Electron Spin Resonance Spectra of the Free Radical Ions of 9,10-Diphenylanthracene[1]

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The e.s.r. spectra of the electrolytically generated free radical anion and cation of 9,10-diphenylanthracene were studied. The free radical spectrum of the cation was the same as that obtained from a solution of 9,10-diphenylanthracene in concentrated sulfuric acid. The cation ion spectrum was analyzed and the various experimental splitting constants were evaluated and found to compare favorably with the theoretical constants.

Introduction

Recent studies[2-4] of the electroluminescence produced by electrolysis of certain organic compounds in solution make it of interest to study and identify the hydrocarbon ions that are electrolytically generated. Visco and Chandross[3] found that electrolysis of 9,10-diphenylanthracene in acetonitrile produced a strong luminescence and attributed this phenomenon to reaction of positive and negative ion free radicals.

Electrochemical generation of free radicals for e.s.r. spectroscopy was first used by Geske and Maki[5] and was exploited fruitfully by other investigators.[6]

Contrary to the behavior of the free radical anions, the free radical cations of aromatic hydrocarbons are generally not very stable under electrolytic conditions and in most instances have been produced by dissolving the hydrocarbon in concentrated sulfuric acid.[7] Examples of such studies have been reported by Yokozawa and Miyashita[8] and by Weissman and co-workers.[9] Electrolytic generation of free radical cations was, however, realized successfully in case of such heteroatom-containing molecules as p-phenylenediamine,[10] derivatives of phenothiazine,[11,12] and most recently, 9-amino-10-phenylanthracene.[13]

In this paper, we are making a brief report of our studies on the electrolytic generation of the cation and anion of 9,10-diphenylanthracene.

Experimental Section

In our experiment, the free radical ions were generated in a cell, constructed according to the "intra mures" technique used by Geske and Maki.[5] The electrolytic compartment of the cell (Figure 1), which was mounted in the resonant cavity of a V-4500 Varian spectrometer, consisted of a flat thin-wall glass tube containing a platinum grid electrode (1). A thin glass capillary served to deaerate and mix the solution by passing an inert gas (nitrogen) through it. A saturated calomel electrode (3) was separated from the rest of the cell by a filter paper plug (2). The potential was calculated from the applied e.m.f. correcting for small potential drop calculated from the known resistance of the cell. The current passed through the cell was 10 μa. The solvent was acetonitrile and the solution was 10^{-3} M with respect to 9,10-diphenylanthracene and 0.1 M with respect to tetraethylammonium perchlorate. All experiments were conducted at 22°.

The free radical cation was generated with +1.5 v. vs. saturated calomel electrode (s.c.e.) on the platinum electrode. At this potential, the blue color reported by Visco and Chandross[3] was observed around the electrode. The free radical anion was generated at a potential of −2.1 v. vs. s.c.e.

Results

The electrolysis of 9,10-diphenylanthracene at 1.5 v. produced the electron spin resonance spectrum shown in Figure 2A. Figure 2B shows the spectrum of the free radical cation produced by dissolving 9,10-diphenylanthracene (3 × 10^{-3} M) in concentrated sulfuric acid (97%). The comparison of the two spectra shows, with the exception of some differences in the intensities, that they are very similar and consist of 41 equally spaced lines with a separation of 0.43 gauss.

When a negative potential of −2.1 v. was applied to the platinum electrode, a blue color was produced and the e.s.r. spectrum obtained for the free radical anion is shown in Figure 3. The spectrum consists of thirteen lines with a spacing of 1.36 gauss.

Discussion

If all the nonequivalent hydrogens in the 9,10-diphenylanthracene had different splitting constants and their effects were resolvable, one would expect 1875 lines in the e.s.r. spectra of its free radical ions. In view of the fact that only 41 equally spaced lines are observed for the free radical cation, it is assumed that the splittings in this cation are multiples or near multiples of the observed line spacing. On the other hand, the much greater widths of the lines of the free radical anion indicate that the assumption of near multiplicity is not applicable in this case, and the observed lines are composed of many closely spaced components.

(1) This investigation was supported in part by Research Grant GM 5144 from the Division of General Medical Sciences, Public Health Service, National Institutes of Health.

(2) D. M. Hercules, *Science*, **145**, 808 (1964).

(3) R. E. Visco and E. A. Chandross, *J. Am. Chem. Soc.*, **86**, 5350 (1964).

(4) K. S. V. Santhanam and A. J. Bard, *ibid.*, **87**, 139 (1965).

(5) D. H. Geske and A. H. Maki, *ibid.*, **82**, 2671 (1960).

(6) P. H. Rieger, L. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *ibid.*, **85**, 683 (1963).

(7) A. Carrington, F. Dravnieks, and M. C. R. Symons, *J. Chem. Soc.*, 947 (1959).

(8) Y. Yokozawa and I. Miyashita, *J. Chem. Phys.*, **25**, 796 (1956).

(9) S. I. Weissman, E. de Boer, and J. J. Conradi, *ibid.*, **25**, 963 (1956).

(10) M. T. Melchior and A. H. Maki, *ibid.*, **34**, 471 (1961).

(11) J.-P. Billon, G. Cauquis, J. Combrisson, and A.-M. Li, *Bull. soc. chim. France*, 2062 (1960).

(12) J.-P. Billon, G. Cauquis, and J. Combrisson, *J. Chim. Phys.*, **61**, 374 (1964).

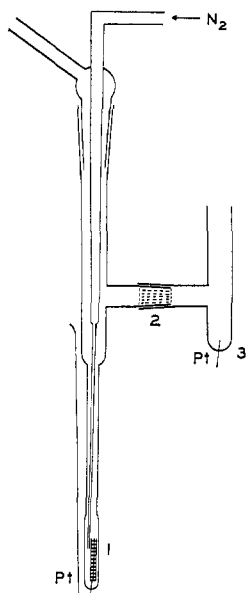(13) F. Tonnard, *Compt. rend.*, **260**, 2793 (1965).

Figure 1. Electrolytic cell for e.s.r. measurements: (1) platinum grid electrode, (2) filter paper plug, (3) calomel electrode.
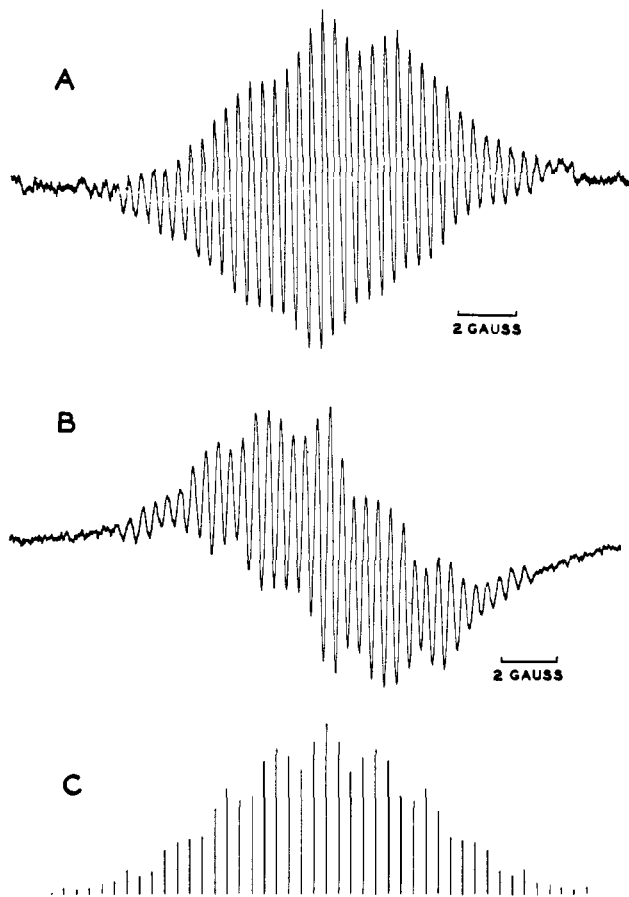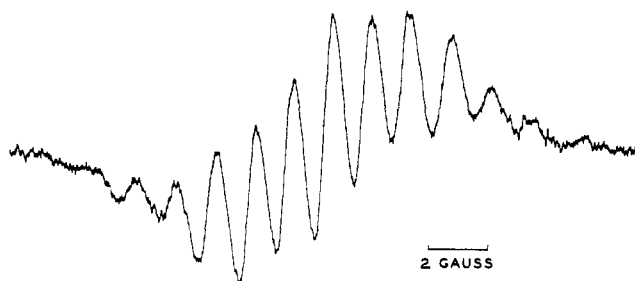

Figure 3. E.s.r. spectrum of the free radical anion of 9,10-diphenylanthracene.

from the unpaired spin densities using the Colpa–Bolton equation $a_H = (Q\rho \pm K\rho^2)$, where ρ is the unpaired spin density equal for both ions. The plus sign is used for the cation and the negative sign for the anion. Q was assumed to be 37 gauss and K, 17 gauss. The resulting unpaired spin densities for both ions and the theoretical splitting constants for the pertinent positions of the cation using Hückel unpaired spin densities are given in Table I. It is seen that the splitting constants are reasonably close to integral multiples of 0.43 gauss.

Table I
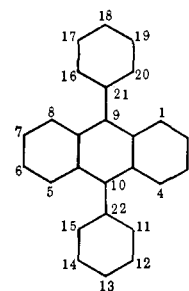
Position	Unpaired spin densities Hückel	McLachlan	Theoret. split. const. of cation, gauss	Multiples of the 0.43 gauss
1	0.0581	0.0680	2.22	2.15
2	0.0338	0.0264	1.28	1.29
11	0.0429	0.0580	1.62	1.72
12	0.0011	−0.0144	0.04	0
13	0.0474	0.0636	1.80	1.72

Figure 2. (A) E.s.r. spectrum of electrolytically generated 9,10-diphenylanthracene free radical cation; (B) e.s.r. spectrum of solution of 9,10-diphenylanthracene in concentrated sulfuric acid; (C) line spectrum built up from theoretical splitting constants of the cation of 9,10-diphenylanthracene.

Hückel molecular orbital and McLachlan[14] calculations were carried out on the radical ions in question and the theoretical splitting constants were calculated

The usually encountered differences between the splitting constants of free radical anions and cations are explained by the Colpa–Bolton theory by means of the C–H bond polarization.[15] Using the above assumptions and calculations, a spectrum for the cation can be constructed (Figure 2C) which is in good agreement with the experimentally observed spectrum.

The splitting constants for the free radical anion do not appear to be very close multiples of any one quantity; consequently, the lines in the spectrum are considerably broader and we have not been successful in interpreting it.

(14) A. D. McLachlan, Mol. Phys., 3, 231 (1960).

(15) J. P. Colpa and J. R. Bolton, ibid., 6, 273 (1963).

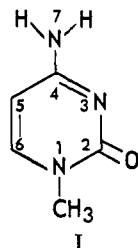# Nuclear Magnetic Resonance Studies of Methyl Derivatives of Cytosine

Edwin D. Becker, H. Todd Miles, and Robert B. Bradley

Contribution from the National Institute of Arthritis and Metabolic Diseases, National Institutes of Health, Bethesda, Maryland 20014. Received August 19, 1965

Proton nuclear magnetic resonance spectra are reported for 1-methylcytosine, its hydrochloride and hydroiodide, and several dimethylcytosine salts. Unequivocal assignments of n.m.r. lines have been made by use of ^{15}N substitution and spin decoupling. Hindered rotation of the amino group has been found in the hydrohalide salts, and in the methylamino derivative this gives rise to geometric isomers. Thermodynamic data for interconversion of the isomers were determined from the n.m.r. spectra, and estimates of the rates of rotation of the amino and methylamino groups are given. Chemical shifts and spin coupling constants are tabulated and discussed, particularly with respect to dependence on salt formation, on the nature of the anion, on the nature of the solvent (SO_2 and dimethyl sulfoxide), and on temperature.

Proton nuclear magnetic resonance (n.m.r.) has been applied in several instances to the structural investigation of cytosine and its nucleosides,[1-6] the work being stimulated in part by the relevance of these substances to nucleic acid structure and function. We present here the results of a detailed n.m.r. study of 1-methylcytosine and a number of its derivatives. In a preliminary report of this work[7] we have shown that the n.m.r. results proved that the only tautomeric form of 1-methylcytosine observed (in dimethyl sulfoxide and in sulfur dioxide solutions) is I, and that in

I

the presence of acid the molecule is protonated at N_3.[8]

In this paper further details of the experiments leading to this conclusion are given, and in addition data are presented on the hindered rotation of the amino group in the protonated molecules, on the presence of stereoisomers in 4-NCH₃ derivatives, on the magnitudes of H–H and ^{15}N–H coupling constants, on the effect of the nature of the anion on the chemical shift of the NH protons, and on the effects of protonation and methyl substitution on the chemical shifts.

Experimental Section

Spectra were obtained with a Varian A-60 spectrometer and 12-in. magnet system, using both a V-6030 room temperature probe (sample temperature 23 ± 1°) and a V-6031 variable temperature probe. The V-6040 variable temperature controller was calibrated to ±2° by using the known chemical shifts of methanol and ethylene glycol.[9] Spectra were scanned routinely at 1 c.p.s./sec. and in certain cases portions of the spectra were scanned at 0.2 c.p.s./sec. The spectrometer frequency calibration was found to be slightly temperature dependent and was calibrated at each temperature by means of audio side bands. Frequencies of sharp peaks are accurate to ±1 c.p.s. (*ca.* 0.02 p.p.m.). Spectral resolution was usually about 0.3–0.4 c.p.s. For the determination of isomer ratios in compound X (see later discussion) integrals were obtained at 1 c.p.s./sec. The values reported are the average of five determinations.

Spin-decoupling measurements were conducted with a Varian HR-60 spectrometer equipped with a Space Avionics single side-band proton–proton decoupler and a V-4331 A variable temperature probe. The sample temperature was measured to ±0.2° with a copper-constantan thermocouple. Spectra were scanned at approximately 0.5 c.p.s./sec. Audio signals used for proton decoupling were measured to ±1 c.p.s.

The hydrochlorides were prepared by passing dry hydrogen chloride into methanolic solutions of the free bases, precipitating the salts, and recrystallizing twice from methanol.

(1) C. D. Jardetzky and O. Jardetzky, *J. Am. Chem. Soc.*, **82**, 222 (1960).
(2) J. P. Kokko, J. H. Goldstein, and L. Mandell, *ibid.*, **83**, 2909 (1961).
(3) L. Gatlin and J. C. Davis, Jr., *ibid.*, **84**, 4464 (1962).
(4) H. T. Miles, *ibid.*, **85**, 1007 (1963).
(5) A. R. Katritzky and A. J. Waring, *J. Chem. Soc.*, 3046 (1963).
(6) O. Jardetzky, P. Pappas, and N. G. Wade, *J. Am. Chem. Soc.*, **85**, 1657 (1963).
(7) H. T. Miles, R. B. Bradley, and E. D. Becker, *Science*, **142**, 1569 (1963).
(8) We have assigned the number 7 to the exocyclic nitrogen in order to avoid unnecessarily cumbersome nomenclature for the methylated derivatives. This convention also permits a clear and succinct designation of the protons attached to this nitrogen, and when necessary, of the isotopic species.
(9) Varian Associates' calibration curve supplied with V-6040 controller.