A Spectroscopic Study of Carbanions and Corresponding Nitranions: Ion Pair Formation in the Ground State and the First Excited State

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The carbanions of fluorene, 4,5-methylenephenanthrene, and indene and the nitranions of carbazole, 4,5-iminophenanthrene, and indole have been investigated by optical absorption and emission spectroscopy. From the influence of alkali counterions on the absorption and emission it appears that in the first excited singlet state the contact ion pairs of the carbanions are converted into solvent-separated ion pairs. The nitranions exhibit stronger interactions with the alkali ions than the corresponding carbanions both in the ground and in the first excited state. The experimental results can be explained by considering the charge distributions in the ground state of the ions and the redistribution of the π electrons after excitation.

THE metallation of fluorene and related compounds, by which the corresponding carbanions are formed, has been described.[1] From optical absorption experiments and conductivity measurements[2] it is known that the cation–carbanion complex of fluorenyl salts can exist as a *contact ion pair* and as a *solvent-separated ion pair.*

Contact ion (c.i.) pairs, in which the distance between the cation and the carbanion is relatively small, are peripherically solvated; they are also referred to as externally solvated c.i. pairs. Formation of these species is favoured if the temperature is high, the radius of the cation is large, and the solvent is not polar. The position of the absorption bands of this type of

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[1] (*a*) M. Gilman and R. D. Gorsisch, *J. Org. Chem.*, 1958, **23**, 550; (*b*) J. J. Eisch and W. C. Kaska, *ibid.*, 1962, **27**, 3745; (*c*) E. G. Janzen and J. L. Gerlock, *J. Organometallic Chem.*, 1967, **8**, 354; (*d*) R. H. Cox, E. G. Janzen, and J. L. Gerlock, *J. Amer. Chem. Soc.*, 1969, **90**, 5906; (*e*) J. v.d. Kooij, N. H. Velthorst, and C. MacLean, *Chem. Phys. Letters*, 1969, **3**, 12.

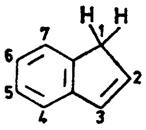
[2] (*a*) T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, 1965, **87**, 669; 1966, **88**, (*b*) 307; (*c*) 318; (*d*) L. L. Chan and J. Smid, *ibid.*, 1968, **90**, 4654; (*e*) T. Ellingsen and J. Smid, *J. Chem. Phys.*, 1969, **73**, 2712.

ion pair is particularly sensitive to the nature of the cation.

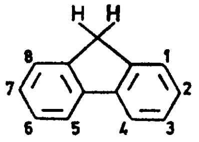
Favourable conditions for the formation of the solvent-separated (s.s.) ion pairs, in which the solvated cations and carbanions are separated by solvent molecules, are opposite to those just mentioned. The position of the absorption bands of this type of ion pair does not depend significantly on the cation and the solvent.

The effect of alkali metal ions on the absorption of carbanions has been the subject of several studies.[2,3] Analogous experiments with emission spectroscopy have not been undertaken; they may give valuable data related to ion pair formation in the excited state. Nitranions (nitrogen analogues of carbanions) have hardly been investigated, either by absorption or by emission spectroscopy.

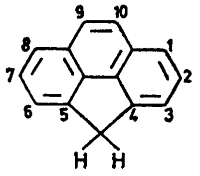
We report here the results of a spectroscopic study of the carbanions of fluorene (FlH^-), 4,5-methylenephenanthrene (MH^-), and indene (InH^-) and of the corresponding nitranions of carbazole (CbN^-), 4,5-iminophenanthrene (ImN^-), and indole (InN^-). We have recorded the absorption and fluorescence spectra of these ions for a temperature range of at least 100°, in several solvents, lithium or potassium ions being the counterions. Remarkable differences in behaviour between the carbanions and nitranions have been found and these are discussed qualitatively in terms of the charge distributions of the ions both in the ground and in the first excited state.



InH_2



FlH_2



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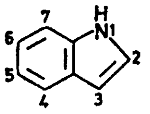
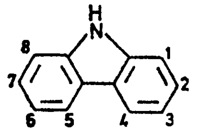
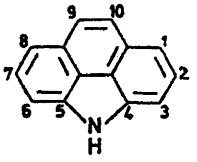


InNH



CbNH



ImNH

EXPERIMENTAL

The carbanions and nitranions were prepared *in vacuo* [reactions (1) and (2)] by treatment of the substrate (ArH_2 or ArNH) with potassium or lithium in 2-methyltetrahydrofuran (MTHF) or 1,2-dimethoxyethane (DME); sodium was used in a few experiments. Solutions of

$$ArH_2 + X \rightleftharpoons ArH^- + X^+ + H \qquad (1)$$

$$ArNH + X \rightleftharpoons ArN^- + X^+ + H \qquad (2)$$

carbanions and nitranions in hexamethylphosphorotriamide (HMP) were obtained from the corresponding MTHF solution by removing MTHF under vacuum and pouring HMP onto the dry salt.

The substrates were taken from stock or obtained from various sources in the purest grade commercially available. They were purified by crystallization, distillation, chromatography, and/or zone refining. The solvents MTHF and DME were of spectroscopic grade. They were refluxed with sodium for several days, then distilled from sodium in nitrogen, and stored in a bulb with sodium and anthracene. HMP was dried with calcium hydride.

Optical absorption spectra of the solutions (*ca.* 5×10^{-4} mol l^{-1}) were recorded with a Cary model 14 spectrophotometer in the region 15—33 kK using an optical cell with a path length of 1 mm. A quartz Dewar flask with optical windows was used for investigations at low temperatures, regulated with a Cryoson TRL-3 ALPHA liquid nitrogen cooling system. Fluorescence experiments were performed on a home-made scanning emission spectrophotometer, described elsewhere.[4]

RESULTS

In general the results (Figures 1 and 2, Table; Ar^-,X^+ denotes a c.i. pair, $Ar^-||X^+$ an s.s. ion pair) can be described by an equilibrium existing between c.i. pairs and s.s. ion pairs, as has been discussed[2] for FlH^- and for MH^-.[3b] The position of the equilibrium varies with the nature of the carbanion and the alkali ion and with the solvating power and the temperature of the medium. In MTHF the fraction of s.s. ion pairs is small in comparison with that in DME, whereas in polar solvents like HMP mainly s.s. ion pairs will be present.

Absorption Spectroscopy.—The general features of the absorption spectra of FlH^- (Figure 1a), MH^- (Figure 1b), and InH^- (Figure 1c) are in agreement with those published.[2a,d,3a,b,5]

In HMP no influence of alkali ions and temperature on the absorptions (a temperature lowering over only *ca.* 20° is possible as the solvent becomes crystalline <0°) was observed.

In MTHF the potassium ion pairs absorb at smaller wavenumber than the corresponding lithium ion pairs. On cooling of the solutions of the potassium salts to −160°, where the solvent has solidified, the positions of the absorption bands are not affected. The absorptions of the carbanions prepared with lithium display a bathochromic shift at decreasing temperature. For FlH^- and MH^- a maximum change of 2·0 and 2·3 kK respectively is reached at *ca.* −60°; for InH^- the maximum shift amounts to 2·8 kK at *ca.* −160°. At these low temperatures the spectra agree with those found in HMP.

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[3] (*a*) A. Streitwieser, jun., and J. I. Brauman, *J. Amer. Chem. Soc.*, 1963, **85**, 2633; (*b*) D. Casson and B. J. Tabner, *J. Chem. Soc.* (*B*), 1969, 572; (*c*) N. H. Velthorst and G. J. Hoijtink, *J. Amer. Chem. Soc.*, 1965, **87**, 4529.

[4] D. Rehm, *Z. Naturforsch.*, 1970, **25a**, 1444.

[5] A. Streitwieser, jun., J. H. Hammons, E. Ciuffarin, and J. I. Brauman, *J. Amer. Chem. Soc.*, 1967, **89**, 59.

The first electronic absorption band (kK) and the fluorescence band (kK) of the carbanions FlH⁻, MH⁻, and InH⁻ and of the nitranions CbN⁻, ImN⁻, and InN⁻

Carbanion/ nitranion of	Absorption c.i. Li⁺	Absorption c.i. K⁺	Absorption s.s.	Fluorescence c.i. Li⁺	Fluorescence c.i. K⁺	Fluorescence s.s.
Fluorene *	21·1 [a]	20·2 [b]	19·2 [c] 20·7 22·1			17·3 [d] 18·5
	28·9	27·8	26·9			
4,5-Methylenephenanthrene	21·7 [a]	20·3 [b]	19·4 [c]			17·3 [d]
Indene	29·5 [e]	27·4 [f]	26·7 [g]			20·3 [h]
Carbazole	25·4 [i] 26·8	24·6 [i] 26·1	23·7 [j] 25·1	22·8s [i] 24·1 25·4	21·7s [i] 22·9 24·1	20·7s [j] 22·0 23·5
4,5-Iminophenanthrene	24·5 [i] 25·4 26·3s	23·6 [i] 24·5 25·3s	22·6s [j] 23·5 25·7	22·2 [i] 23·3	21·3 [i] 22·4	20·4 [j] 21·3
Indole	33·9 [d]	33·9 [d]	33·9 [d]	27·5 [k]	25·1 [k]	

* It is impossible to establish the exact position of the broad first absorption band; the next band has also been given. s = Shoulder.

[a] MTHF, +20°. [b] MTHF, +20°, −160°; DME, +20°. [c] HMP–K⁺, +20°; HMP–Li⁺, +20°; MTHF–Li⁺, −80°; DME–K⁺, −80°; DME–Li⁺, +20°, −80°. [d] Insensitive to solvent, cation, and temperature. [e] MTHF, +20°; DME, +20°. [f] MTHF, +20°, −160°; DME, +20°, −80°. [g] HMP–K⁺, +20°; HMP–Li⁺, +20°; MTHF–Li⁺, −160°; DME–Li⁺, −80°. [h] Insensitive to solvent and cation; dependent on temperature; +20°: σ = 20·3 kK; −160°: σ = 22·4 kK. [i] MTHF and DME; independent of temperature. [j] HMP–K⁺, +20°; HMP–Li⁺, +20°. [k] MTHF, +20°; sensitive to temperature and cation

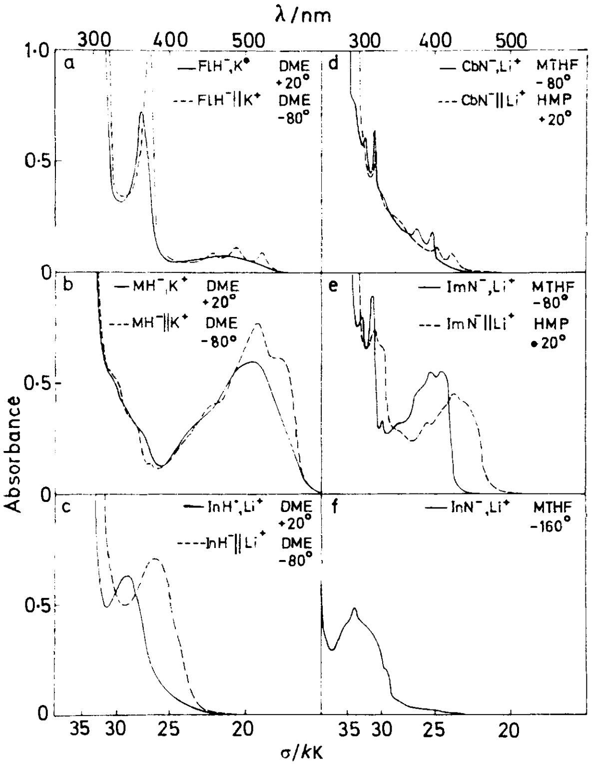

FIGURE 1 The electronic absorption spectra of the carbanions of fluorene, 4,5-methylenephenanthrene, and indene and of the nitranions of carbazole, 4,5-iminophenanthrene, and indole

In DME the results obtained for the potassium ion pairs of FlH⁻ and MH⁻ at +20° are nearly equal to those in MTHF. A lowering of the temperature results in a red shift with a maximum of 0·9 kK for both carbanions; at −80° the absorption maxima have the same positions as measured in HMP. The data for the corresponding lithium salts at +20° and at low temperatures are identical with those for HMP.

The phenomena observed for InH⁻ in DME are practically the same as for the MTHF solutions of InH⁻. Even at −80° the absorption maximum of the potassium ion pair is not shifted to smaller wavenumber, in contrast with the results for the corresponding FlH⁻ and MH⁻ solutions.

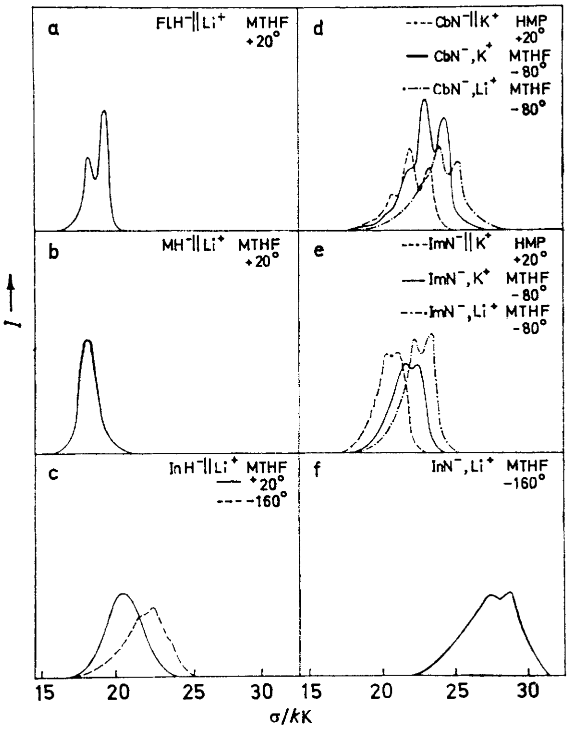

FIGURE 2 The fluorescence spectra of the carbanions of fluorene, 4,5-methylenephenanthrene, and indene and of the nitranions of carbazole, 4,5-iminophenanthrene, and indole

The absorption spectra of the nitranions CbN⁻, ImN⁻, and InN⁻ are given in Figures 1d—f. The absorptions appear to be nearly independent of temperature. In HMP related potassium and lithium ion pairs of the nitranions mentioned absorb at the same wavenumbers. In MTHF and DME the absorption bands of CbN⁻ and ImN⁻ display a blue shift compared with those recorded in HMP; the changes amount to *ca.* 1·0 kK for the potassium salts and to about 1·8 kK for the lithium salts.

The absorption of the InN⁻ ion pairs is completely insensitive to the solvent, the alkali ion, and temperature. Under all conditions chosen the maximum of the first absorption band is at 33·9 kK.

Fluorescence Spectroscopy.—The fluorescence of the carbanions FlH⁻, MH⁻, and InH⁻ (Figures 2a—c) exhibits hardly any dependence on the solvent, the alkali ion, or the temperature. Only the emission wavenumber of InH⁻ in MTHF increases by 2·1 kK on lowering the temperature to −160°.

The fluorescence spectra of the nitranions CbN^- and ImN^- are, in contrast with those of the corresponding carbanions, fairly sensitive to the nature of the solvent and the alkali ion used, whereas the temperature effect on the fluorescence can be neglected. In HMP the position of the fluorescence bands of CbN^- and ImN^- are not affected by the alkali ion.

In MTHF and DME the maxima of the fluorescence bands of the potassium ion pairs of CbN^- and ImN^- are shifted to smaller wavenumber relative to those of the lithium ion pairs ($\sigma_{Li^+} - \sigma_{K^+} \approx 1{\cdot}1$ kK). Compared with the fluorescence, observed in HMP it appears that the emission of the potassium salts in DME and MTHF takes place at higher energies. The changes amount to about 1·1 and 2·0 kK for the potassium and lithium ion pairs, respectively.

The lithium and potassium salts of InN^- emit at different wavenumbers at 20° ($\sigma_{Li^+} - \sigma_{K^+} = 2{\cdot}4$ kK). The fluorescence of InN^- is rather sensitive to temperature. The experimental data are not consistent, so that further investigations are needed to elucidate the behaviour as a function of the temperature.

DISCUSSION

Association Phenomena in the Ground State.—The phenomena observed with absorption spectroscopy pertain to the ground state of the ions. The results demonstrate the occurrence of s.s. ion pairs and c.i. pairs. From the data in Table 1 it appears that the interaction between the carbanions and the alkali ions is stronger for InH^- than for FlH^- and MH^-. A larger temperature decrease is required for the conversion of the c.i. pair InH,Li^+ into the s.s. ion pair $IH^-\|Li^+$ than for the same transformation of FlH^-,Li^+ and MH^-,Li^+, whereas the ion pair InH^-,K^+ is not converted at all, not even at −160°.

The strong interaction is understandable from the charge distributions of the carbanions. SCF calculations * show that *ca.* 70% of the excess of charge is located in the five-membered ring of InH^-; for FlH^- and MH^- the surplus amounts to *ca.* 40%. The differences between the excesses will cause greater electrostatic interaction in the species InH^-,X^+ than in the ion pairs FlH^-,X^+ and MH^-,X^+.

In an analogous way the results for the nitranions CbN^- and ImN^- can be described in terms of s.s. ion pairs and c.i. pairs. In MTHF and DME c.i. pairs are are invariably formed, but in HMP only s.s. ion pairs are generated. The absorption bands of the c.i. pairs display a blue shift relative to those of the s.s. ion pairs. This phenomenon, agreeing with the results obtained for carbanions,[2a,3b,c] can be explained [2b,3c,6] by a change of charge distribution over the negative part of the ion pair after excitation. According to the Franck–Condon principle an electronic transition takes place without modification of the nuclear arrangement during the transition. Therefore the alkali ion will occupy an energetically less favourable position in the excited state. Consequently it may be expected that the absorption bands of the c.i. pairs will display a blue shift relative to the absorption bands of the s.s. nitranions. The smaller the radius of the alkali ion, the greater the effect of the electrostatic perturbation and hence the greater the hypsochromic shift will be.

In the preceding considerations, it was not taken into account that a third type of ion can exist, *i.e. free ions*.[2a] In order to establish whether these ions are present or not the concentration of counterions (5×10^{-4} mol l^{-1}) was increased a hundred-fold by addition of sodium tetraphenylborate to the solutions. The absorption bands were not altered with respect to the original spectra recorded for DME and HMP solutions of the carbanions and nitranions prepared with sodium as the reducing agent. This behaviour indicates that the distinction between free ions and s.s. ion pairs is irrelevant in the solvents used.

The results, which are different for the carbanions and the nitranions may be qualitatively explained by the charge distribution in these ions. From quantum chemical calculations it is known that the excess of charge, δ, on the nitrogen of the nitranions are larger than those on the corresponding carbon of the carbanions (FlH^-, $\delta = 0{\cdot}31$; CbN^-, 0·55; MH^-, 0·32; ImN^-, 0·56; InH^-, 0·25; and InN^-, 0·49). As a consequence of the large δ values for the nitrogen atom the nitranions will interact strongly with the alkali ions. To obtain s.s. nitranions solvents more polar than MTHF and DME are required.

The behaviour of the nitranion InN^- deviates from that of the others studied. The position of the π electron absorption band of InN^- σ 33·9 kK) is not a sensitive function of the solvating power of the medium or of the radius of the alkali ion. In view of the strong interaction which may be expected to exist between the nitranion and the counterion the presence of s.s. ion pairs is excluded. For this reason it is concluded that the alkali ion is so oriented that it does not affect the π electron energy. It is most likely that the alkali ion is located in the molecular plane of InN^- close to the nitrogen atom, the non-bonding electrons of this atom being predominantly concerned in the bonding with the alkali ion. This bond is apparently rather strong; even in the polar solvent HMP the spectra do not give any indication for the existence of s.s. ion pairs.

Association Phenomena in the Excited State.—Under all conditions chosen the fluorescence of the carbanions FlH^-, MH^-, and InH^- is insensitive to the alkali ions. This result may be attributed to a transformation of the c.i. pairs into s.s. ion pairs involving an emission from the first excited state of the s.s. ion pairs. The charge distribution in these ions before and after excitation seems to justify this supposition.

On the other hand the fluorescence emission of the nitranions CbN^- and ImN^- in MTHF and DME displays

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* Quantum chemical calculations will be published in a separate paper.

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

an alkali dependence. We suppose that the c.i. pairs of the nitranions are the emitting species in the solvents mentioned. The excess of charge, δ, on the atom are lowered by excitation [CbN^-, $\delta = 0{\cdot}55$, $\delta^* = 0{\cdot}20$; and ImN^-, $\delta = 0{\cdot}56$, $\delta^* = 0{\cdot}28$ [δ^* refers to the excited state]. However, the δ^* values approximate to the corresponding δ values of the carbanions FlH^- and MH^-, resulting in an interaction of the same order of magnitude. The existence of the carbanions FlH^- and MH^- as c.i. pairs in the ground state supports the assumption that the nitranions CbN^- and ImN^- may be present as c.i. pairs in the excited state.

The maxima of the emission bands of the c.i. pairs of the nitranions have been shifted to larger wavenumber compared with those of the s.s. nitranions, recorded in HMP. The most pronounced change is found in the presence of lithium ions, as in the case of the absorption spectra of the nitranions. Förster and Renner have reported the same sequence for the emission bands of alkali salts of amino-compounds such as 1- or 2-naphthylamine and 1- or 2-aminoanthracene.[7]

The carbanion InH^- and the nitranion InN^- show some deviations from the other carbanions and nitranions under study. First, attention will be paid to the large difference, $\Delta\sigma$, between the absorption and fluorescence maxima ($\Delta\sigma = \sigma_{abs} - \sigma_{fl}$), which amounts to at least 6·4 kK (see Table). Because of the Franck–Condon principle, excitation does not directly lead to the equilibrium conformation of the excited state, but to a conformation (the so-called F.C. excited state) which has a solvent cage identical to that in the ground state. The more the charge distribution of the solute in the excited state differs from that in the ground state the larger the stabilization of the fluorescent state with respect to the F.C. excited state will be, as a result of solvent reorientation. From charge density calculations it appears that 30—40% of the excess of charge is located in the six-membered ring of InH^- and InN^- in the ground state; in the first excited state the surplus amounts to 70—80%. This extensive displacement of negative charge will cause a large energy difference between the F.C. excited state and the equilibrium excited state. The same reasoning holds for the emission of InH^- and InN^-. Transition occurs from the equilibrium excited state to a F.C. ground state which will persist until the solvent molecules have been rearranged to the equilibrium orientation belonging to the ground state. These features give rise to the relatively large value for $\Delta\sigma$.

The blue shift of the fluorescence band of InH^- in MTHF at -160 and $+20°$ ($\Delta\sigma = 2{\cdot}1$ kK) may be explained in the same way. In a solid matrix, *e.g.* in MTHF at $-160°$, stabilization of the F.C. excited state can occur only to a small extent, resulting in an emission from this state to the equilibrium ground state. Consequently, a blue shift will be observed in contrast to the spectra obtained of the ions in a MTHF solution where stabilization of the F.C. excited state is realized. As the energy difference between the F.C. excited state and the equilibrium excited state is small for FlH^- and MH^- compared with InH^-, the fluorescence band of these carbanions will be only slightly sensitive to variations in the temperature.

The emission phenomena of the nitranion indolyl are rather complicated. Contrary to the absorption, the fluorescence depends on the alkali metal used, involving a change of the π electron energy levels. It may be that the nature of the bonding between the nitranion and the alkali ion is modified by the redistribution of the excess of charge ($\delta_N = 0{\cdot}49$; $\delta_N^* = 0{\cdot}32$). As a consequence the bond between the ions of the complex partly loses its σ character.

The influence of the temperature on the fluorescence spectrum of InN^- has not completely been elucidated and will be subject of a further study. The investigations will be extended to other solvents.

The experimental assistance of Mr. G. P. Hoornweg is gratefully acknowledged.

[1/1807 *Received*, 4*th October*, 1971]

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[7] Th. Förster and H. Renner, *Z. Elektrochem.*, 1957, **61**, 340.