hydrogen from slow elimination from VIII or XII. Since the initial secondary hydrogen presumably arises from VII, these results can be accommodated by either approximately equal quantities of VI–VIII or a more complex mixture including unsymmetric products as well.

Experimental

Cyclohexene–phosphorus–oxygen reaction products were prepared as previously described, separated by filtration under moisture-free conditions, and stored in closed containers.

Lead Salts of Oxidative Hydrolysis Products.—A sample of cyclohexene reaction product (0.92 g., 0.0044 mole) was added to 5 cc. of 45% HNO_3 in a small flask and placed on a steam-bath. In a few seconds a vigorous reaction occurred and the flask was set aside for 10 min., then diluted with 35 cc. of water and heated for an hour at 85°. On addition of 0.013 mole of $Ba(OH)_2$ solution and enough NH_4OH to render the mixture basic, $Ba_3(PO_4)_2$ was precipitated, 1.15 g., theory 1.3 g. Treatment of the filtrate with lead nitrate (0.0048 mole) gave 1.6 g. of pale yellow lead salt which was slurried with 95% ethanol, filtered and dried. *Anal.* Found: Pb, 57.43, 57.55; P, 7.74. Calcd. for $C_6H_9PO_3Pb$: Pb, 56.4; P, 8.42. Similar treatment of an isobutylene reaction product, 1.8 g., gave the calculated yield of barium phosphate and 2.5 g. (theory 3.6 g.) of lead salt. *Anal.* Found: Pb, 57.87; P, 8.41. Calcd. for ($C_4H_8(OH)PO_3Pb$): Pb, 57.6; P, 8.64. Calcd. for ($C_4H_7PO_3Pb$): Pb, 60.7; P, 10.0.

Amine Salts of Hydrolysis Products.—A 5-g. sample of the cyclohexene product was hydrolyzed with nitric acid, the solvent removed *in vacuo*, and the residue taken up in 95% ethanol. Addition of cyclohexylamine precipitated a mixture of salts. Fractional crystallization from alcohol and then aqueous acetone removed amine phosphate as the more soluble component leaving finally 1 g. of material, m.p. 220–228°. *Anal.* Found: N, 7.77; P, 11.26. Calcd. for the tricyclohexylamine salt of β-phosphatocyclohexane phosphonic acid: N, 7.53; P, 11.1. By continuous ether extraction of a similar hydrolysis mixture and evaporation of the ether, a viscous residue was obtained which, on treatment with cyclohexylamine and recrystallization, gave a small amount of salt, m.p. 246–250°. *Anal.* Found: N, 8.28; P, 9.30. Calcd. for tetracyclohexylamine salt of the same acid: N, 8.55; P, 9.45. Refluxing a sample of cyclohexene product for two hours with potassium bromate solution followed by continuous ether extraction again yielded a residue which on treatment with aniline and recrystallization from methanol gave what was evidently the aniline salt of cyclohexenephosphonic acid or its polymer since it had the correct neutralization equivalent (129, calcd. 128). Here elimination was complete since the extracted aqueous solution gave the calculated yield of magnesium ammonium phosphate on treatment with magnesium and ammonium ions.

Potentiometric Titrations.—Weighed samples of cyclohexene reaction products were dissolved in water and aliquots titrated with standard NaOH solution using a glass electrode in the conventional manner. In the case of alcoholysis products the weighed samples were dissolved in absolute methanol and aliquots titrated after dilution with water. In order to establish that hydrolysis of intermediate esters was negligible during the titration, diethyl phosphite was added to one of these diluted samples without significant effect on the titration curve.

Isolation of Dialkyl Phosphites from Alcoholysis Products.—A sample of cyclohexene reaction product, 20.8 g., was dissolved in 100 cc. of absolute ethanol and refluxed for 5 hours. A small amount of yellow precipitate was removed by filtration, and the filtrate distilled *in vacuo*. In addition to the excess alcohol, only 4 g. of volatile material was obtained, b.p. on redistillation 62° (6 mm.), $n^{25}{}_D$ 1.4052, with an infrared spectrum identical with diethyl phosphite. The light brown viscous residue remaining yielded no further product, but darkened and decomposed on further heating. A similar alcoholysis using *n*-butyl alcohol yielded dibutyl phosphite, b.p. 101° (4 mm.), $n^{25}{}_D$ 1.4243, with the correct infrared spectrum.

Esterification of Alcoholysis Products.—A methanol solution of the cyclohexene product was treated with an ether solution of excess diazomethane which reacted immediately with evolution of nitrogen. Methanol was removed and the residue taken up in benzene in which it was now soluble. The remaining methanol was removed by azeotropic distillation and the solution treated with additional portions of diazomethane until the yellow color of the latter persisted. After the reaction mixture had stood overnight an attempt was made to distil it *in vacuo*. No volatile material other than a small amount of dimethyl phosphite and trimethyl phosphate could be obtained and the viscous residue was evidently polymeric since it had a Rast molecular weight of 410. Its analysis C, 41.85; H, 6.76; P, 18.60, corresponded to no obvious composition. Another experiment in which an ethanol alcoholysis product was heated with triethyl phosphite similarly gave no distillable product containing the cyclohexene ring, but only a viscous residue. The method, incidentally, appears to be a good one for further esterifying phosphate esters. Thus a mixture of triethyl phosphite and mixed mono- and diethyl phosphates gives diethyl phosphite and triethyl phosphate in good yield.

NEW YORK 27, N. Y.

[CONTRIBUTION FROM WASHINGTON UNIVERSITY AND THE CHEMICAL LABORATORY, THE FREE UNIVERSITY, AMSTERDAM]

Electron Spin Resonance Spectra of Aromatic Mononegative and Monopositive Ions[1]

BY E. DE BOER AND S. I. WEISSMAN

RECEIVED MARCH 17, 1958

The electron spin resonance (E.S.R.) spectra of the mononegative ions of anthracene, tetracene, phenanthrene, biphenyl, terphenyl, perylene, pyrene, triphenylene, coronene, fluoranthene, acenaphthylene, acepleiadylene, acenaphthene and acepleiadiene are reported. In addition, the E.S.R. spectra of the positive ions of perylene, tetracene, anthracene, acepleiadylene and acepleiadiene have been measured. The spectra are compared with those calculated on the assumption of a linear relationship between hyperfine coupling constant with a proton and the π-spin density on the adjacent carbon. The latter were calculated by a single configuration Hückel molecular orbital treatment. The spectra of the negative ions of all the alternant hydrocarbons except pyrene are in satisfactory agreement with the calculations. The spectra of the negative ions of the non-alternant hydrocarbons fluoranthene and acenaphthylene agree with the calculations, while the spectrum of acepleiadylene ion does not. Among the positive ions, the spectra of the ions of perylene, tetracene and anthracene agree with the calculations; the spectrum of the positive ion of acepleiadiene does not. The ions of the partially saturated hydrocarbons acepleiadiene and acenaphthene have high coupling constants with the methylene protons and are not satisfactorily treated by simple molecular orbital theory.

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Introduction

Hydrocarbon mono- and dinegative ions formed by the reduction of aromatic hydrocarbons with alkali metals in tetrahydrofuran, 1,2-dimethoxyethane and in solvents with similar properties[2-4] display electron spin resonance (E.S.R.) absorption spectra with a remarkable hyperfine structure.

Recently Yokozawa and Miyashita[5] reported that a solution of perylene in concentrated sulfuric acid showed paramagnetism. They attributed this to perylene being in a triplet state and to free radicals ($S = {}^1/_2$). From further investigations[6,7] it became clear that the paramagnetism was caused by the formation of monopositive ions. It was found that of the hydrocarbons considered in this paper not only perylene, but also tetracene, anthracene and acepleiadylene, formed positive ions on solution in sulfuric acid and their E.S.R. spectra exhibit well-resolved hyperfine patterns.

The hyperfine structure of the E.S.R. spectra of the monopositive and mononegative ion arises from the interaction between the magnetic moment of the unpaired electron and the magnetic moments of the protons in the aromatic system. Since the odd electron in the monopositive and mononegative ion is a π-electron and the protons are located in the nodal plane of the π-orbitals, the spin densities at the positions of the protons will be zero unless interaction occurs between the π-electron and the σ-electrons of the carbon hydrogen bonds.[8-12] Extended and elegant treatments of the $\sigma-\pi$ interaction have been given by McConnell and Chestnut[13] and by McConnell.[14] In brief, these treatments demonstrate that electrostatic exchange interactions between π- and σ-orbitals lead to the production of spin density in the σ-bonds of aromatic free radicals. Further, the resulting hyperfine coupling with each carbon is approximately proportional to the density of unpaired π-electron on the adjacent carbon atom.[15] If we adopt a single configuration molecular orbital description of each free radical, the π-spin density at each carbon atom is approximately equal to the square of the coefficient of its 2p function in the singly occupied molecular orbital.[16]

The one-electron m.o. method is a better approximation for hydrocarbon mono- and dinegative ions than for hydrocarbon molecules.[17] If the unpaired electron in alternant hydrocarbons does not bring about an appreciable change in the distribution of the other electrons in the molecule, which is approximately true for large aromatic systems, it may be considered to move in the field of the neutral carbon atoms. Indeed, from experimental data it is known that asymmetrical alternant hydrocarbons have negligible dipole moments.[18] In agreement with this, Hückel's m.o. treatment as well as the more elaborate calculations of Pariser[19] and Pople,[20] including interaction between the π-electrons, lead to a uniform distribution of the π-electrons in alternant hydrocarbons. In non-alternant hydrocarbons the π-distribution is not uniform, so that the odd electron in the mononegative ion cannot be considered to move in the field of the neutral carbon atoms. When, however, the aromatic system does not deviate too much from an alternant hydrocarbon, reasonable results might be expected from the calculations on the various properties of these anions by applying the Hückel m.o. method.

The question may arise whether the one-electron treatment is reliable for the positive ions as well as for the negative ions of alternant hydrocarbons. For the positive ions, the following picture may be presented on the analogy of the theory of the semi-conductors. Suppose an electron is removed from a molecule. The resulting vacancy may be considered as a "positive hole." Imagine such a "positive hole" is added to a hydrocarbon, thus creating the monopositive ion. This "positive hole" can be described quantum-mechanically in the same way as the added electrons in the negative ions, making the same plausible assumption that the neutral molecule is not much disturbed by the "positive hole." Therefore a theory similar to the one developed for the mononegative ions[17] may be given for the monopositive ions. For alternant hydrocarbons the following relations hold for the coefficients of the molecular orbitals[21]

$$\left.\begin{array}{l} C_{s,j} = +C_{s,k} = s = \text{starred} \\ C_{s,j} = -C_{s,k} = s = \text{unstarred} \end{array}\right\} k = 2n + 1 - j$$

here the subscripts j and k refer to one of the $2n$ m.o.'s, s to the division of the carbon atoms in starred and unstarred ones, which is a general procedure used to distinguish the alternant from the non-alternant hydrocarbons. According to these relations both mononegative and monopositive ions ought to yield similar E.S.R. spectra, as has actually been observed.[4] The only difference is that the E.S.R. spectra in sulfuric acid are somewhat longer and better resolved, which is particularly the case with tetracene. Similar reactions between the coefficients of the m.o.'s of non-alternant hydrocarbons do not exist. The spectra of the negative and positive ions of acepleiadylene are in fact quite different from each other. However, we should note

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(2) D. Lipkin, D. E. Paul, J. Townsend and S. I. Weissman, *Science*, **117**, 534 (1953).

(3) G. J. Hoijtink, E. de Boer, P. H. van der Mey and W. P. Weijland, *Rec. trav. chim.*, **75**, 487 (1956).

(4) D. E. Paul, D. Lipkin and S. I. Weissman, THIS JOURNAL, **78**, 116 (1956).

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

(6) S. I. Weissman, E. de Boer and J. J. Conradi, *ibid.*, **26**, 963 (1957).

(7) G. J. Hoijtink and W. P. Weijland, *Rec. trav. chim.*, **76**, 836 (1957).

(8) S. I. Weissman, J. Townsend, D. E. Paul and G. E. Pake, *J. Chem. Phys.*, **21**, 2227 (1953).

(9) H. M. McConnell, *ibid.*, **24**, 764 (1956).

(10) S. I. Weissman, *ibid.*, **25**, 890 (1956).

(11) R. Bersohn, *ibid.*, **24**, 1066 (1956).

(12) B. Venkataraman and G. Fraenkel, *ibid.*, **24**, 737 (1956).

(13) H. McConnell and D. Chestnut, *ibid.*, **28**, 107 (1958).

(14) H. McConnell, *ibid.*, **28**, in press (1958).

(15) We refer here to the diagonal elements of the π-spin density matrix; see ref. 14.

(16) S. I. Weissman, T. R. Tuttle and E. de Boer, *J. Phys. Chem.*, **61**, 28 (1957).

(17) P. Balk, S. de Bruin and G. J. Hoitjtink, *Rec. trav. chim.*, **76**, 907 (1957).

(18) B. and A. Pullman, "Les theories electroniques de la chimie organique," Masson, et Cie, Paris, 1952, p. 393.

(19) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).

(20) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

(21) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (*London*), **A192**, 16 (1948).

that in this case the simple molecular orbital theory[22] predicts the same spectrum for positive and negative ions. The predicted spectrum does not resemble either of the observed spectra.

Experimental Methods

The preparations of the solutions of the negative ions are given in previous articles.[4,23] In all experiments potassium was used as reducing agent, tetrahydrofuran as solvent. No special arrangements were made for the preparation of the positive ions in concentrated sulfuric acid.

The hydrocarbons under investigation were taken from stock. To prepare *p*-deuteriobiphenyl, 3-deuteriopyrene and 3,5,8,10-tetradeuteriopyrene, the well-known metal-halogen interconversion reaction was applied. As starting materials for the metal-halogen interconversion reaction, *p*-bromobiphenyl, taken from stock, and 3-bromopyrene and 3,5,8,10-tetrabromopyrene, synthesized according to the methods given by Lock[24] and Vollman,[25] respectively, were used. The *p*-deuteriobiphenyl was prepared following a procedure described by Gilman.[26] The bromo compounds of pyrene were treated in an analogous manner. The reaction between 3,5,8,10-tetrabromopyrene and butyllithium leads after decomposition of the reaction mixture with heavy water to dideuteriodibromopyrene, m.p. 221°. Repeating the reaction with the latter compound we were able to replace the two remaining bromine atoms and isolate the 3,5,8,10-tetradeuteriopyrene.

The optical spectra of the negative ions of the deuterated compounds, measured with the aid of a Cary spectrophotometer, were identical with those of the undeuterated ones.

The electron spin resonance measurements were carried out with an apparatus designed and constructed by Professor J. Townsend. To achieve a high sensitivity, the magnetic field was modulated at a frequency of 100 kc./sec. The klystron operated at about 9000 Mc./sec. Since the amplitude of the modulating field was small as compared with the line width, the derivative of the absorption curve was recorded. In our experiments, hyperfine components in the E.S.R. spectra of the negative and positive ions of the aromatic compounds at distances of about 0.6 and 0.4 oersted from each other, could just be distinguished.

Results and Discussion

On the basis of the theoretical considerations outlined in the foregoing section, the experimental E.S.R. spectra of various hydrocarbon mononegative and monopositive ions will be interpreted.

Using as a reference a solution of peroxylamine disulfonate ion in water, whose g_e value and hyperfine splitting are well-known,[27] we determine the g_e value and the width of the spectra of the aromatic ions considered. It appeared that the g_e values of the hydrocarbon ions approach the g_e value of the free electron. Hence it may be concluded that the spin-orbit interaction in the aromatic ions is negligible, which is usually the case in polyatomic molecules having a low molecular symmetry and light nuclei.

Taking the linear relation between the spin density on a carbon atom and the hyperfine splitting of the proton attached to this carbon atom as a basis, we constructed the theoretical E.S.R. spectra. The way in which the theoretical spectra are constructed has been described in detail by Fraenkel, *et al.*[28] In comparing these spectra with the experimental curves it should be borne in mind that peaks in the spectra of the mononegative ions with a spacing of less than 0.6 oersted cannot be distinguished. For the monopositive ions the situation is slightly better; in this case the limit of the resolving power is 0.4 oersted.[29] The odd electron density, normalized so that the sum of the densities at the various atoms is unity, is placed around the structural formulas.

With each paramagnetic sample several runs were made, each time diluting the sample till the width of the lines did not decrease any further. In Table I are listed the values for the total width of the E.S.R. spectra; column (a) contains the width of the spectra measured between the points where the resonance signal could just be distinguished from the noise line, column (b) the width measured between centers of extreme peaks. The latter has only been stated for those ions which give a well-resolved hyperfine pattern. The accuracy of the data is given by twice the standard deviation from the mean.

In the naphthalene negative ion, symmetry requires that the singly occupied orbital has zero spin densities on the two central carbon atoms to which no protons are attached. If there is a single constant of proportionality for all C–H bonds in different aromatic compounds, the total widths of the spectra of the other aromatic ions could be calculated with the aid of the spin distribution, using the total width of the naphthalene negative ion as a reference. On considering Table I, it appears that such a general proportionality constant does not exist. For instance the spectrum of the negative ion of acenaphthylene should be 10.6% shorter; it was found 0.7% longer than the total width of the naphthalene negative ion (column a). Recently, the E.S.R. spectrum of benzene negative ion has been measured.[16] The total hyperfine splitting should be equal to the splitting in the naphthalene negative ion, but it amounts, however, to only 22.5 oersteds.

We should note that the variations in total length of the spectra may result not only from lack of proportionality between π-density and proton splitting, but also from the existence of negative spin densities. In the single configuration molecular orbital approximation we have used, the π-spin densities are everywhere positive, but small admixtures of other π-configurations may lead to negative spin densities.

Interpretation of the E.S.R. Spectra

The spectra will now be discussed in detail.

Biphenyl Mononegative Ion.[30]—The calculated spin densities, theoretical spectrum, and observed spectrum are given in Fig. 1. The agreement is as good as the resolution permits. As a further check, the spectrum of the negative ion of *p*-deuteriobi-

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[22] We are indebted to Professor B. Pullman for the coefficients of the orbitals in acepleiadylene.

[23] P. Balk, G. J. Hoijtink and J. W. H. Schreurs, *Rec. trav. chim.*, **76**, 813 (1957).

[24] G. Lock, *Ber.*, **70**, 926 (1937).

[25] H. Volman, H. Becker, M. Corell and H. Streeck, *Ann.*, **531**, 1 (1937).

[26] H. Gilman, W. Langham and F. W. Moore, THIS JOURNAL, **62**, 2327 (1940).

[27] G. E. Pake, J. Townsend and S. I. Weissman, *Phys. Rev.*, **85**, 683 (1952).

[28] B. Venkataraman and G. K. Fraenkel, THIS JOURNAL, **77**, 2707 (1955).

[29] The resolution was apparently limited by minimum line breadth attainable. In subsequent experiments improvements in the sensitivity of the apparatus have permitted resolution of lines separated by about 0.1 oersted.

[30] E. de Boer, *J. Chem. Phys.*, **25**, 190 (1956).

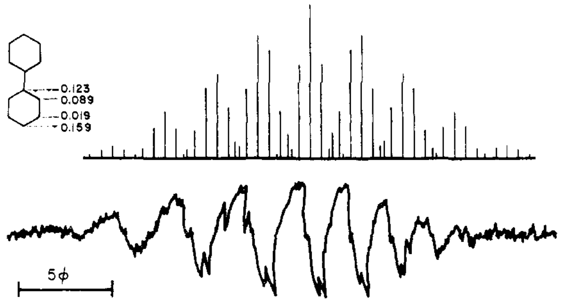

Fig. 1.—Calculated spin densities, theoretical spectrum (above) and observed spectrum (below) for biphenyl anion.

phenyl was measured. Again the agreement is good, both to the structure of the spectrum and its length. The latter, because of the smaller magnetic moment of the deuteron, is expected to be 3.5 oersteds shorter than the spectrum of the ion of normal isotopic composition. We found 3.8 ± 0.4 oersteds.

TABLE I

WIDTH OF THE E.S.R. SPECTRA

Hydrocarbon	(a) oersteds	(b) oersteds
(Biphenyl)$^-$	24.2 ± 0.2	21.0 ± 0.2
(p-Deuteriobiphenyl)$^-$	20.4 ± .1	....
(Naphthalene)$^-$	29.2 ± .3	27.2 ± .3
(Anthracene)$^-$	28.2 ± .2	26.4 ± .2
(Perylene)$^-$	30.3 ± .3	26.0 ± .2
(Tetracene)$^-$	26.5 ± .2	24.7 ± .1
(Phenanthrene)$^-$	24.9 ± .2	23.1 ± .1
(Terphenyl)$^-$	21.0 ± .2	....
(Pyrene)$^-$	32.0 ± .2	30.3 ± .2
(3-Deuteriopyrene)$^-$	28.0 ± .2	....
(3,5,8,10-Tetradeuteriopyrene)$^-$	17.0 ± .4	....
(Coronene)$^-$	22.5 ± .4	....
(Triphenylene)$^-$	16.0 ± .2	....
(Acenaphthylene)$^-$	31.0 ± .2	27.4 ± .1
(Fluoranthene)$^-$	22.9 ± .1	20.9 ± .1
(Acepleiadylene)$^-$	25.5 ± .3	22.4 ± .2
(Acepleiadiene)$^-$	33.1	28.8
(Acenaphthene)$^-$	45.2	43.0
(5-Deuterioacenaphthene)$^-$	44.8	....
(1,1,2,2-Tetradeuterioacenaphthene)$^-$	26.0	....
(Anthracene)$^+$	33.2 ± 0.3	31.5 ± 0.3
(Tetracene)$^+$	30.8 ± .2	29.0 ± .2
(Perylene)$^+$	32.7 ± .2	28.7 ± .1
(Acepleiadylene)$^+$	45.9 ± .2	43.1 ± .2
(Acepleiadiene)$^+$	64.0 ± 1.0	61.0 ± 1.0

Naphthalene Negative Ion.—This ion already has been studied in detail. Both the α- and β-monodeuterio ions have been prepared. Excellent agreement with predictions of the Hückel theory is found.[16,31]

Anthracene Negative and Positive Ions.—Owing to the fact that the spin densities in the univalent ions of anthracene are in the ratio of 4:2:1, many lines coincide and we expect the appearance of only 21 lines. The E.S.R. spectra of both the mononegative and the monopositive ion (Fig. 2) show the predicted 21 lines, while in addition, the intensity distribution is in accordance with the theory. To distinguish the very weak outermost lines clearly, a spectrum was measured of a more concentrated solution of the anthracene negative ion; the low-field portion of this spectrum is represented in Fig. 2, which leaves no doubt about the presence of the number of lines mentioned. The only difference between the spectra of the mononegative and the monopositive ion of anthracene is that the spectrum of the positive ion of anthracene in sulfuric acid is about 5.0 oersteds longer than that of the negative ion in tetrahydrofuran or 1,2-dimethoxyethane.

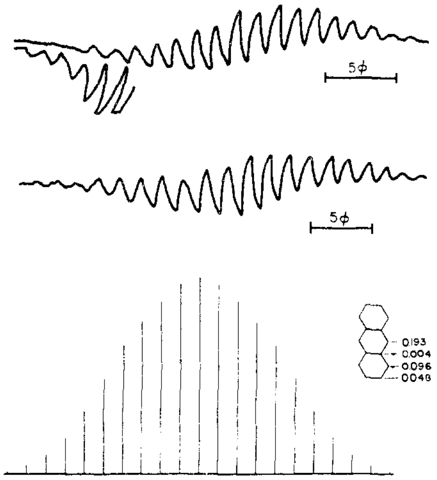

Fig. 2.—Above, spectrum of anthracene negative ion with a portion of the spectrum at higher intensity; center, spectrum of anthracene positive ion; below, theoretical spectrum.

Perylene Mononegative and Monopositive Ions.—The spectrum of the negative ion of perylene consists of nine equally spaced groups of lines (Fig. 3). Included in the figure is a close-up of the first and last two peaks, measured on a more concentrated solution. As a consequence of the increased concentration the fine structure has vanished due to concentration broadening. The spectrum of perylene positive ion, taken with improved apparatus, is shown in Fig. 4, as well as the theoretical spectrum. In addition to the lines displayed in the spectra, there are two weak groups of five lines each at the extremities. These have been observed but are not included in Fig. 4 because of their low intensities. The agreement with Hückel's theory is remarkably good. Because of the magnitude of the coupling constants, small changes in them would greatly alter the pattern. The

Fig. 3.—Calculated spin densities and observed spectrum of perylene negative ion.

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(31) T. R. Tuttle, R. L. Ward and S. I. Weissman, *J. Chem. Phys.*, **25**, 189 (1956).

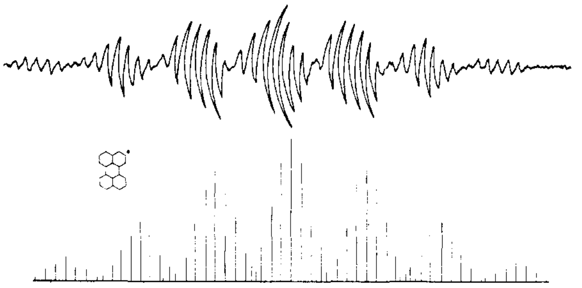

Fig. 4.—Observed spectrum of perylene positive ion and theoretical spectrum. Both observed and theoretical spectra contain two sets of five weak lines, each at the extreme; they are not shown in the figure.

agreement between observed and calculated spectrum requires that the ratios of the calculated coupling constants are correct within 5%.

It should be noticed that the resolution of the spectrum obtained in sulfuric acid is better than that in tetrahydrofuran. One of the reasons might be, apart from the greater extension in field, a different relaxation time in this medium and accordingly a change in the line width of the hyperfine components. The difference in width between the two spectra amounts to 2.7 oersteds (measured between centers of extreme peaks).

Tetracene Mononegative and Monopositive Ions.[4]—Comparing the spectrum of the mononegative ion and of the monopositive ion (Fig. 5) there seems to be no correspondence at all. The reason for this difference in hyperfine pattern is the increased resolution in sulfuric acid. The spectrum of the positive ion contains at least 33 lines, whereas in the spectrum of the negative ion only 19 lines occur. Again the spectrum of the positive ion is longer, in this case 4.3 oersteds. The observed divergence can be understood by comparing the two experimental curves with the theoretical spectrum based on the entire spin distribution in the univalent ion. According to the calculated spectrum a rather complicated hyperfine pattern is to be expected. The interval between the various lines, however, is too small for complete resolution to be effected with our apparatus. Only a partial resolution is obtained, resulting in more lines for the positive than for the negative ion for the abovementioned reasons. Taking this into consideration the different shapes of the two spectra can be accounted for. In both cases the number of lines is in good agreement with what could be expected.

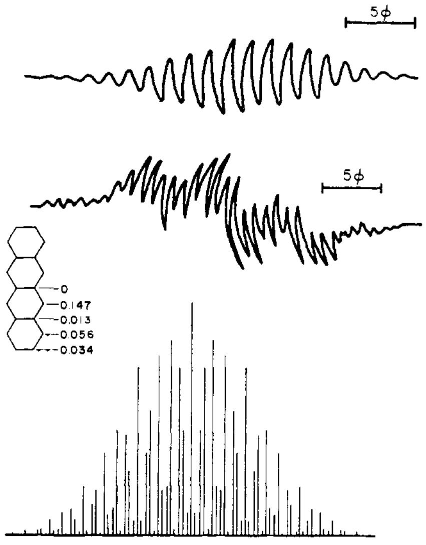

Fig. 5.—Above, observed spectrum of tetracene negative ion; center, positive ion; and below, theoretical spectrum.

A very close similarity exists between the optical absorption spectra of the monopositive and mononegative ions measured by Hoijtink and Weijland.[32] They are almost indistinguishable in shape. On theoretical considerations it may be expected that the monopositive and mononegative ions would yield similar electronic and E.S.R. spectra. The resolution being insufficient, it is impossible to observe complete correspondence in the latter case.

Phenanthrene Mononegative Ion.—An abundance of lines is to be expected. The distance between the lines is too small for complete resolution of the spectrum to be obtained. Only the most outstanding peaks could be recorded separately. The experimental spectrum shows seven peaks, all of them displaying a complex structure, which indicates the existence of more lines. Qualitatively, this behavior is in agreement with the theory. The spectra are presented in Fig. 6.

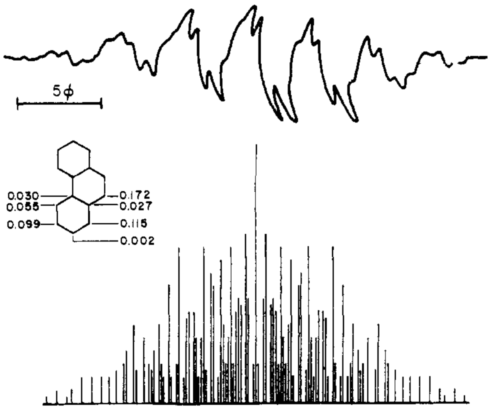

Fig. 6.—Observed spectrum, calculated spin densities, and theoretical spectrum for phenanthrene negative ion.

Terphenyl Negative Ion.—According to the spin distribution, 239 lines should occur, which leads to an average interval between the lines of about 0.1 oersted. This is beyond the resolving power of the resonance spectrometer. Consequently, the mononegative ion of terphenyl yields a spectrum of a single broad line. It is presented in Fig. 7.

Pyrene Mononegative Ion.—The spectrum of the pyrene negative ion (Fig. 8) consists of five groups of nine lines each; the total splitting is 32 oersteds.

A serious discrepancy exists between the spectrum expected according to the squares of the Hückel coefficients on the carbon atoms and the experimental one. In the Hückel approximation the odd electron occupies a π-orbital which is entirely antisymmetric with respect to the x- and y-axes of the molecule. Consequently, the maximum number of lines the E.S.R. spectrum should contain is 25. An attempt to explain the large

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(32) G. J. Hoijtink and W. P. Weijland, to be published.

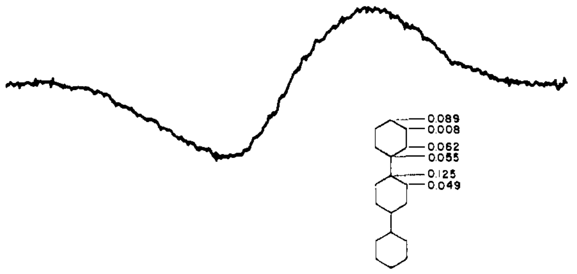

Fig. 7.—Observed spectrum and calculated spin densities for terphenyl negative ion.

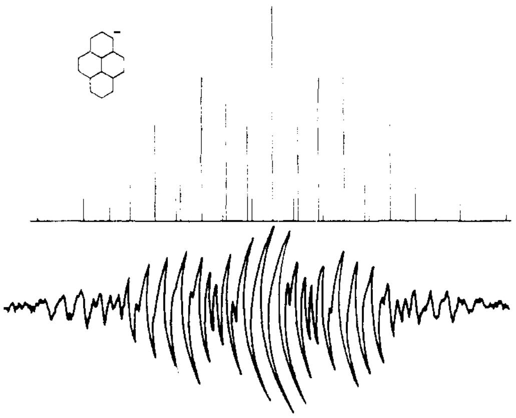

Fig. 8.—Theoretical spectrum and observed spectrum of pyrene negative ion.

number of lines found by assuming a complex of the structure (pyrene)$^-$K$^+$(pyrene)$^-$ or (pyrene)$^-$K$^+$(pyrene) failed; the hyperfine pattern constructed according to this model is quite different from the spectrum observed. Further, use of lithium rather than potassium yields the same spectrum, but with somewhat improved resolution. If the singly occupied orbital is not anti-symmetric with respect to the y-axis, interaction between the electron magnetic moment and the two magnetic moments of the protons lying along the long axis of the molecule may occur and thus the appearance of more than 25 lines is possible.

The five groups of lines in the spectrum suggest that there are four positions of very high spin density in the anion. To obtain more information about this, experiments were carried out with the mononegative ions of 3,5,8,10-tetradeuteriopyrene and 3-monodeuteriopyrene. The splendid spectrum of the pyrene negative ion changes drastically upon deuteration; in the case of the anion of tetradeuteriopyrene it collapses to a single line and the total width is considerably reduced. From this result it follows unambiguously that the deuterated positions are the four positions possessing a high spin density. The coupling constant associated with the 3-, 5-, 8- and 10-positions, derived from the experimental curve, amounts to 5.8 oersteds. Assuming this value, the spectra of the monodeuteriopyrene and tetradeuteriopyrene mononegative ions must be 4.0 and 16.0 oersteds shorter, respectively. Experimentally, we found 4.0 ± 0.4 and 15.0 ± 0.6, respectively.

Apart from assigning coupling constants to the deuterated positions, we are unable to analyze the spectrum further. The question remains whether or not the two protons along the long axis of the molecule give rise to hyperfine interaction. Although it seems unlikely, the excessive number of lines may be caused by interaction between the ion and the protons of the solvent. Pyrene negative ions dissolved in tetrahydrofuran or in 1,2-dimethoxyethane, however, yield E.S.R. spectra that are indistinguishable as far as their shape is concerned.

Coronene Mononegative Ion.—The singly occupied orbital in coronene negative ion is presumably degenerate. Accordingly, a Jahn–Teller distortion of the molecule is expected.

If the transitions between various distorted configurations are rapid compared with the hyperfine frequencies, a sharply averaged spectrum of thirteen lines is expected. The observed spectrum (Fig. 9) is poorly resolved and suggests strongly that a Jahn–Teller distortion does in fact contribute. (The comparable situation in benzene negative ion does, however, lead to sharp averaging; these matters are deferred for a later publication).

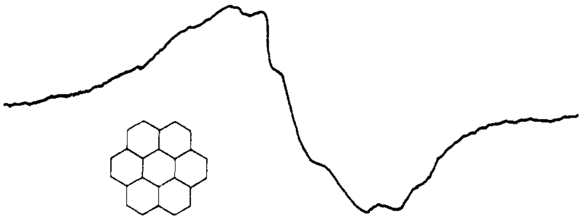

Fig. 9.—Observed spectrum of coronene negative ion.

Triphenylene Mononegative Ion.—The situation in triphenylene, as in coronene, is complicated by a possible Jahn–Teller effect. The spectrum of triphenylene negative ion is given in Fig. 10.

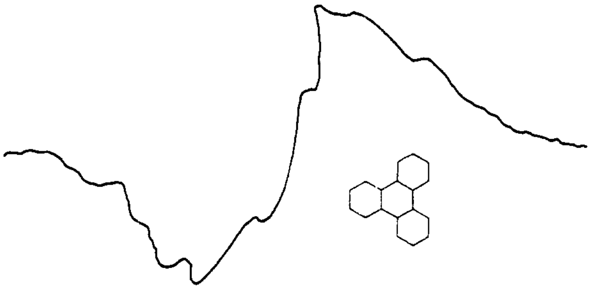

Fig. 10.—Observed spectrum of triphenylene negative ion.

Acenaphthylene Mononegative Ion.—The experimental spectrum (Fig. 11) shows eleven peaks. Without doubt each is composed of several other ones; the line width and the shape of the peaks point to the presence of more lines. However, the resolving power of the present apparatus is insufficient to prove their existence. Considering the resolution limit of 0.6 oersted, the predicted number of lines and the intensity distribution are in good agreement with the hyperfine pattern observed.

Fluoranthene Mononegative Ion.—The spectrum of the mononegative ion of fluoranthene consists of 17 equally spaced lines with a very characteristic intensity distribution (Fig. 12). The behavior of the spectrum suggests that the lines are not single in nature but have a more complex structure.

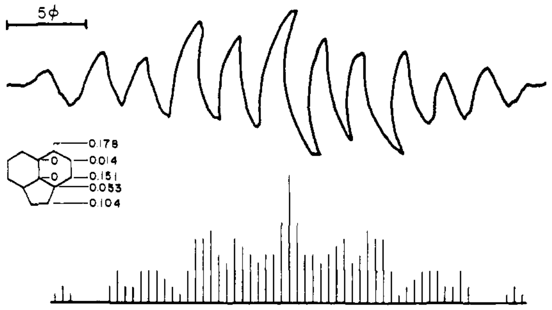

Fig. 11.—Observed spectrum, calculated spin densities, and theoretical spectrum of acenaphthylene negative ion.

If the low values of 0.022 and 0.015 are neglected, the spectrum calculated on the basis of this assumption is in very good agreement with the spectrum observed. No correspondence exists when we take into account the entire distribution of the odd electron as indicated in the structure formula. From the fairly good similarity of the theoretical and the experimental spectrum, it may be inferred that the spin densities of 0.022 and 0.015 are still too high and should be about 0.010. Assuming this value, we are able to describe the spectrum in all details.

Acepleiadylene Negative and Positive Ions.—These species yield well resolved spectra. They do not resemble each other and neither resembles the spectrum calculated for it by simple molecular orbital theory.

Substances Containing Methylenic Hydrogens.—The spectrum of the negative ion of acenaphthene exhibits a primary splitting into five groups of at least seven lines each. The primary splitting is 7.0 oersteds between centers of groups. The spectrum of acenaphthene completely deuterated in the methylene position reveals that the large primary splitting is produced by the hydrogens in these positions. Similarly, the wide spectra of the positive and negative ions of acepleiadiene suggest high spin densities at the positions of the methylene hydrogens.

Conclusions

An interesting conclusion which may be drawn from the hyperfine structure observed in aromatic hydrocarbon ions is that a small spin polarization exists in the covalent C–H bond, brought about by interaction between σ- and π-electrons.

It has been shown in the foregoing section that in many cases a linear relationship exists between the spin density on a carbon atom, calculated with the aid of Hückel's m.o. treatment, and the hyperfine splitting caused by the proton bonded to this particular atom. The E.S.R. spectra of the negative ions of biphenyl and naphthalene and those of the positive and negative ions of anthracene and perylene are in excellent agreement with the theoretical spectra. The resonance absorption curves of the negative ions of phenanthrene and terphenyl and the positive and negative ions of tetracene did not display any clear deviation from the predictions. As regards the alternant hydrocarbon ions, only one serious discrepancy was found, *viz.*, the spectrum of the pyrene negative ion, which could not be explained on the basis of the spin distribution calculated. Although the one-electron treatment is not as reliable for non-alternant as for alternant hydrocarbons, the agreement between theoretical and experimental spectra was quite satisfactory in the case of the negative ions of fluoranthene and acenaphthylene, unlike the spectra of the acepleiadylene positive and negative ions which are different from the predicted ones based on the Hückel coefficients.

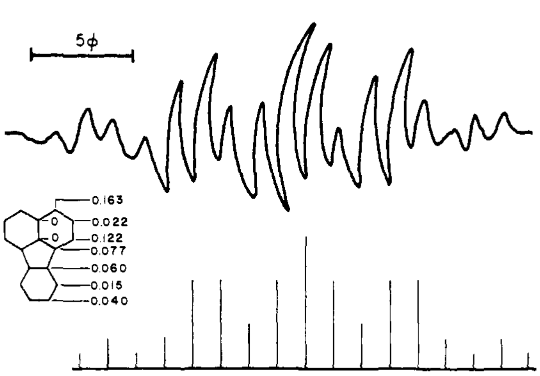

Fig. 12.—Observed spectrum, calculated spin densities and theoretical spectrum for fluoranthene negative ion.

More evidence for a linear relation between hyperfine splitting and spin density is provided by Brovetto and Ferroni,[33] who, applying the valence bond method, computed the odd electron distribution in triphenylmethyl and were able to interpret the entire proton hyperfine splitting of this compound with the aid of the calculated spin densities on the carbon atoms. Bersohn[11] carried out quantitative calculations on the semiquinone ions, using the valence bond method. They, too, produced coupling constants for the ring protons of the semiquinone radicals, which are of the correct order of magnitude.

The large splittings by methylene hydrogens, however, are not accounted for by the simple approximations and undoubtedly require introduction of refinements such as hyperconjugation.

It may be concluded from the results of these investigations that calculations on the spin distribution in paramagnetic aromatic compounds are very useful in analyzing the E.S.R. spectra and, conversely, the study of the hyperfine structures provides a powerful means to obtain information on the electron distribution in paramagnetic substances.

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[33] P. Brovetto and S. Ferroni, *Il Nuovo Cimento*, **5**, 142 (1957).