

OPTICAL AND NMR INVESTIGATIONS ON ALKALI ION PAIRS OF CARBANIONS AND NITRANIONS

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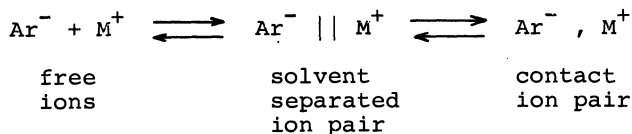
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Abstract - The ion pair formation of some cyclic conjugated carbanions and nitranions has been studied by absorption and fluorescence spectroscopy. From the spectra, recorded as a function of temperature, solvent and counter ion it becomes clear that the absorption spectra of contact ion pairs are always shifted to high energy with respect to the spectra of solvent separated ion pairs, but in the fluorescence spectra shifts in both directions have been found. The observed phenomena can be explained satisfactorily by theoretical π -electron charge distributions in the ground and first excited states.

Also with ^1H and ^{13}C NMR spectroscopy valuable information concerning the ion pairing has been obtained. An apparent discrepancy between the structure of the contact ion pair of the carbanion indenyl inferred from calculations and from ^1H NMR is resolved by a theoretical examination of the effects of the cationic field on the proton chemical shifts. The ^{13}C NMR data support the interpretation of the temperature dependence of the ^1H chemical shifts in terms of a "direct" and an "indirect" effect of the cation. In order to explain the ^1H chemical shifts of some anions with 16 π -electrons the occurrence of paramagnetic ring currents has to be postulated. ^7Li NMR data give evidence for the structure of the contact ion pairs, σ - or π -complex. The influence of ion pair formation on the reaction rate of the symmetrical proton exchange reaction between a carbanion and its parent molecule has been studied from the exchange line broadening for the system indene/indenyl in various solvents.

INTRODUCTION

It is well-known that ion pairs of aromatic anions and alkali metal cations can exist in three distinguishable forms (1,2 & 3):



The FREE IONS predominate in strongly polar solvents like hexamethylphosphoric triamide (HMPT), but only minor amounts are present in aliphatic and alicyclic ethers.

In a SOLVENT SEPARATED or LOOSE ION PAIR the cation and anion are separated by a solvation shell (of the cation). The optical spectra of this type are (nearly) identical to those of the free ions. Smid et al have used conductivity measurements to distinguish them (4 & 5).

In a CONTACT or TIGHT ION PAIR the ions are not separated by solvent molecules, although the ion pairs can be solvated externally. The proximity of the cation induces displacements - called ION PAIR SHIFTS - of the absorption (6 - 10), emission (8,9,11 & 12) and NMR (13 - 22) spectra of the anion. The contact ion pairs can still be divided into σ - and π -complexes (9,16 - 20). In this paper a review will be given of the ion pair formation of some cyclic conjugated carbanions and nitranions with alkali metal ions. We will pay

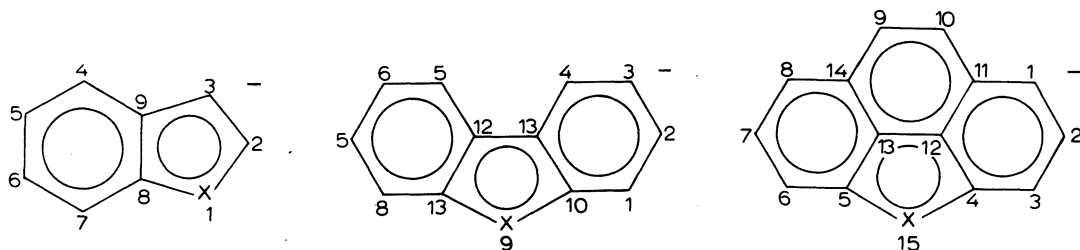
attention to the influences of the cation and anion size, of the introduction of heteroatoms and of the excitation to the first excited singlet state on the ion pair structure.

The anions have been prepared in vacuo by treatment of the parent molecules with alkali metal (Li, Na, K) or with sodium amide (8 & 23). The measurements have been performed in various solvents: tetrahydrofuran (THF), 2-methyl-tetrahydrofuran (MTHF), 1,2-dimethoxyethane (DME) and HMPT as a function of temperature. The maximal ranges are from room temperature down to respectively -110, -160, -80 and 0 °C.

The experimental results are analysed with the aid of energy level diagrams, which in turn will be correlated with molecular orbital charge density calculations. The quantummechanical quantities have been calculated with the semi-empirical π -electron Variable Electronegativity Self Consistent Field (VESCF) method (24,9 & 10), which is an extension of the well-known Pariser, Parr and Pople method and gives a more realistic description of the charge distribution (25).

ALKALI ION PAIRS OF CARBANIONS AND NITRANIONS

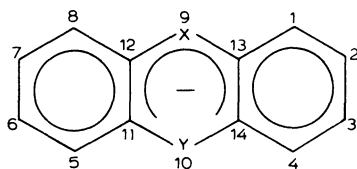
The optical absorption and emission spectroscopy are useful techniques to study ion pair formation, as the positions of the bands are sensitive to association phenomena. The fluorescence and/or absorption spectra of the following ions have been recorded as a function of temperature, solvent and counter ion. The experimental results can be interpreted in terms of contact



X = CH: InH⁻
indenyl
X = N: Idl⁻
indolyl

X = CH: FlH⁻
fluorenyl
X = N: Cb⁻
carbazolyl

X = CH: MH⁻
4,5-methylenepheneanthrenyl
X = N: Im⁻
4,5-iminopheneanthrenyl



X = CH Y = CH₂: AH⁻
9,10-dihydroanthracenyl
X = CH Y = O: XH⁻
xanthenyl
X = CH Y = S: TxH⁻
thioxanthenyl

ion pairs and solvent separated ion pairs. Under some experimental conditions both types of ion pairs are present.

Ion pair formation in the ground state

For the CARBANIONS the results observed are as expected (4 & 6): in ethereal solvents the equilibrium between contact ion pairs and solvent separated ion pairs is shifted to the latter type with increasing solvent polarity and with decreasing cation radius and temperature. The temperature effect is demonstrated in Fig. 1 for InH⁻ prepared in MTHF with Li (9).

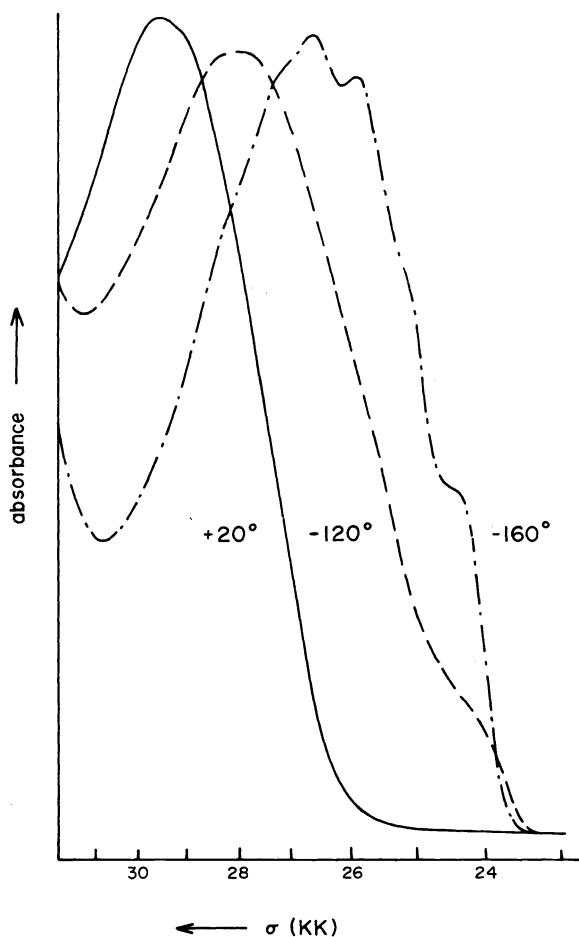


Fig. 1. The absorption spectrum of indenyl-lithium in MTHF at different temperatures; 1 kK = 1000 cm^{-1} .

The spectral positions of the bands of the carbanions FlH^- and InH^- are represented schematically in Fig. 2. It is clear that the ABSORPTION ION PAIR SHIFT, defined as the spectral displacement on formation of a contact ion pair from a solvent separated ion pair, is always to high energy; the shift increases in the order K^+ , Na^+ , Li^+ .

It has been found that the pairing properties of FlH^- and MH^- are similar (8 & 26). The CONVERSION TEMPERATURES, defined as the temperatures at which the concentrations of contact ion pair and solvent separated ion pair are equal, differ, on the average, less than 20 $^{\circ}\text{C}$. Besides, the ground state acidities of the parent molecules FlH_2 and MH_2 , respectively 20.5 and 20.0 in DMSO (27) and also the calculated π -electron charge distributions of FlH^- and MH^- (see Fig. 3) are similar (26). All these data indicate that the cation - anion attraction energies in both systems are nearly equal. This leads to the conclusion that the vinylene group in MH^- does hardly enhance the delocalization of the negative charge.

On the other hand InH^- has a greater tendency to form contact ion pairs than FlH^- (8 & 9). The conversion temperature amounts for $\text{InH}^- \text{Li}^+$ in MTHF -120 $^{\circ}\text{C}$, for $\text{FlH}^- \text{Li}^+$ in MTHF 0 $^{\circ}\text{C}$. This can be explained by supposing that in the three ring system FlH^- the negative charge is more delocalized than in the two ring system InH^- . Charge density calculations (9) confirm this supposition (see Fig. 4).

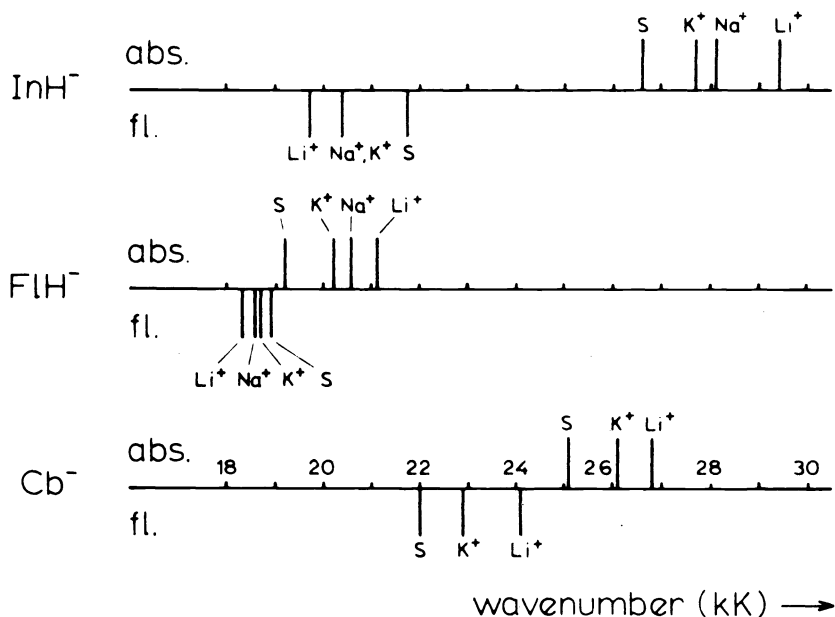


Fig. 2. The absorption and fluorescence spectral positions of InH^- , FlH^- and Cb^- . The positions of the spectral maxima (InH^- and Cb^-) or the 0-0 transitions (FlH^-) are indicated for the solvent separated ion pairs (denoted by S) and the contact ion pairs (denoted by the cation involved). The maxima in different solvents have been averaged for each type of ion pair. The fluorescence wavenumbers of the contact ion pairs of FlH^- have been taken from ref. 11.

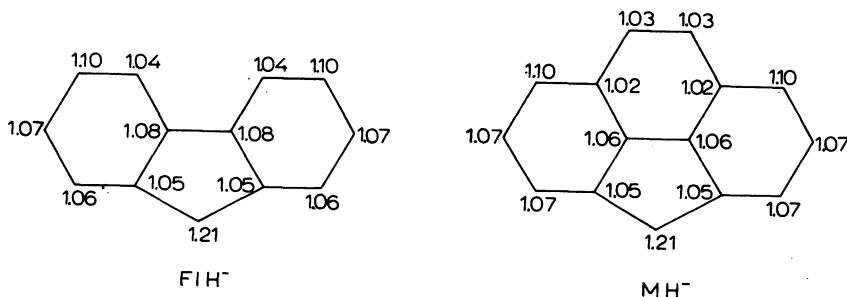


Fig. 3. π -Electron charge densities of the carbanions FlH^- and MH^- , calculated with the VESCF method.

From the absorption spectra of the NITRANIONS Idl^- , Cb^- and Im^- it appears that in ethereal solvents contact ion pairs always predominate (8 & 26). A strongly polar solvent like HMPT is needed to separate the ions. The absorption ion pair shift is to high energy, as has been represented schematically in Fig. 2 for the nitranion Cb^- ; the shifts increase in the order K^+ , Na^+ , Li^+ , just as for the carbanions (9).

The nitranions have a higher affinity towards alkali cations than the analogous carbanions. This could be expected (9) as in the nitranions the

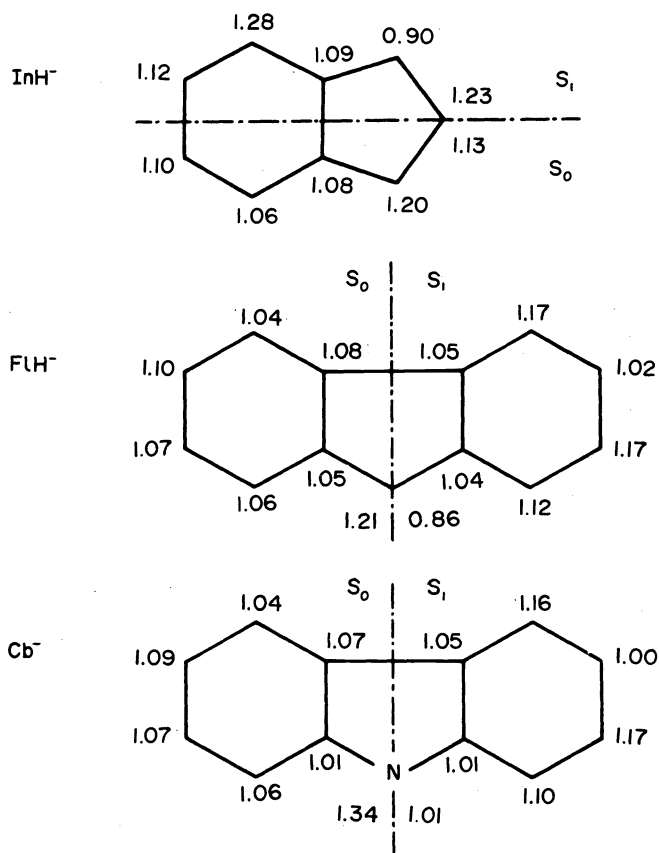
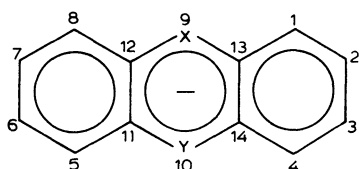


Fig. 4. π -Electron charge densities of InH⁻, FlH⁻ and Cb⁻ in the ground state (S₀) and the first excited singlet state (S₁), calculated with the VESCF method.

π -electron charge is strongly concentrated on the nitrogen atom (see Fig. 4). In addition, the lone pair on the nitrogen atom can interact with the cation. In general, a competition will take place between these two interactions. If the π -electron contribution dominates a π -contact ion pair will be formed, if the lone pair contribution dominates a σ -contact ion pair.

For the TRICYCLIC CARBANIONS AH⁻, XH⁻ and TxH⁻ a temperature dependent equilibrium between contact and solvent separated ion pairs is observed (10). The absorption ion pair shifts are to high energy and increase in the order K⁺, Na⁺, Li⁺, just as for the anions considered until now. However, the shifts for these tricyclic carbanions with a central six-membered ring are larger than those observed for the tricyclic carbanions FlH⁻ with a central five-membered ring. The differences in wavenumbers between the solvent separated ion pairs and the lithium contact ion pairs amount about 3100, 3400, 3800 and 2000 cm⁻¹ for respectively AH⁻, XH⁻, TxH⁻ and FlH⁻. There is an important difference between XH⁻ and TxH⁻ on the one hand and the anions containing a five-membered ring on the other hand (10). As the hetero-atoms oxygen and sulphur contribute two electrons to the π -electron systems, XH⁻ and TxH⁻ have a $4n$ ($n=4$) π -electron perimeter, whereas the other anions under study contain $4n+2$ π -electrons. Accordingly XH⁻ and TxH⁻ are partially PARATROPIC (28), which means that paramagnetic ring currents are induced by a magnetic field. The anions with a five-membered ring are completely DIATROPIC; in other words XH⁻ and TxH⁻ are less "aromatic" than the homocyclic carbanions under study (29). This difference is reflected for XH⁻ in the acidity constant of its parent molecule xanthene. The high acidity constant of xanthene with respect to the homocyclic molecules indene, fluorene and methylenephenanthrene, 27.1, 18.2, 20.5 and 20.0 respectively (30 & 27) may be accounted for by a smaller stabilization of XH⁻ as compared with FlH⁻.

The partially paratropic character of XH^- and TxH^- can be inferred from the proton chemical shifts (31). These are drawn schematically for a series of carbanions in Fig. 5 (32). In this series two anions with a central seven-membered ring have been included (33). The most striking feature is the



X = CH Y = CH=CH: DbcH⁻
 carbanion of 5H-dibenzo[a,d]cycloheptene
 X = N Y = CH=CH: Dba⁻
 nitranion of 5H-dibenzo[b,f]azepine

strong displacement of the chemical shifts to high field in comparison with the corresponding chemical shifts for FlH^- ; for proton 9 in the carbanion DbcH⁻ even a shift upfield to TMS has been observed. It is clear from Fig. 5 that for a given anion the displacements for protons in a similar position

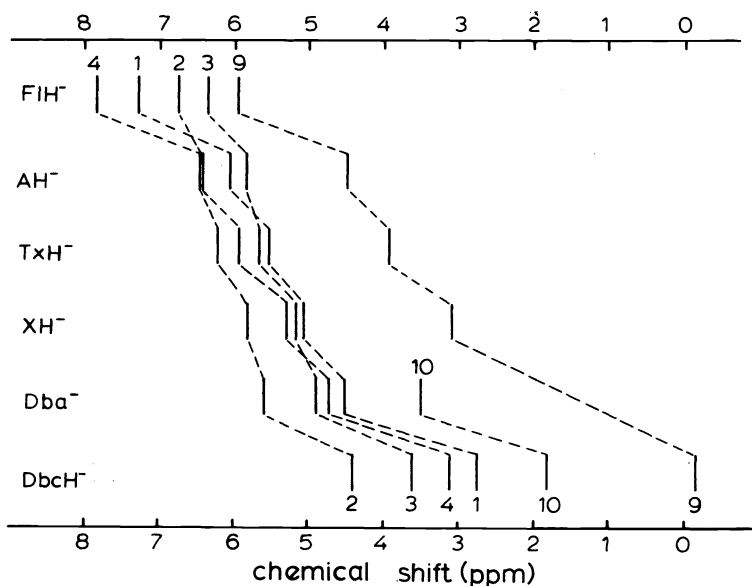


Fig. 5. The chemical shifts of FlH^- , AH^- , TxH^- , Dba^- and $DbcH^-$, expressed in ppm relative to TMS.

have nearly the same values. Moreover they decrease with increasing distance to the central ring. These data can only be explained with the occurrence of a paramagnetic ring current in the central ring of the $4n$ π -electron systems, resulting in a less "aromatic" character for these systems. This less "aromatic" character is also reflected in the lower reaction rates of xanthene and thioxanthene with alkali metal and in the instability of the formed carbanions, which are light sensitive (10).

In summary, the absorption spectra of XH^- and TxH^- show the same dependence on solvent polarity, cation size and temperature as has been found for homocyclic carbanions. The conversion from contact ion pairs into solvent separated ion pairs occurs approximately in the same temperature regions as

for FlH^- . This means that the introduction of an oxygen or a sulphur atom in the central ring of FlH^- does not have an important influence on the ion pairing properties in the ground state.

As we have seen nitrogen containing anions like Cb^- form exclusively contact ion pairs in ethereal solvents. Apparently the influence of the "pyridine"-like nitrogen atom in Cb^- on the stability of the contact ion pairs is much greater than the influence of the oxygen atom in XH^- . The oxygen atom is not as "ether"-like as it seems; it may be described as "furan"-like (10).

Ion pair formation in the first excited singlet state

The fluorescence spectra of the anions have been measured as a function of temperature, solvent and counter ion. They consist in general of broad bands as is demonstrated in Fig. 6 for InH^- (8,9 & 10). The absence of any displacement in the fluorescence spectra of the CARBANIONS FlH^- and MH^- indicates

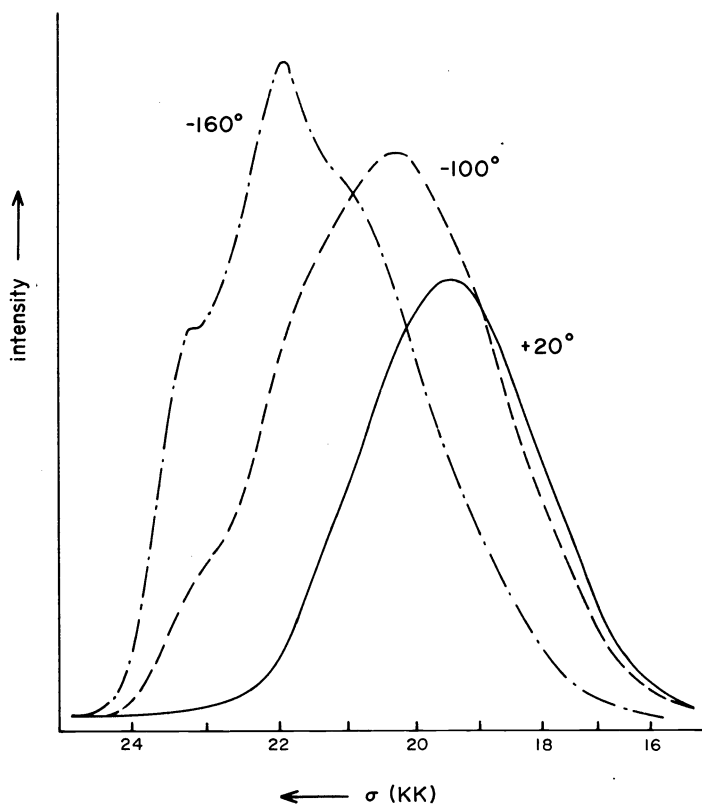


Fig. 6. The fluorescence spectrum of indenyl-lithium in MTHF at three different temperatures. The intensities of the spectra at $+20$ and -100°C are multiplied by factors 16 and 8, respectively.

that the fluorescent state in MTHF, DME and HMPT is a solvent separated ion pair (8 & 26). Hogen-Esch et al (11 & 12) have shown that FlH^- forms contact ion pairs in the excited state in solvents which are less polar than MTHF, such as tetrahydropyrane and dioxane. Obviously, the tendency to form solvent separated ion pairs is larger in the first excited state than in the ground state. If contact ion pairs are present in the ground state they can be converted into solvent separated ion pairs after excitation; the lifetime of the excited state - according to Hogen-Esch et al $\approx 10^{-8}$ sec (12) - is long enough for such a process.

The fluorescence spectra of InH^- (see Fig. 6), on the contrary, are temperature dependent (9). InH^- can form contact and solvent separated ion pairs in the first excited singlet state. The conversion temperatures are approximately -110°C with Li^+ in MTHF and -50°C with Li^+ in DME; these tempera-

tures are comparable with those for the ground state. These data lead to the conclusion that the tendency to form contact ion pairs is roughly equal for the ground and the excited states of InH^- . From the graphical representation of the fluorescence maxima for InH^- and FlH^- (see Fig. 2) it is obvious that the fluorescence maxima of the contact ion pairs are shifted to low energy with respect to those of the solvent separated ion pairs. Hence, the FLUORESCENCE ION PAIR SHIFTS are for these carbanions to low energy, which is opposite to the absorption ion pair shifts. However, the fluorescence ion pair shifts, just as the absorption ion pair shifts, increase in the order K^+ , Na^+ , Li^+ . Moreover, for FlH^- the fluorescence ion pair shifts are smaller than the absorption ion pair shifts, whereas there is only a small difference for InH^- (9).

The fluorescence spectra of the NITRANIONS Cb^- and Im^- in ethereal solvents, which are cation dependent, indicate the presence of contact ion pairs in the excited state (8). These systems do not show ion pair conversion when the temperature is varied over the usual range. The fluorescence ion pair shifts are to high energy, just like the absorption ion pair shifts (see Fig. 2). The shifts increase in the order K^+ , Na^+ , Li^+ . The absorption and fluorescence ion pair shifts of Cb^- and Im^- are approximately equal in magnitude (9). The nitranion Idl^- also forms in the first excited state only contact ion pairs. However, the fluorescence spectra of Idl^- show a rather complicated temperature dependence (20) and will be left out of consideration in this review.

In summary, for the carbanions the tendency to form contact ion pairs is lower in the first excited singlet state than in the ground state. The cation-anion attraction is greater for the nitranions than the analogous carbanions. The most remarkable difference between carbanions and nitranions is encountered in the fluorescence ion pair shifts: for carbanions to low energy, which is in opposite direction as the absorption ion pair shifts; for nitranions to high energy, which is in the same direction as the absorption ion pair shifts. For FlH^- the absolute values of the ion pair shifts are considerably smaller in the fluorescence than in the absorption spectra; for the other anions under study the absolute values of corresponding shifts differ slightly.

DISCUSSION OF THE ABSORPTION AND FLUORESCENCE ION PAIR SHIFTS

In order to explain the results of a number of structurally related carbanions and nitrogen - containing anions we will consider in detail the energy level diagrams, which describe the absorption and fluorescence ion pair shifts. These diagrams are related with the charge distributions, calculated for ground and first excited singlet states. We restrict ourselves to three typical systems, namely InH^- , FlH^- and Cb^- .

The absorption ion pair shifts

The absorption ion pair shifts can be explained by the redistribution of the

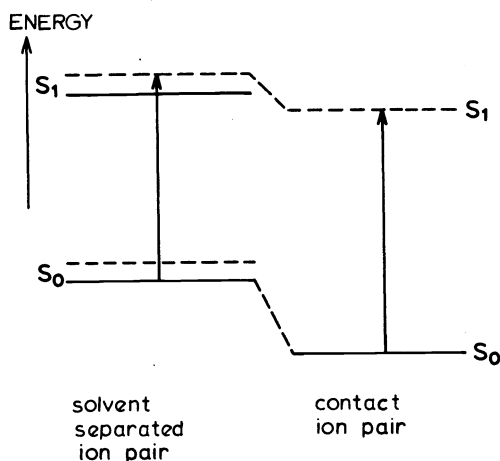


Fig. 7. Energy level diagram which describes the absorption ion pair shift.

negative charge of the anion on excitation (6). From the calculated π -electron charge densities for InH^- , FlH^- and Cb^- in the ground and first excited singlet states (see Fig. 4) a decrease of the cation-anion interaction on excitation has to be expected, as the cation retains its position. In energy terms this means, that for the contact ion pair with respect to the solvent separated ion pair the Franck Condon excited state, in which the system is immediately after excitation, is less stabilized than the ground state (see Fig. 7). It is obvious that a spectral shift to high energy occurs when a solvent separated ion pair is converted into a contact ion pair.

Fluorescence ion pair shifts

For the discussion of the fluorescence ion pair shifts we start from the incomplete energy level diagram in Fig. 7, in which arbitrary values have been given to the absorption energies of the solvent separated and contact ion pairs and to the fluorescence energy of the solvent separated ion pair. Moreover we suppose that the Franck Condon destabilization energies of the ground and excited states of a certain system have the same value. The related absorption and fluorescence transitions have been drawn in Fig. 8a. The question arises where we have to draw the missing levels in the energy diagram of the contact ion pair. In other words: which values have the equilibrium stabilization energies and the Franck Condon energy. To answer this question we have to establish which factors influence the energy terms mentioned.

At first we consider the EQUILIBRIUM STABILIZATION ENERGIES. Their values are determined by the depths of the minima in the corresponding potential energy curves which depend, on its turn, on the extent of charge localization. VESCF calculations supply the following data (9). For InH^- the minima for the ground and first excited singlet states amount, respectively, to -4.92 and -4.90 eV; for FlH^- the values are respectively -4.68 and -4.56 eV. These results imply that the ground and excited states of the contact ion pair of InH^- are stabilized in the same extent with respect to those of the solvent separated ion pair, whereas for FlH^- the ground state of the contact ion pair is more stabilized than the excited state.

Secondly the FRANCK CONDON DESTABILIZATION ENERGY of the contact ion pair has to be determined. This energy is related to the difference in geometry between the lowest vibronic ground state and the first excited singlet state. Contributions will arise, among others, from the change in anion geometry on the formation of contact ion pairs and from the change in the equilibrium position of the cation with respect to the anion on excitation. The first contribution will be of minor importance; the second one will strongly influence the Franck Condon destabilization energy. If the position of the potential energy minimum or the area of charge localization is displaced on excitation the Franck Condon stabilization energy increases on formation of contact ion pairs.

From calculated charge densities (see Fig. 4) it is clear that for InH^- in the ground state the charge for the larger part is localized in the five-membered ring. Excitation to the first excited singlet state is accompanied by a displacement of the charge and thus of the position of the potential minimum from the five- to the six-membered ring. As a result the Franck Condon destabilization energy will be larger for the contact ion pair than for the solvent separated ion pair.

For FlH^- in the ground state the charge is slightly localized in the central ring, but in the excited state the negative charge is predominantly localized in the side rings (see Fig. 4). Just as for InH^- the position of the potential minimum is displaced on excitation, resulting in an enhanced value of the Franck Condon destabilization energy in the contact ion pair compared with the solvent separated ion pair.

With the theoretical results discussed above we can complete the energy level diagram and determine the direction and the absolute value of the fluorescence ion pair shifts.

For the contact ion pair of InH^- the equilibrium stabilization energies of the ground and first excited states have the same value. The Franck Condon destabilization is larger for the contact ion pair than for the solvent separated ion pair. From the resulting diagram (Fig. 8c) follows a fluorescence ion pair shift to low energy which is in the opposite direction as the absorption ion pair shift. The absolute values of the absorption and fluorescence ion pair shifts are of the same order. The experimental results (see Fig. 2) are in agreement with these predictions.

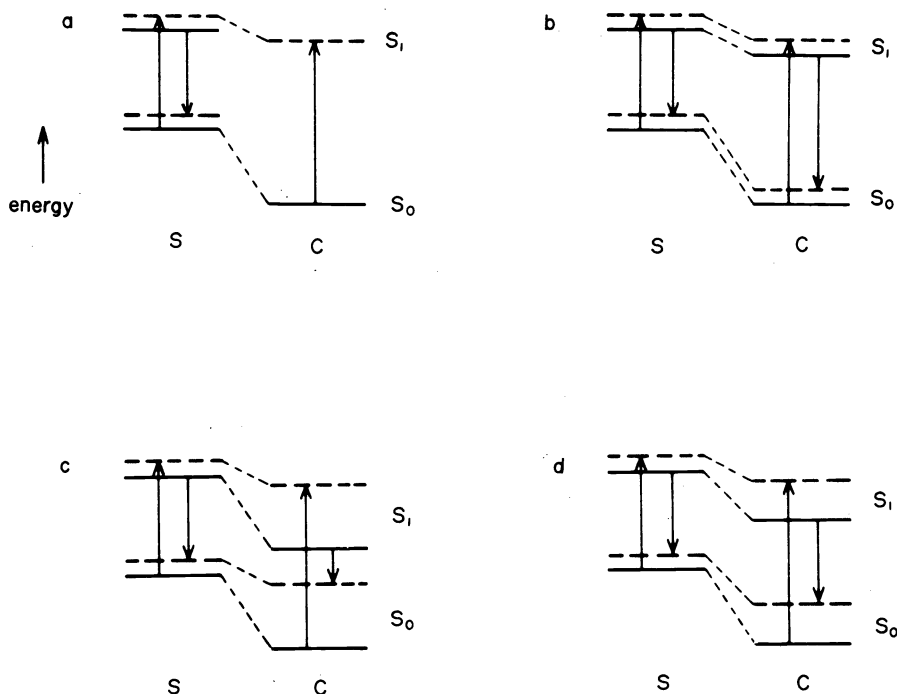


Fig. 8. Energy level diagrams which describe the absorption and fluorescence ion pair shifts. S and C denote respectively solvent separated and contact ion pairs.

For FlH^- the equilibrium stabilization energies of the contact ion pairs in ground and first excited states and the Franck Condon energies of the solvent separated and contact ion pairs are different (Fig. 8d). Depending on the absolute values of these energy terms a red or blue fluorescence ion pair shift may occur; besides this shift may be small in comparison with the absorption ion pair shift. The experimental results of FlH^- with a small fluorescence ion pair shift to low energy and a larger absorption ion pair shift to high energy (see Fig. 2) satisfy this "intermediate" model. The calculated results for Cb^- don't differ considerably from those of FlH^- . However, the experimental results of Cb^- (see Fig. 2) are not in agreement with the energy level diagram that describes the results of FlH^- satisfactorily (Fig. 8d). It is most probable that the influence of the nitrogen atom, which is more electronegative than the corresponding carbon atom in FlH^- and in addition possesses a lone pair, has to be taken into consideration. If the cation is co-ordinated to this electron lone pair, both in the ground and first excited states, the potential minimum will not be displaced on excitation. As for Cb^- charge delocalization occurs on excitation (see Fig. 4) a decrease of the depth of the potential minimum has to be expected. Incorporation of these data lead to an energy level diagram for Cb^- as represented in Fig. 8b. This model indeed predicts fluorescence and absorption ion pair shifts in the same direction and absolute values which are of the same order. In the next section we will see that NMR data also give evidence for the formation of a σ -contact ion pair rather than a π -contact ion pair.

The systems discussed show that the various experimental results for the fluorescence ion pair shifts may be interpreted by a careful analysis of the different energy contributions. In nitrogen containing anions the specific interaction of the cation with the nitrogen lone pair electrons has to be taken into account.

NMR EVIDENCE FOR THE ION PAIR STRUCTURES

The diamagnetic carbanions and nitranions, which are closed shell systems, display high resolution NMR spectra (34 & 35). As the chemical shifts are sensitive to association phenomena ^1H and ^{13}C NMR spectroscopy are useful for a study of ion pair formation; the counter ion has a minor effect on the spin-spin coupling constants. Moreover valuable information concerning ion pairs can be obtained from the chemical shift of the cation nucleus.

 ^1H NMR

A cation positioned above the π -electron system of the anion will displace the electron density in the C-H bonds towards the carbon atoms. As a result the shielding of the protons will decrease and the proton resonances will be shifted downfield with respect to the proton chemical shifts of the solvent separated ion pair. The extent of the displacement will be larger the closer the cation is located to the C-H bond. This implies that the low field shift increases when the size of the alkali ion decreases. Hence we can expect from this so-called "direct" effect that the order for the proton chemical shifts in the contact ion pairs and the solvent separated ion pair is from high to low field: S^+ , K^+ , Na^+ , Li^+ .

The proton chemical shifts for the lithium and sodium salts of InH^- in DME, measured as a function of temperature, have been represented in Fig. 9. For InH Li^+ the shift from low to high field at decreasing temperature has to be

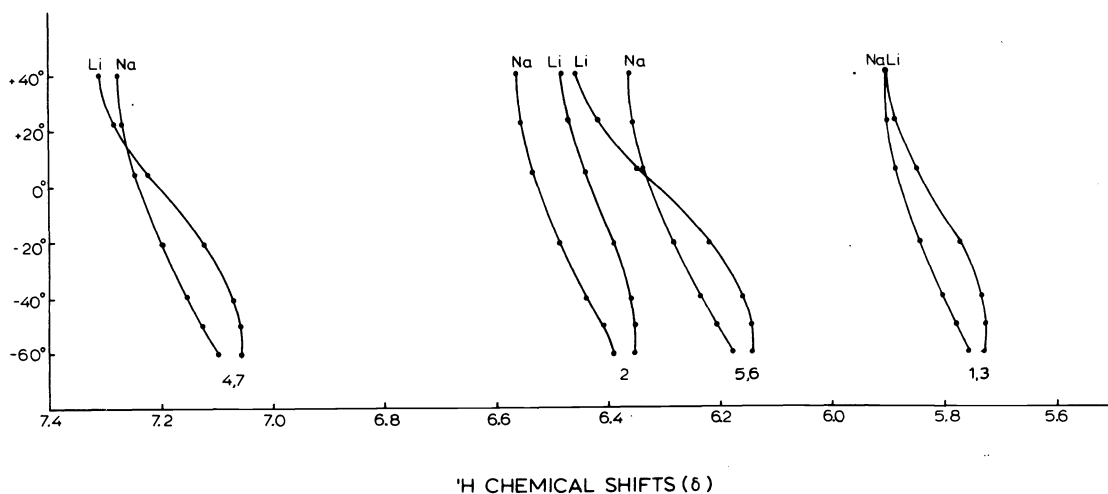


Fig. 9. The temperature dependence of the ^1H chemical shifts (δ) of indenyl-lithium and -sodium in the solvent DME. δ is given in ppm from TMS.

attributed to a conversion of contact ion pair into solvent separated ion pair. For InH Na^+ the temperature dependence is less pronounced. The fraction of solvent separated ion pair at -60°C will be smaller than for InH Li^+ , which is in agreement with optical measurements.

As at $+40^\circ\text{C}$ mainly contact ion pairs are present we expect to observe the proton lines of InH Li^+ at lower field than the corresponding lines of InH Na^+ . However, only the lines belonging to protons in the six-membered ring display this order. Moreover, the differences between the proton chemical shifts of InH Li^+ at $+40$ and -60°C are larger for the protons in the six-membered than for those in the five-membered ring. From these observations, we should conclude that the lithium cation is located over the six-membered ring. This seems to be in disagreement with the theoretical result, that in the ground state the negative charge is localized in the five-membered ring and thus the cation is located over this ring. The discrepancy may be resolved by taking into account a so-called "indirect" effect of the cation, which causes a redistribution of the excess negative charge in the anion and modifies the C-H bond polarization (9). If the alkali ion resides above the five-membered ring the negative charge in this ring will be enhanced and an upfield shift for the protons 1, 2 and 3 is expected.

Furthermore the decreased negative charge in the six-membered ring will lead to a downfield shift for the protons 4, 5, 6 and 7. For the alkali ion above the six-membered ring the displacements will be in the opposite direction. It is obvious from the schematic diagram (Fig. 10) for InH^- , in which the alkali ion is placed above the five-membered ring,

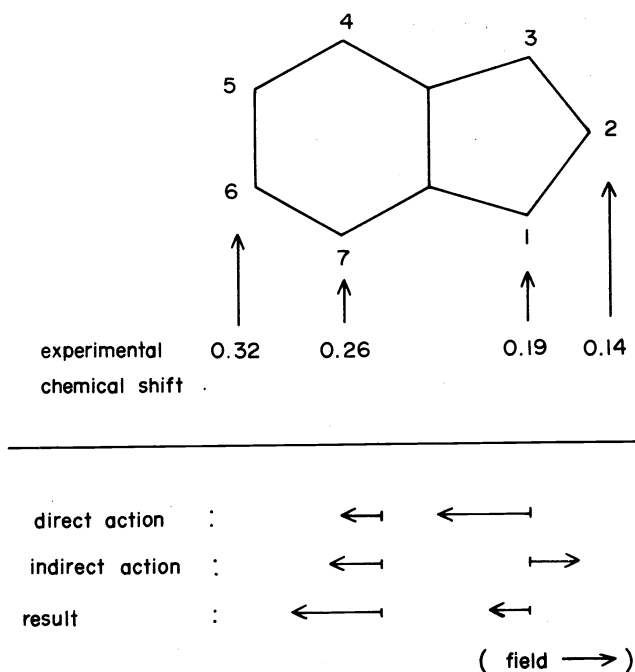


Fig. 10. The experimental differences in proton NMR shifts (in ppm) between contact and solvent separated ion pairs; bottom, schematic indication of the effects on the proton chemical shifts arising from a cation located above the five-membered ring.

that the combined influence of the "direct" and "indirect" effect may result in a larger downfield shift for the protons 4, 5, 6 and 7 than for the protons 1, 2 and 3. This prediction is in agreement with the experimental data.

¹³C NMR

The occurrence of a "direct" and an "indirect" effect is a restriction for the applicability of proton NMR in this type of research (9). This disadvantage is removed for the greater part in ¹³C NMR, as ¹³C chemical shifts depend strongly on the π -electron charge densities on the carbon nuclei (21, 36, 37 & 38). In first approximation, only the "indirect" effect of the cation will contribute to the displacements (22).

The ¹³C chemical shifts of the lithium and sodium salts of InH^- in DME have been represented in Fig. 11 as a function of temperature. The larger cation-anion attraction for $\text{InH}^- \text{Li}^+$ in comparison with $\text{InH}^- \text{Na}^+$ is demonstrated by the stronger temperature dependence of the ¹³C chemical shifts as well as by the higher conversion temperature. Particular attention has to be paid to the slopes of the graphs, which differ for the carbon atoms in the six- and five-membered ring. The temperature coefficient, defined as $d\delta/dT$, is negative for the carbon atoms of the five-membered ring and positive for the carbon atoms of the six-membered ring. As a negative sign means an increase of the π -electron charge density and a positive sign a decrease we must conclude that the formation of contact ion pairs is accompanied by a displacement of negative charge from the six- to the five-membered ring. These data corroborate the conclusions from optical and ¹H NMR measurements, that in the contact ion pair the cation

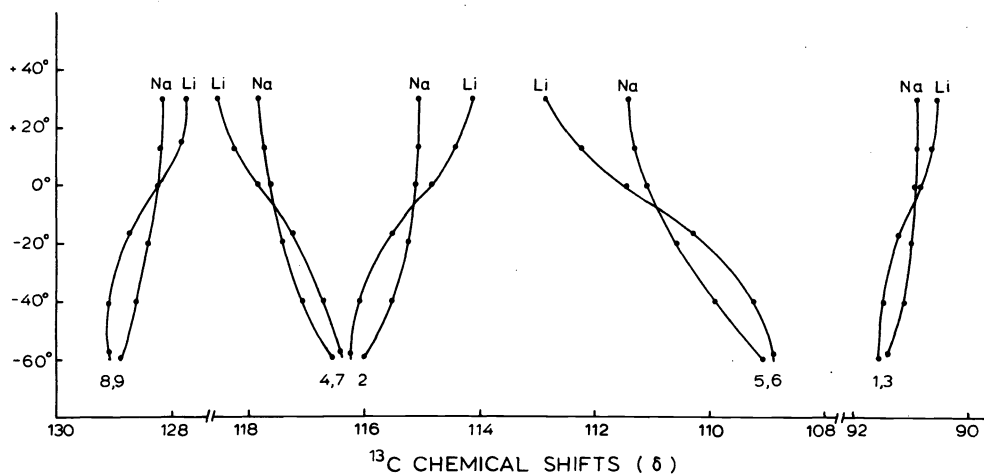


Fig. 11. The temperature dependence of the ^{13}C chemical shifts (δ) of indenyl-lithium and -sodium in the solvent DME. δ is given in ppm from TMS.

is located over the five-membered ring.

Apparently, ion pair aggregates, which may be present in the NMR samples (1) do not seriously affect the chemical shift data.

^7Li NMR

Dixon, Cox and others (16,17,18 & 19) have shown that ^7Li NMR is a useful technique to distinguish various types of ion pairs: solvent separated ion pairs, σ - and π -type contact ion pairs.

According to the ring current theory (39,40 & 41) it may be expected that a cation in a π -complex will be shielded in comparison with a free ion, whereas a cation in a σ -complex will be deshielded (see Fig. 12). It is known from the literature, that the ^7Li resonance of solvent separated ion pairs is observed 1 to 3 ppm upfield from 1 mol/l aqueous LiCl. For π -complexes the upfield shift amounts to 6-9 ppm. For σ -complexes, with Li^+ in the deshielding region of the anion, a downfield shift with respect to the solvent separated ion pairs can be expected.

In Table 1 the ^7Li chemical shifts of some anions in various solvents have been summarized (20). From these data it is clear that for FlH^- in THF a

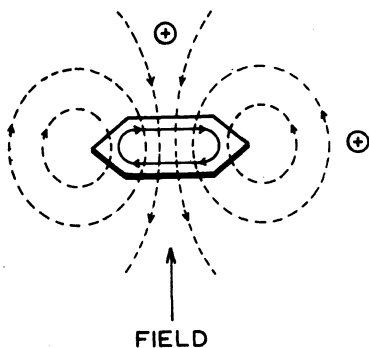


Fig. 12. The shielding and deshielding of a cation in a π - and σ -type contact ion pair.

TABLE 1. ^7Li NMR chemical shifts of some anions in various solvents, expressed in ppm relative to 1 mol/l aqueous LiCl

anion	solvent	chemical shift
Idl^-	MTHF	-0.55
	THF	-0.47
	DME	-0.16
	DG*	-0.13
Cb^-	MTHF	-0.71
	THF	-0.62
	DME	-0.10/-0.13 ^{a)}
FlH^-	THF	-1.88/+2.07 ^{b)}
	Et_2O^*	+6.95 ^{b)}

* DG = Diglyme; Et_2O = Diethylether

a) from ref. 17

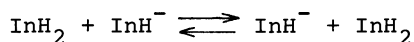
b) from ref. 18 & 19

solvent separated ion pair predominates. The large upfield shift in Et_2O proves that FlH^- in this solvent is present as a π -complex. For Cb^- and Idl^- the ^7Li chemical shifts indicate a coordination between Li^+ and the nitrogen lone pair, thus forming a σ -complex. These data affirm the assumption made to explain the fluorescence ion pair shift of Cb^- : Both for Cb^- and Idl^- the ^7Li nuclei are more deshielded in MTHF and THF than in DME and DG. A stronger external solvation of the cation in the latter two solvents may cause this difference.

PROTON EXCHANGE REACTION BETWEEN INDENE AND INDENYL

In the foregoing sections we have considered the ion pair formation in ground and first excited singlet states and the structures of the contact ion pairs.

It is well-known that the various types of ion pairs can also be distinguished by their reactivities in chemical reactions (1 & 3). We have observed such a difference for the symmetrical proton exchange reaction between indene and indenyl (23).



In general the reaction rate can be studied from the exchange line broadening. In the low temperature region, where the exchange is very slow, the NMR spectra of mixtures of InH_2 and InH^- are superpositions of the spectra of the components (see Fig. 13). The temperatures, at which line broadening becomes visible, depend on the InH_2 concentration and the solvent used. For the polar solvent HMPT the exchange line broadening starts already at about 40 °C (see Fig. 13). The reaction rate amounts to about 10 l mol⁻¹ s⁻¹. In the ethereal solvents DME and DG the reaction proceeds more slowly and line broadening becomes detectable only above respectively 180 and 150 °C. This specific solvent effect may be correlated with ion pairing phenomena. The enhanced reaction rate in the strong polar solvent HMPT might be attributed to the presence of free solvated ions or solvent separated ion pairs.

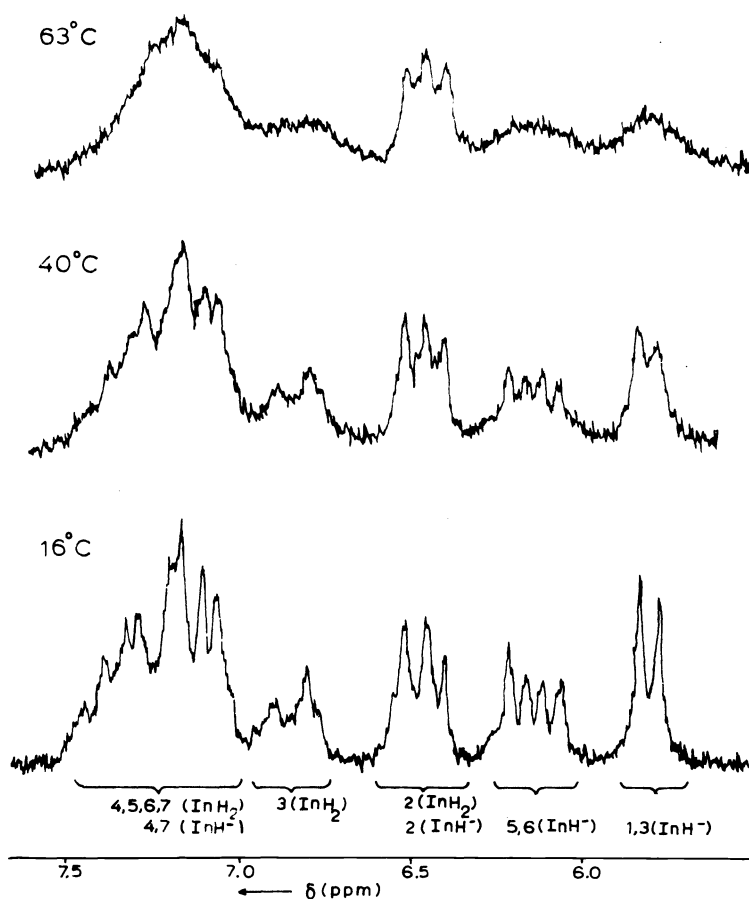


Fig. 13. The 60 MHz ^1H NMR spectra of a mixture of InH_2 (0.64 mol/l) and InH^- (0.44 mol/l) in HMPT at three temperatures. Chemical shifts are denoted in ppm from TMS.

CONCLUDING REMARKS

Optical and NMR spectroscopy are useful techniques to study ion pair formation of cyclic conjugated anions and alkali ions. In ethereal solvents nitranions form exclusively contact ion pairs in ground and first excited singlet states, whereas carbanions can be present both as contact and solvent separated ion pairs. The percentage of solvent separated ion pair is for FlH^- and MH^- larger in the excited state than in the ground state. For the relative small delocalized system InH^- the formation of contact ion pairs is favoured. The conversion of solvent separated ion pairs into contact ion pairs is accompanied with a blue shift in the absorption spectra and a blue or red shift in the fluorescence spectra. The direction and the absolute value of the displacements depend on the extent of localization of the negative charge and the area of charge localization in ground and first excited singlet states. The size of the alkali ion influences the absolute values; the shifts increase in the order K^+ , Na^+ , Li^+ . The position of the alkali ion with respect to the anion can be predicted from calculated π -electron charge densities. NMR measurements reveal that the contact ion pairs of the carbanions are π -type complexes and of the nitranions σ -type complexes. The introduction of an oxygen or sulphur atom in the central ring of FlH^- , resulting in the heterocyclic carbanions XH^- and TxH^- , does not have an important influence on the ion pairing properties. The less "aromatic"

character of the $4n \pi$ -electron systems XH^- and TxH^- is reflected in the strong high field displacements of all proton chemical shifts in comparison with those of FlH^- .

From a 1H NMR study in various solvents it has been derived, that ion pairing may have an effect on the reaction rate of the proton exchange reaction between indene and indenyl.

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