 (1963).

(52) M. Hirayama, *Bull. Chem. Soc. Jap.*, **40**, 2530 (1967).

(53) F. J. Adrian, *J. Chem. Phys.*, **28**, 608 (1958).

(54) L. O. Wheeler, Ph.D. Dissertation, The University of Texas, 1967.

(55) H. Eyring, *J. Am. Chem. Soc.*, **54**, 3191 (1932).

(46) J. A. Pople and D. L. Beveridge, *J. Chem. Phys.*, **49**, 4725 (1968).

(47) H. Suzuki, *Bull. Chem. Soc. Jap.*, **32**, 1340 (1959).

(48) H. Weiler-Feichenfeld, E. D. Bergman, and A. Hirschfeld, *Tetrahedron Lett.*, 4129 (1965).

equation $E_{CH} = 2.3E_{HH}$.⁵³ The purpose of these calculations was to compare 9,10-DPA with 9,10-DNA and to establish the order of importance of the various possible steric interactions.

A previous calculation for 9,10-DPA which considered only the H-H interactions indicated an energy minimum at 55°. ⁵⁴ The inclusion of the pertinent C-H interactions caused the position of this minimum to move to an angle of 60°. The C-H interaction was included because it was found to be a large source of steric repulsion energy in the case of 9,10-DNA. The 1-8' C-H interaction was found to be comparable in magnitude to the 1-8' interaction. The C-H interaction found in 9,10-DPA and between positions 8 and 2 of 9,10-DNA was much less. The complete calculation for 9,10-DNA indicated an energy minimum between 65 and 70°. Although quite crude, these calculations were useful, as they confirmed the experimental finding that 9,10-DNA was more severely twisted than 9,10-DPA. They also indicated the importance of the 1-8' type of C-H interaction and further confirmed our belief that, in the case of these highly hindered molecules, the molecular geometry is almost entirely controlled by steric factors. Certainly more complete types of calculations are known, but it was our belief that the small additional information content did not warrant further calculations.

The most remarkable aspect of this study has been its consistency, both internally and with previously published work. The electrochemical behavior of 9,10-DNA is exactly as anticipated, and there is excellent reason to believe that the twist angle between the aromatic nuclei is about 75°. This value is exactly that which is expected on the basis of previous measurements of other molecules. The compilation of these previous measurements also gives rise to a totally empirical classification system which relates the type of steric interaction to the twist angle. The anion, cation, and neutral forms of 9,10-DNA all seem to be twisted to the same extent, which emphasizes the predominance of steric effects over resonance effects in molecules of this sort.

Experimental Section

Chemicals. The 9,10-DNA was procured from Alfred Bader Chemicals and used as received. N,N'-Dimethylformamide was dried over Linde 4A molecular sieves and vacuum distilled under nitrogen from a suspension of anhydrous copper sulfate. Dimethoxyethane was dried and distilled over lithium aluminum hydride and stored on the vacuum line over pieces of sodium. Hexamethylphosphoramide was vacuum-distilled from sodium and then from a solution of 9,10-DNA and sodium. A solution of this solvent with tetraethylammonium perchlorate supporting electrolyte was found to provide an excellent polarographic background out to -2.7 V. Methylene chloride was dried over calcium hydride and distilled. Tetra-*n*-butylammonium perchlorate was obtained from Southwestern Analytical Chemicals (Austin, Texas) and dried in a vacuum oven before use. Tetraethyl ammonium perchlorate was prepared from the bromide, recrystallized several times, and dried in a vacuum oven.

Electrochemical Experimentation. With the exception of the RDE experiments, all electrolyses and voltammetric measurements were carried out on a vacuum line using procedures which have been described previously.¹⁷ The electrochemical instrumentation was completely conventional. Slow voltammetric measurements were made with a multipurpose instrument employing vacuum tube operational amplifiers, and rapid measurements were made with a solid-state instrument which employed positive feedback compensation of uncompensated resistance.⁵⁵ This instrument was used for all measurements in methylene chloride since the uncompensated resistance of these solutions was found to be 1000 ohms or greater. The potentiostat and integrator used for coulometric experiments were previously described.^{32,33} The electrode rotator was of the tachometer-generator type and was built by Electrocraft Corp. (Hopkins, Minn.). The areas of the Pt electrodes used were 2.17×10^{-2} , 2.2×10^{-1} , and 1.2×10^{-2} cm² for RDE, slow and fast voltammetry, respectively. All potentials are reported in respect to an aqueous SCE.

Esr Experimentation. The esr spectrometer was a Varian V-4502 with standard accessories which have been previously described.¹³⁻¹⁵ Details of the calculations and spectral simulations have also been discussed.¹³⁻¹⁵

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(56) E. R. Brown, D. E. Smith, and G. L. Booman, *Anal. Chem.*, **40**, 1411 (1968).