

Protonation of Aromatic Hydrocarbon Dinegative Ions. A Spectroscopic Study¹

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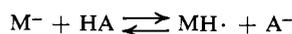
The electronic absorption spectra of the primary proton adducts (the carbanions MH^-) of the dinegative ions of naphthalene, anthracene, tetracene, and pyrene have been measured and compared with the spectra of the corresponding carbonium ions MH^+ . The electrical conductances of solutions of the carbanions show that these ions tend to associate with alkali ions. The influence of the ion-pair formation on the electronic spectra of the carbanions shows that the distortion of the negative ion by the alkali ion increases as the radius of the cation decreases.

Introduction

When a proton donor is added to a solution of an aromatic hydrocarbon dinegative ion one may expect the formation of the carbanion MH^- as the primary reaction product.



Similarly these carbanions may be obtained by protonation of the mononegative ion.

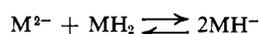


The second reaction is due to the fact that the radical MH^\cdot has a much higher electron affinity than the corresponding hydrocarbon molecule M .²

The present paper deals with the carbanions MH^- derived from a number of aromatic hydrocarbons; in particular with their tendency toward association with the alkali ion and with their absorption spectra.

Experimental Section

We have investigated a number of aromatic hydrocarbons, using as a proton donor either stearyl alcohol or the dihydro compound of the hydrocarbon under investigation. In the latter case the reaction proceeds according to



Not all hydrocarbon dinegative ions appear to give the carbanion MH^- . In some cases the carbanion MH^- proves to be unstable and disproportionates. An explanation of this behavior will be given in a separate paper.

In the present paper we report the spectra of the carbanions MH^- derived from naphthalene, anthracene,

tetracene, and pyrene. The latter one proved to be unstable, but the rate of disproportionation was slow enough to enable us to measure the absorption spectrum.

In order to know whether the carbanion was "free" or associated with the alkali ion we determined the electrical conductances of the solutions from which the spectra were measured. The concentrations of these solutions were 10^{-4} M. For details concerning the spectral and the conductivity measurements we refer to a previous paper.³

Results and Discussion

In a recent paper³ the association of aromatic hydrocarbon negative ions with alkali ions has been discussed in detail. A summary of the conclusions we arrived at may be given by considering Figure 1, where the molar conductances of some alkali salts of pentacene in 2-methyltetrahydrofuran have been plotted against the temperature. In this figure the curve for the lithium salt (M^-Li^+) shows the normal decrease of conductance with temperature, which is due to the temperature dependence of the viscosity of the solvent. Looking at the curve for the sodium salt (M^-Na^+) we see that the conductivity first increases and at lower temperature reaches the same temperature dependence as the lithium salt.

Our conclusion was that under the conditions of the experiment (10^{-4} M solutions) the lithium salt is completely dissociated at room temperature, whereas the sodium salt at the same temperature is still partly associated. At lower temperature the sodium salt dissociates. The same behavior is found for the potassium salt (M^-K^+).

The fact that the maximum in the curve of the latter salt is located towards lower temperature than the maximum of the sodium salt points to a stronger tendency to association for K^+ than for Na^+ .

This brings us to the first conclusion drawn in our previous paper, *viz.*, that the tendency towards association increases with increasing radius of the cation.

This is analogous to what Kunze and Fuoss⁴ have found for the alkali halides in dioxane-water mixtures. Obviously the solvation of the cation plays a dominant role in the dissociation of the ion pairs.

Looking at the right-hand part of Figure 1 we see that the molar conductances increase in the order Li^+ , Na^+ , K^+ . This is similar to what is found for the same ions in water and which is generally ascribed to the fact that the smaller ions carry thicker solvent spheres with them.

(3) K. H. J. Buschow, J. Dieleman, and G. J. Hoijtink, *J. Chem. Phys.*, **42**, 1993 (1965).

(4) R. W. Kunze and R. M. Fuoss, *J. Phys. Chem.*, **67**, 914 (1963).

(1) These investigations have been carried out under the auspices of the Netherlands Foundation for Chemical Research (S.O.N.) and with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

(2) G. J. Hoijtink, J. van Schooten, E. de Boer, and W. Y. Aalbersberg, *Rec. trav. chim.*, **73**, 355 (1954).

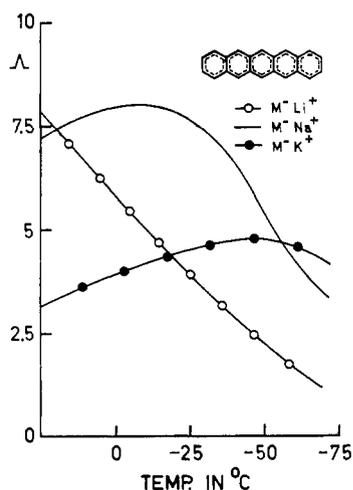


Figure 1. Temperature dependence of molar conductance in $\text{ohm}^{-1} \text{cm.}^2 \text{mole}^{-1}$ of alkali salts of the pentacene mononegative ion in MTHF.

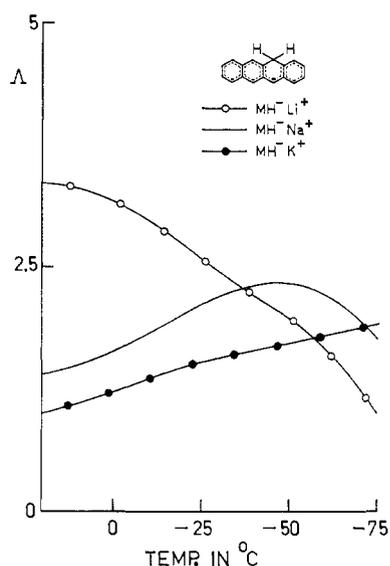


Figure 2. Temperature dependence of molar conductance in $\text{ohm}^{-1} \text{cm.}^2 \text{mole}^{-1}$ of alkali salts of the tetracene carbanion in MTHF.

Another important conclusion from our previous paper is that the tendency towards association increases with decreasing size of the hydrocarbon negative ion. The smaller the ion the less the negative charge is smeared out and so the stronger the electrostatic interaction with the cation.

Turning now to Figure 2 we see a similar behavior for the carbanions MH^- derived from tetracene. The curve for the lithium salt ($\text{MH}^- \text{Li}^+$) (the small dip at -25° very likely has no real significance as the accuracy of the conductance measurements is not very high) shows a much lower conductance at room temperature than the lithium salts of anthracene, tetracene, and pentacene ($\text{M}^- \text{Li}^+$) in the same solvent, which all turned out to be completely dissociated at room temperature.³ This means that the lithium salt $\text{MH}^- \text{Li}^+$ is still partially associated at room temperature. We further see that as in other cases³ the tendency towards association increases in the sequence Li^+ , Na^+ , K^+ .

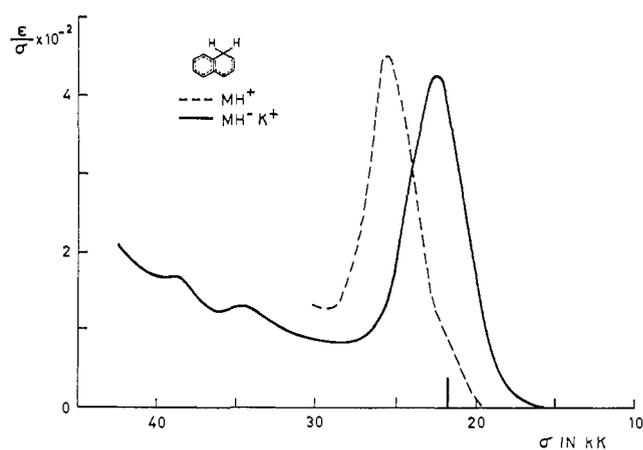


Figure 3. Electronic absorption spectra of the naphthalene carbonium ion and carbanion. The spectrum of the carbonium ion is taken from ref. 5a. As we are not quite sure about the absorption of the carbonium ion at wave numbers higher than 30.0 kK, we have only drawn the spectrum from 10.0 to 30.0 kK. We could not measure the absorption spectrum of the free carbanion (see the text); therefore we have drawn the spectrum of the potassium associate; the maximum of the first absorption band of the free carbanion have been marked at 21.8 kK.

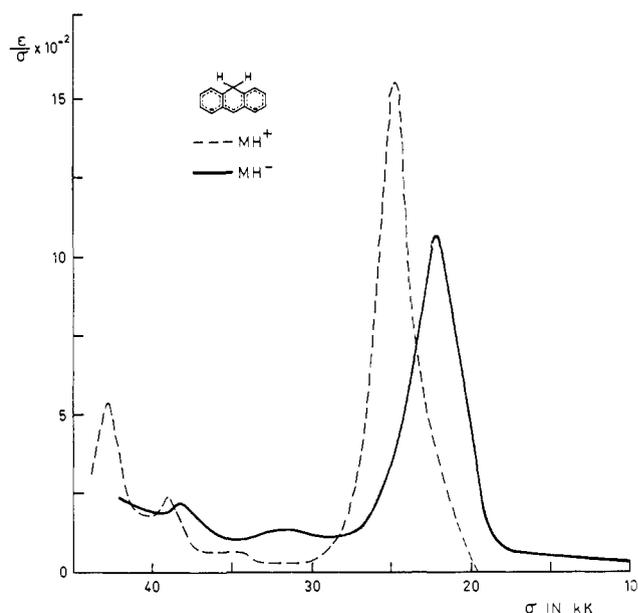


Figure 4. Electronic absorption spectra of the anthracene carbonium ion and carbanion. The spectrum of the carbonium ion is taken from ref. 5a.

A possible explanation for the fact that the ions MH^- show a stronger tendency toward association than the ions M^- is that in the former the negative charge is more concentrated in a smaller part of the ion, thus giving rise to a stronger interaction with the alkali ion.

Guided by these results we were able to choose experimental conditions such that either the free ion or its associate was present.

All the spectra were measured at room temperature. The free ions were measured from solutions in 1,2-dimethoxyethane. In this solvent all the ions appeared to be free at room temperature except the carbanion derived from naphthalene. For the latter we could only obtain the location of the first strong absorption

Table I^a

MH ⁻ Li ⁺		MH ⁻ Na ⁺		MH ⁻ K ⁺		MH ⁻	
σ	D	σ	D	σ	D	σ	D
Naphthalene							
24.3	0.72	23.0	0.79	22.6	0.80	21.8	...
35.0		34.9		34.6			
39.0		39.1		38.9			
Anthracene							
25.1	1.50	23.3	1.69	22.3	1.74	22.0	1.85
34.0-35.0		32.8-35.0		32.1-33.5		30.5-32.5	
39.2		38.9		38.7		38.4	
Tetracene							
18.0		17.3		17.0		16.4	
23.8	1.46	22.3	1.65	21.3	1.76	20.6	1.93
33.0		32.4		32.0		31.8	
39.9		39.7		39.6		39.5	

^a σ in kK., D in 10^{-18} cm.². All these data were obtained from spectral measurements at room temperature (see the text). The free ions were measured from solutions in 1,2-dimethoxyethane, the associates from solutions in 2-methyltetrahydrofuran.

band of the free ion. The spectra of the associates were obtained from solutions in 2-methyltetrahydrofuran at room temperature. In some cases small corrections had to be made for the presence of free ions. The results of the spectral measurements are given in Table I and in the Figures 3-6.

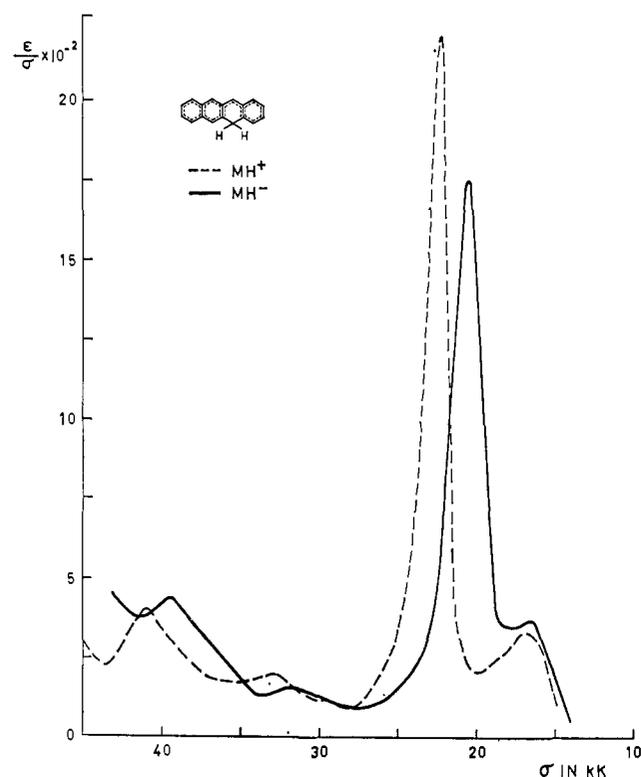


Figure 5. Electronic absorption spectra of the tetracene carbonium ion and carbanion. The spectrum of the carbonium is taken from ref. 5b.

From Table I it appears that the association with the alkali ions leads to a blue shift of the absorption bands. This shift increases in the order K^+ , Na^+ , Li^+ . The most plausible explanation for this phenomenon is that in the ground state of the ion MH^- the alkali ion will have a high density probability near the carbon atom(s) with a high negative charge. According to

the Franck-Condon principle the strongly allowed electronic transition will take place without change of the nuclear arrangement, so that in the excited state the alkali ion will occupy an energetically less favorable position. This implies that the ground state will be more stabilized by the interaction with the cation than the excited state, thus leading to a blue shift of the absorption band.

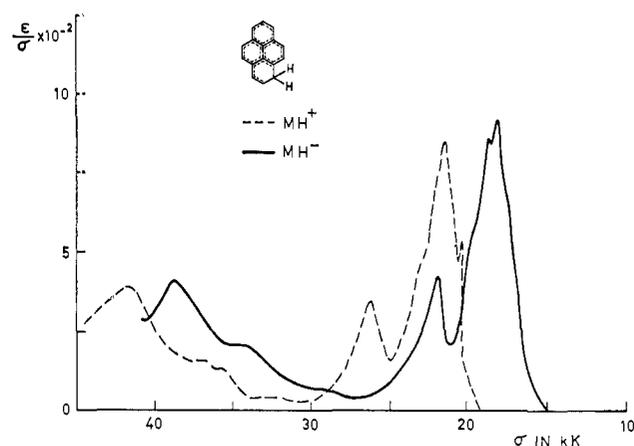


Figure 6. Electronic absorption spectra of the pyrene carbonium ion and carbanion. The spectrum of the carbonium ion is taken from ref. 5a.

Streitwieser and Brauman,⁵ who studied carbanions of comparable size, recently came to an opposite conclusion. According to them the perturbation of the carbanion by the alkali ion increases in the order Li^+ - Cs^+ . In their experiments they used cyclohexylamine or 1,2-dimethoxyethane and diethyl ether as a solvent. The authors, however, did not measure the electrical conductances of the solutions from which the spectra were measured. It seems probable to us that their lithium salts in dimethoxyethane and cyclohexylamine, which are both good solvents for cations,

(5) A. Streitwieser, Jr., and J. I. Brauman, *J. Am. Chem. Soc.*, **85**, 2633 (1963).

were dissociated or very weakly associated,^{5a} whereas the lithium salts in diethyl ether were associated. On this supposition, their results become consistent with ours and with those obtained by Carter, McClelland, and Warhurst⁶ for some metal ketyls and with those found by Jones and Weissman⁷ for the alkali salts of tri-*p*-nitrophenylmethyl.

In Figures 3, 4, 5, and 6 the spectra of the carbanions derived from naphthalene, anthracene, tetracene, and pyrene are compared with the spectra of the carbonium ions MH⁺. The latter spectra have been studied in detail by Mackor, *et al.*⁸

From the theoretical study by Brickstock and Pople⁹ we may expect the spectra of the positive and negative ions of odd alternant hydrocarbons to be very similar. The same conclusion was drawn some years ago with regard to the positive and negative ions of even alternant hydrocarbons.¹⁰

From the figures it appears that the spectra of the carbanions and the carbonium ions are very much alike. The absorption bands of the negative ions are somewhat broader, but the over-all intensities are practically the same, which leaves no doubt that the structure of the ions MH⁻ and MH⁺ are equal.

MacLean, van der Waals, and Mackor¹¹ have shown by n.m.r. measurements that the CH₂ group in the carbonium ions has a real aliphatic character. Hence we may safely say that proton addition to a hydrocarbon dinegative ion also leads to the formation of a normal carbon-hydrogen bond.

The structure of the carbonium ions considered in this paper have been well established by Mackor, *et al.*,¹² both from a study of atom localization energies

(5a) NOTE ADDED IN PROOF. Recent investigations by Hagen-Esch and Smid [T. E. Hagen-Esch and J. Smid, *J. Am. Chem. Soc.*, **87**, 669 (1955)] have shown that in addition to free ions and ion pairs, weakly bound ion pairs may occur. The electronic spectra of the latter associates are practically indistinguishable from those of the free ions. The only clear distinction is the electrical conductance.

(6) H. V. Carter, B. J. McClelland, and E. Warhurst, *Trans. Faraday Soc.*, **56**, 455 (1960).

(7) M. T. Jones and S. I. Weissman, *J. Am. Chem. Soc.*, **84**, 4269 (1962).

(8) (a) G. Dallinga, E. L. Mackor, and A. A. V. Stuart, *Mol. Phys.*, **1**, 123 (1958); (b) A. A. V. Stuart and E. L. Mackor, *J. Chem. Phys.*, **27**, 826 (1957).

(9) A. Brickstock and J. A. Pople, *Trans. Faraday Soc.*, **50**, 901 (1954).

(10) (a) W. P. Weijland, Thesis, Free University, Amsterdam, 1958; (b) G. J. Hoijtink, Colloque International sur le Calcul des Fonctions d'Onde Moléculaires, C.N.R.S., Paris, 1958; (c) A. D. MacLachlan, *Mol. Phys.*, **2**, 271 (1959).

(11) C. MacLean, J. H. van der Waals, and E. L. Mackor, *ibid.*, **1**, 247 (1958).

(12) (a) G. Dallinga, A. A. V. Stuart, P. J. Smit, and E. L. Mackor, *Z. Elektrochem.*, **61**, 1019 (1957); (b) E. L. Mackor, A. Hofstra, and J. H. van der Waals, *Trans. Faraday Soc.*, **54**, 66, 186 (1958).

and from experimental structure determinations. This leads us to the structures of the carbanions as given in the Figures 3-6.

Following the same reasoning as the above-mentioned authors, we may say that proton addition will be most likely to occur at that carbon atom of the dinegative ion which has the lowest localization energy, *i.e.*, the energy required to localize two π electrons on it. Within the scope of the Hückel theory, the localization energy at a carbon atom of a hydrocarbon dinegative ion differs only by a constant from the localization energy at the same atom in the corresponding molecule. This would mean that the proton is added to the same carbon atom in the molecule and in its dianion. So far the experimental results confirm the theoretical expectations.

In the foregoing discussion the influence of the methylene group on the energy of the π electronic part of the ions has not been taken into account. One of the effects of the CH₂ group will be that the symmetry between positive and negative ions of odd alternant hydrocarbons as discussed by Brickstock and Pople⁹ will not hold as strictly as this theoretical approach predicts. The CH₂ group causes a distortion, which leads to a divergence from this symmetry. This may explain the fairly large difference in location for corresponding absorption bands of carbanions and carbonium ions. Another contribution to this shift may be produced by solvent effects. The carbonium ions have been measured in solvents with much higher dielectric constant than the solvents used for the carbanions. Hence we may expect a blue solvent shift for the carbonium ions which is indeed observed.

The perturbation of the π -electronic system by the CH₂ group will also influence the localization energies. This may be important in those cases where two or more chemically distinct carbon atoms in the aromatic hydrocarbon (and accordingly in its dinegative ion) have about the same localization energies. For the molecules considered in this paper this is not the case.

A qualitative interpretation of the spectra analogous to that for the negative and positive ions of the polyacene and polyphenyl molecules¹³ cannot be given because of the very low symmetry. As a result of this, the number of excited states that must be considered is so large that a rigorous quantum mechanical calculation must be made.

(13) (a) G. J. Hoijtink, N. H. Velthorst, and P. J. Zandstra, *Mol. Phys.*, **3**, 533 (1960); (b) K. H. J. Buschow, J. Dieleman, and G. J. Hoijtink, *ibid.*, **6**, 1 (1964).