192. *Unstable Intermediates. Part IV.* Electron Spin Resonance Studies of Univalent Aromatic Hydrocarbon Ions.*

By A. CARRINGTON, F. DRAVNIEKS, and M. C. R. SYMONS.

The electron spin resonance spectra of the positive and negative ions of anthracene, naphthacene, and perylene have been analysed and the hyperfine splitting constants obtained. Some aspects of the chemistry of the positive ions are discussed.

MANY workers have observed electron spin resonance absorption from solutions of aromatic hydrocarbons in sulphuric acid. These have usually been attributed to hydrocarbon positive ions although in no case has it been proved that the electron spin resonance spectrum arises exclusively from one paramagnetic entity. Indeed, Yokozawa and Miyashita[1] suggest that the spectrum they obtain from a solution of perylene in concentrated sulphuric acid arises in part from appreciable population of the perylene triplet state and in part from the presence of a separate free radical. The most convincing evidence in favour of the positive ion postulate was obtained by Weissman, de Boer, and Conradi[2] who showed that the spectra obtained from the sulphuric acid solutions were very similar in their general appearance to those obtained from the well-authenticated hydrocarbon negative ions, and that this was in accord with molecular-orbital theory.

The published electron spin resonance spectra of both positive and negative ions are not too well resolved and only for the naphthalene negative ion[3] was it possible to analyse

---

* Part III, *J.*, 1959, 277.

[1] Yokozawa and Miyashita, *J. Chem. Phys.*, 1956, **25**, 796.

[2] Weissman, de Boer, and Conradi, *ibid.*, 1956, **26**, 963.

[3] Tuttle, Ward, and Weissman, *ibid.*, 1956, **25**, 189.

the spectrum completely and obtain values of the splitting constants for the non-equivalent protons contributing to the hyperfine structure. The demonstration that the splitting due to a proton attached to an aromatic carbon atom is, to a good approximation, proportional to the unpaired electron density at that carbon atom [4] led to the appreciation that the electron spin resonance method should provide a powerful tool for the investigation of electron distributions. This potentiality has not yet been fully realised because few complex hyperfine patterns have been completely and successfully analysed.

We have almost completely resolved the hyperfine structure in the spectra obtained from the positive and negative ions of anthracene, naphthacene, and perylene. This has enabled us to assign precise values to the splitting constants and to show that, for sulphuric acid solutions, the spectra can be interpreted unambiguously in terms of a single paramagnetic species.

EXPERIMENTAL

The electron resonance experiments were made with a spectrometer employing a reflection cavity operating in the TE 0116 mode at 9200 Mc./sec. A magnetic field of approximately 3300 gauss was provided by a magnetically shimmed 6 inch magnet with a battery power supply. The field was modulated at 100 kc./sec. by using one turn of wire around the sample inside the cavity. The signal was amplified at 100 kc./sec., fed through a phase-sensitive detector and recorded on a Sanborn Dual Channel Recorder as the first derivative of the absorption with respect to magnetic field, against the magnetic field. The chart paper was calibrated in gauss by the proton resonance technique and *g*-values were measured with respect to the diphenylpicrylhydrazyl free radical. The splitting constants in Table 1 are believed to be accurate to ±0·05 gauss and the *g*-values are accurate to the fourth decimal place, a value of 2·0039 for diphenylpicrylhydrazyl being used.

The positive ions were prepared by dissolving the hydrocarbon in 98% sulphuric acid, the concentrations being 0·01M—0·02M although the line widths were not very dependent upon the concentration. The spectrum of the anthracene positive ion persisted for about 1 hr., but with naphthacene and perylene good spectra were obtained for several weeks after preparation. In no case was any change in symmetry or relative line intensities observed and we can conclude with certainty that only one free radical was formed in each system.

The negative ions were prepared by vacuum distillation of tetrahydrofuran from phosphoric oxide into a tube containing the hydrocarbon and a small piece of potassium. The tubes were sealed off, warmed to melt the potassium, and examined in the spectrometer. The line width in all cases depended very strongly on the hydrocarbon concentration, as has been discussed by Ward and Weissman.[5] With anthracene an interesting sequence was observed. As the potassium dissolved, the radical concentration increased and a spectrum of 21 broad lines was observed. However, the line width decreased with time and after several days we obtained the spectrum shown in Fig. 1. We suggest that the initial line width is due to electron exchange between the radical ion and unchanged anthracene but that exchange between the radical ion and the products must be slow. The sample containing the perylene negative ion still gave a strong well-resolved spectrum after two months.

The hydrocarbons were all recrystallised from ethanol and their m. p.s checked.

RESULTS

The spectra obtained are shown in Figs. 1, 2, and 3, the spectra for the two ions of any one hydrocarbon being shown under identical sweep conditions. The spectra were analysed and the reconstruction shown under each spectrum was computed once the splitting constants for protons occupying different symmetry sites had been determined. The latter are determined largely by trial and error, but once the correct constants have been obtained the agreement between the computed and experimental spectra should be perfect with respect to both relative line intensity and position. Ease of such an analysis depends on the resolution.

The splitting constants are listed in Table 1; positions α, β, and γ are defined in structures (I)—(IV). We have included our values for the naphthalene negative ion since we have been

---

[4] McConnell, *J. Chem. Phys.*, 1956, **24**, 632.

[5] Ward and Weissman, *J. Amer. Chem. Soc.*, 1954, **76**, 3612.

FIG. 1. *Electron spin resonance absorption spectra of the anthracene positive and negative ions.*

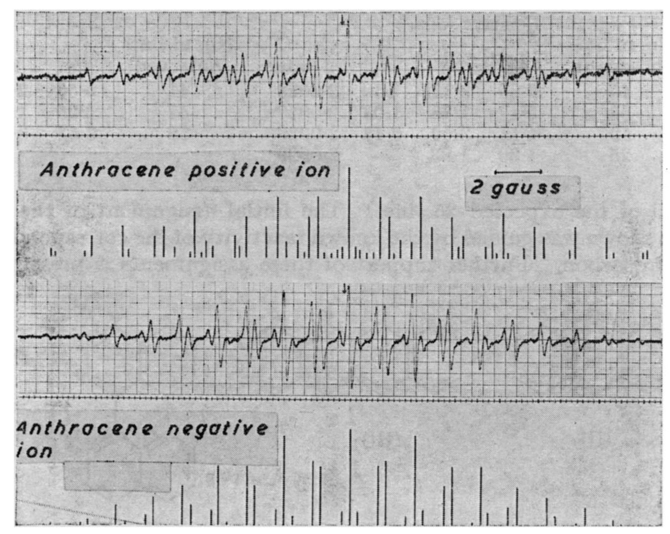


FIG. 2. *Electron spin resonance absorption spectra of the naphthacene positive and negative ions.*

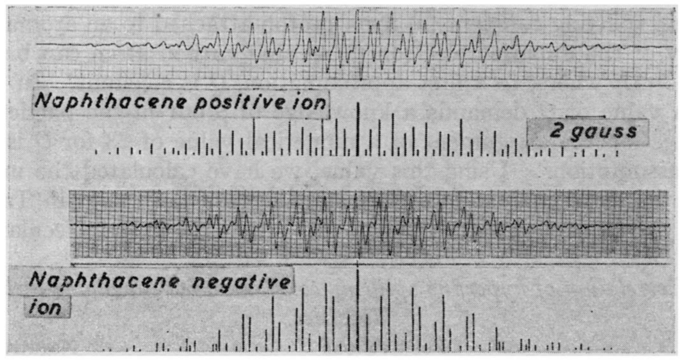


FIG. 3. *Electron spin resonance absorption spectra of the perylene negative and positive ions.*

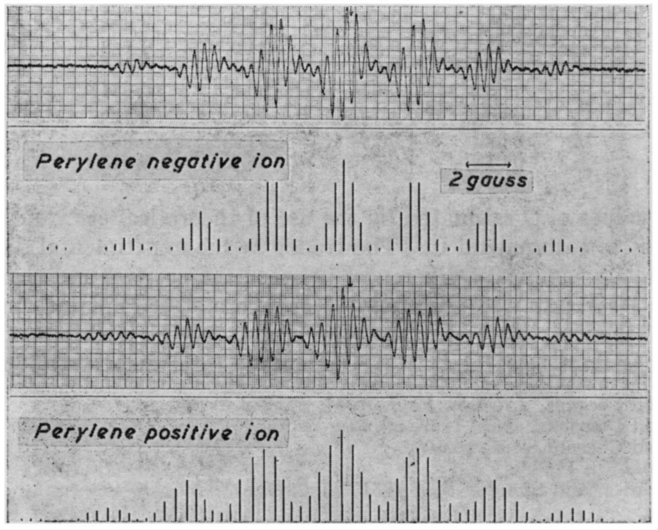
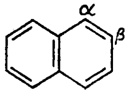


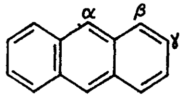
TABLE 1. *Values of the hyperfine splitting constants (in gauss).*

	Positive ions					Negative ions				
Hydrocarbon	No. of lines observed	a_α	a_β	a_γ	g-value	No. of lines observed	a_α	a_β	a_γ	g-value
Anthracene ...	45	6·65	3·11	1·40	2·0028	41	5·56	2·74	1·57	2·0029
Naphthacene ...	63	5·17	1·74	1·03	2·0028	57	4·25	1·49	1·17	2·0029
Perylene	59	4·11	3·09	0·46	2·0028	59	3·53	3·09	0·46	2·0029
Naphthalene ...	25	4·90	1·83	—	2·0029					

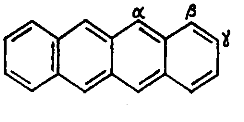
able to resolve all of the expected 25 lines. The initial assignment of the constants to the particular protons shown was guided by the known reactivity of the corresponding ring positions in the parent hydrocarbon. Further support of these assignments is presented below.



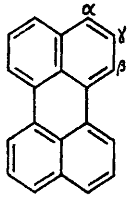
(I)



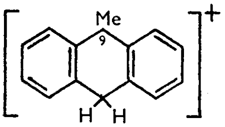
(II)



(III)



(IV)



(V)

DISCUSSION

McConnell and his co-workers [6-9] have found that the relationship between the experimental hyperfine splitting constant (a) for a proton attached to an aromatic carbon atom and the density of the unpaired electron (ρ) at that carbon atom can be represented by the equation $a = Q\rho$ where, to a first approximation, Q is constant. In the general case derivation of a value of Q demands a knowledge of ρ but in the particular case of the benzene negative ion the assignment of a numerical value of 23 for Q is independent of any arbitrary assumptions. Using this value, we have calculated the unpaired electron densities from the experimental hyperfine splitting constants and in Table 2 these are compared with the electron densities calculated [10] from Hückel's molecular-orbital theory.

TABLE 2. *Correlation of hyperfine splitting constants with calculated unpaired electron densities.*

		Positive ions			Negative ions		
		ρ (calc.)	ρ (obs.)	" Q "	ρ (calc.)	ρ (obs.)	" Q "
Anthracene	α	0·192	0·289	34·6	0·192	0·242	28·9
	β	0·096	0·135	32·4	0·096	0·119	28·5
	γ	0·047	0·061	29·8	0·047	0·068	33·4
Naphthacene	α	0·148	0·225	34·9	0·148	0·185	28·7
	β	0·056	0·076	31·1	0·056	0·065	26·6
	γ	0·034	0·045	30·3	0·034	0·051	34·4
Perylene	α	0·108	0·179	38·1	0·108	0·153	32·7
	β	0·083	0·134	37·2	0·083	0·134	37·2
	γ	0·013	0·020	35·3	0·013	0·020	35·3

We also include values of Q estimated by the use of theoretical electron densities but this procedure has less to recommend it. The trends in the experimental data are worthy of comment. There are significant differences between the positive and negative ions which, as Weissman, de Boer, and Conradi [2] pointed out, cannot be explained in terms of simple molecular-orbital theory. The differences are largest for the positions of highest electron density. Also, one finds that the Q values calculated from the experimental data increase

---

[6] McConnell and Chesnut, *J. Chem. Phys.*, 1957, **27**, 984.
[7] McConnell and Dearman, *ibid.*, 1958, **28**, 51.
[8] McConnell and Chesnut, *ibid.*, p. 107.
[9] McConnell, *ibid.*, p. 1188.
[10] Fukui, Yonezawa, and Shingu, *ibid.*, 1952, **20**, 722.

with increasing size of the hydrocarbon. Without carefully defining what we mean by the electron density at a carbon atom, these values of Q have little significance. Despite the approximations involved, the simple relationship is of great value and in many cases supports the predictions of simple molecular-orbital theory. Hoijtink[11] has recently considered the application of molecular-orbital theory to these problems and concludes that the simple theory is suited to the interpretation of the electron spin resonance spectra of the hydrocarbon mononegative ions since the basic assumption of this theoretical approach, *i.e.*, that the unpaired electron may be considered as moving in the field of the carbon atoms, is not too far removed from reality. In other cases, where the unpaired electron in a neutral alternant hydrocarbon radical forms an integral part of the system, the simple theory is not satisfactory. Simple valence-bond theory gives a better description of such systems.[12]

Chemistry of the Positive Ions.—When an aromatic hydrocarbon is dissolved in concentrated sulphuric acid, three reactions are well established, namely, protonation, oxidation, and sulphonation. There is much chemical evidence for oxidation to form positive ions, much of which has been summarised by Weiss.[13] The mechanism of this oxidation is of interest. Kon and Blois[14] pointed out that the ability of a hydrocarbon to form a positive ion in sulphuric acid follows the ease of protonation (atom localisation energies) rather than the ionisation potentials. This can be understood in terms of the following sequence for anthracene (A):

$$A + H_2SO_4 \rightleftharpoons AH^+ + HSO_4^- \quad \ldots\ldots\ldots \quad (1)\ (\text{rapid})$$

$$A + AH^+ \rightleftharpoons {\cdot}AH + A^+ \quad \ldots\ldots\ldots\ldots \quad (2)$$

$${\cdot}AH + 2H_2SO_4 \rightleftharpoons A^+ + 2H_2O + SO_2 + HSO_4^- \quad \ldots\ldots \quad (3)$$

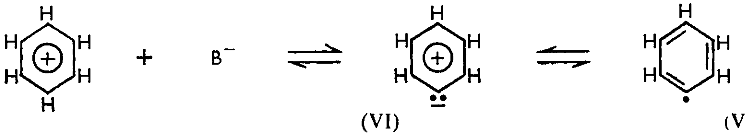
The radical ·AH will be a powerful hydride-ion or hydrogen-atom donor, and stage (3) is simply one of several possible subsequent reactions. It is noteworthy that in oxygen-free HF, which cannot accept hydride ions or hydrogen atoms, only protonation can be detected.

In the specific case of anthracene in acid solution, the evidence for protonation is very strong. Gold and Tye[15] have pointed out the formal similarity between the diphenylmethyl carbonium ion (Ph_2HC^+) and anthracene protonated in the 9-position. Their ultraviolet and visible absorption spectra are, in fact, remarkably similar, the long-wavelength bands having maxima at 4400 Å and 4300 Å respectively. If 9-methylanthracene is dissolved in sulphuric acid under protonating conditions, then a long wavelength band at 4130 Å is found.[16] The methyl group has effected a shift of 170 Å to shorter wavelengths. Protonated 9-methylanthracene (V) bears the same relationship to protonated 1 : 1-diphenylethylene as protonated anthracene (AH^+) bears to the diphenylmethyl carbonium ion. In fact the methyldiphenylmethyl carbonium ion has a peak at 4240 Å, the shift to shorter wavelengths being 160 Å, almost identical with the expected value. These considerations make the assumed structures seem highly plausible, and absence of electron spin resonance absorption from these solutions is also in accord with these postulates.

It is probably correct to assume that the positive ions are entirely separate from the anion HSO_4^-. Concentrated sulphuric acid is an extremely good ionising solvent and electron spin resonance gives no indication of ion pairing. This is equally true of the negative ions in ether solutions. Here, because of the lower dielectric constant, one might expect to find some ion pairing even in dilute solutions, but evidently this cannot be construed as involving covalent bonding since Adam and Weissman's[17] recent results on salts of the type $Ph_2CO^-Na^+$ show strikingly that if the ions are adjacent some charge transfer occurs and the hyperfine structure due to sodium is resolved.

[11] Houtink, *Mol. Phys.*, 1958, **1**, 157.
[12] Brovetto and Ferroni, *Nuovo Cim.*, 1957, **5**, 142.
[13] Weiss, *Nature*, 1941, **147**, 512.
[14] Kon and Blois, *J. Chem. Phys.*, 1958, **28**, 743.
[15] Gold and Tye, *J.*, 1952, 2173 *et seq.*
[16] Grace and Symons, *J.*, 1959, 958.
[17] Adam and Weissman, *J. Amer. Chem. Soc.*, 1958, **80**, 1518.

It is interesting to consider the corresponding conjugate acids and bases of the hydrocarbon ions. In a sufficiently basic medium, hydrocarbon positive ions could lose ring protons. For ease of presentation the benzene positive ion is depicted.



(VI) (VII)

Structure (VI) is converted into (VII) by electron transfer from the sp^2 hybridised lone pair to the ring. When phenyl radicals react they do so invariably as if they had structure (VII), so one can infer that (VII) is a closer representation of the ground state than (VI). However, if phenyl-type radicals were formed in strongly acidic media, protonation should occur, with a consequent decrease in free-radical reactivity.

This work was supported in part by the U.S. Air Force Office of Scientific Research. One of us (A. C.) is indebted to Professor J. E. Wertz for the opportunity to work in his laboratory during the tenure of a Research Fellowship at the University of Minnesota.

UNIVERSITY OF MINNESOTA, MINNEAPOLIS 14, MINNESOTA, U.S.A.
THE UNIVERSITY, SOUTHAMPTON (*present address,*
A. C. *and* M. C. R. S.).

[*Received, August* 11*th*, 1958.]