Indolyl Alkali-metal Ion Pairs in the Excited State. Part 2.[1] The Influence of Temperature on the Position of the Counterion

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The structures of the fluorescent ion pairs of indolyl (Idl^-) alkali-metal salts in 2-methyltetrahydrofuran (MTHF) as a function of temperature have been elucidated on the basis of the absorption and fluorescence ion-pair shifts. For the determination of these shifts the complex of IdlK with the cryptand [2.2.2] has been used as a reference system. From the values of the ion pair shifts and the Stokes shifts it has been concluded that at −180 °C the emitting Li^+, Na^+, and K^+ ion pairs have a σ-type structure. At this temperature the solvent-excited solute relaxation of Idl^- in the first excited singlet (S_1) state is slow on the fluorescence time scale so that the counterion cannot change its position before emission occurs. The temperature dependence of the fluorescence band position strongly suggests that for Idl^-, Li^+ this relaxation only involves a reorientation of the neighbouring solvent molecules, but that for Idl^-, Na^+, and Idl^-, K^+ intramolecular migration of the counterion takes place simultaneously. The 'stable' ion pair structure in the S_1 state is a σ-complex for Idl^-, Li^+, but a π-complex for Idl^-, Na^+, and Idl^-, K^+. The possible positions for the counterion in the π-complexes have been discussed and for this purpose also the ion-pair shifts of the 7-methylindolyl salts have been measured.

THE structure of ion pairs consisting of aromatic carbanions and alkali-metal cations have been the subject of many spectroscopic studies.[2,3] Both optical and n.m.r. spectroscopy have been used as tools to investigate ion pair formation. A great number of papers has appeared on ion pair structures in the *ground state*; considerably fewer reports are concerned with ion pair structures in the *excited state*.

Among others, studies on the ion pairs of fluorenyl anion (FlH^-), indenyl anion (InH^-), and their aza-analogues, carbazolyl anion (Cb^-) and indolyl anion (Idl^-), in the excited state have been published.[1,4-6] It has been shown [1,4] that the experimental data can be conveniently interpreted on the basis of the absorption and fluorescence ion pair shifts, defined as the displacements of the absorption with respect to the fluorescence band positions on formation of a contact ion pair from a solvent-separated ion pair, and of calculated π-electron charge densities. For the carbocyclic aromatic systems the absorption ion-pair shifts are towards blue, whereas the fluorescence ion-pair shifts are in the opposite direction. On the contrary, for Cb^-, the aza-analogue of FlH^-, the absorption and fluorescence ion pair shifts are in the same direction, *i.e.* towards blue. In all cases the shifts increase in the order K, Na^+, Li^+. It has been concluded [1,4] that, in the carbocyclic aromatic systems mentioned, in the ground state the counterion is located above the five-membered ring, but in the excited state above the six-membered ring. For Cb^- both in the ground and excited states the counterion is co-ordinated with the nitrogen lone pair electrons of the anion, thus forming a σ-type complex.

The spectra of Idl^-, the aza-analogue of InH^-, display some interesting features.[1] Whereas the absorption ion-pair shifts are towards blue in the order $Li^+ > Na^+ > K^+$, the fluorescence ion-pair shifts are, probably, towards blue for Li^+, but towards red for Na^+ and K^+ and in addition, the shift is larger for K^+ than for Na^+. Furthermore, although there is no change from a contact ion pair to a solvent-separated ion pair in the ethereal solvents used, the fluorescence band positions of the latter two salts strongly depend on temperature. In Part 1,[1] only a preliminary interpretation of the results could be given, as the values for the fluorescence ion-pair shifts of Idl^- were not available. It has been suggested that in the first excited singlet (S_1) state for IdlNa and IdlK two types of contact ion pair occur, *i.e.* σ- and π-type complexes, whereas in the ground (S_0) state, as for Cb^-, only σ-type complexes are formed. In the present study a more detailed investigation of the alkali-ion pairs of Idl^- and 7-methylindolyl ($MeIdl^-$) in 2-methyltetrahydrofuran (MTHF) is reported.

EXPERIMENTAL

The indolyl and 7-methylindolyl alkali-metal salts in MTHF (*ca.* 10^{-3} mol dm^{-3}) and in hexamethylphosphoric triamide (HMPT) have been prepared as described elsewhere.[7,8] The [2.2.2] cryptates of IdlK and MeIdlK have been obtained by adding *ca.* 4.10^{-3}M-cryptand [2.2.2] dried on the vacuum line by gentle heating *in vacuo* to the corresponding potassium salts.

Details of the absorption and fluorescence spectrometers have been given previously.[9] In the fluorescence equipment a quartz instead of a flint-glass prism has been used because of the low response of the latter at the shortest wavelengths of operation. The fluorescence band position was set equal to the mean values of the wavenumbers at half-peak height, thus eliminating the influence of differences in the band structure. As a result there is a systematic shift in fluorescence band position with respect to those reported in Part 1[1] of *ca.* 400 cm^{-1}, but the general features of the temperature dependence are not affected.

RESULTS

In Figure 1 absorption spectra of IdlK at room temperature are presented. It is obvious that the addition of cryptand [2.2.2] affect the spectrum in MTHF considerably, which suggests the formation of a cryptate denoted as $Idl^-[2.2.2]K^+$. This is supported by the observation that its spectrum strongly resembles the spectrum of the free solvated anion Idl$^-$ in HMPT (Figure 1b). Although the absorption of the solvent HMPT slightly disturbs the spectrum of IdlK, it is clear that the positions of the maxima in Figures 1b and c are equal within experimental accuracy.

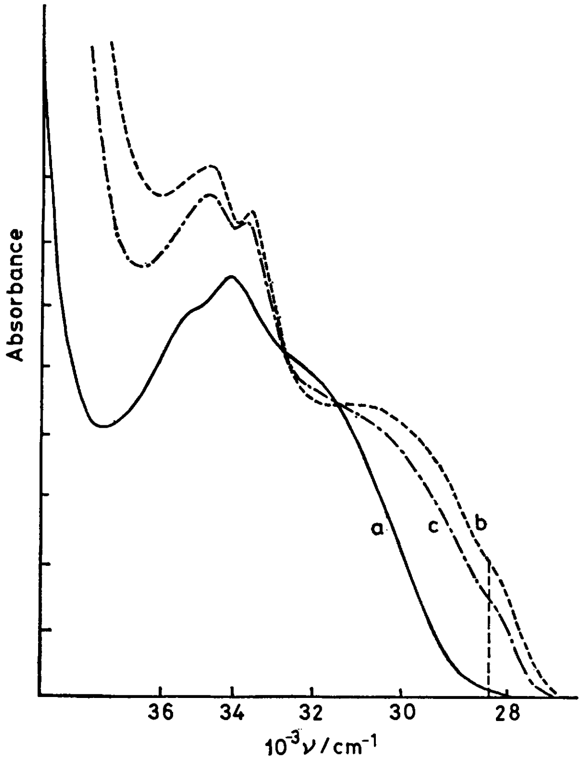

FIGURE 1 Absorption spectra of *ca.* 10^{-3}M-IdlK at room temperature (a) in MTHF, (b) in HMPT, (c) in MTHF after addition of *ca.* 4.10^{-3}M-cryptand[2.2.2]

Figure 2 shows the temperature dependence of the fluorescence band position for the salts Idl–Li, –Na, and –K and for the complex Idl$^-$[2.2.2]K$^+$ in MTHF in the range -180 to $+20$ °C. Dilution to 10^{-4}M does not affect the results. As will be argued later, Figure 2 additionally gives the fluorescence ion-pair shifts for Li$^+$, Na$^+$, and K$^+$ as a function of temperature since the points of zero shift are represented by the curve of Idl$^-$[2.2.2]K$^+$.

The shape of the fluorescence spectra also depends on temperature. Whereas above -140 °C a structureless band is observed, at lower temperatures the spectra show some structure and at -180 °C three or four maxima are clearly visible (see Table 1). The corresponding Stokes shifts and ion pair shifts in absorption and fluorescence are given in Table 2.

TABLE 1

Fluorescence spectral maxima of indolyl alkali-metal ion pairs in MTHF at -180 °C (10^{-3} ν/cm^{-1})

Li$^+$	29.5	28.2	27.3	
Na$^+$	29.1	27.8	27.0	
K$^+$	28.8	27.6	26.6	
K$^+$ [2.2.2]	28.1	26.9	25.9	24.5

The fluorescence quantum yields ϕ_f for the systems under study are independent of the counterion and temperature from -180 to -60 °C (they gradually decrease at higher temperatures) within the experimental accuracy of ± *ca.* 10%. The same holds for τ_f as $\phi_f = k_f^\circ \cdot \tau_f$, where k_f° is the intrinsic radiative rate constant.

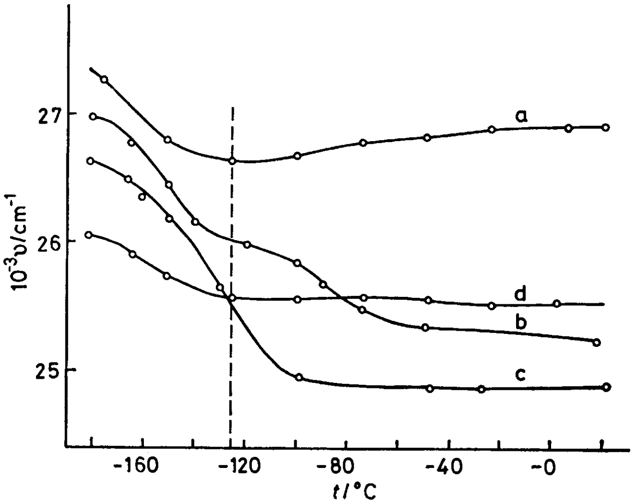

FIGURE 2 Temperature dependence of the fluorescence band position of Idl$^-$ in MTHF with (a) Li$^+$, (b) Na$^+$, (c) K$^+$, and (d) K$^+$[2.2.2]

For 7-methylindolyl salt analogous results have been obtained. The absorption spectrum of MeIdl$^-$[2.2.2]K$^+$ is identical with the spectrum of MeIdlK in HMPT. The fluorescence band positions as a function of temperature are depicted in Figure 3. One striking difference with Figure 2 should be noted: at room temperature the order of the band

TABLE 2

Stokes shifts and ion pair shifts of indolyl (10^{-3} ν/cm^{-1}) at -180 °C

	Li$^+$	Na$^+$	K$^+$	K$^+$ [2.2.2]
0–0 Absorption transition	29.9 [a]	29.6 [a]	29.2 [a]	28.5
0–0 Fluorescence transition	29.5	29.1	28.7	28.1
Stokes shift	0.4	0.5	0.4	0.4
Absorption ion pair shift [b]	+1.4	+1.1	+0.7	0
Fluorescence ion pair shift [b]	+1.4	+1.0	+0.6	0

[a] Reported in Part 1.[1] [b] The positive sign indicates a blue shift.

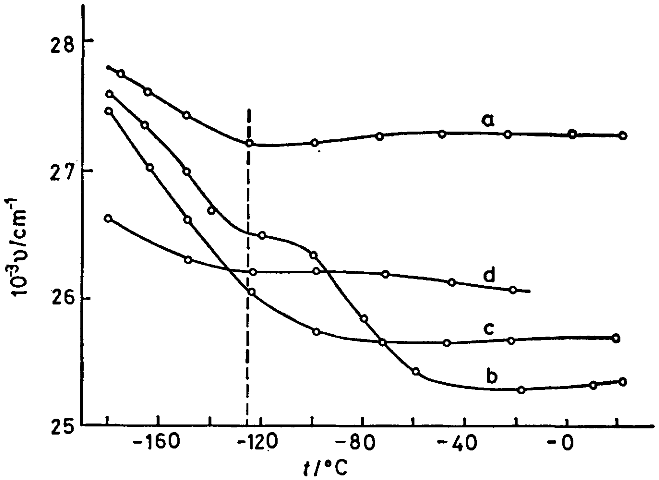

FIGURE 3 Temperature dependence of the fluorescence band position of MeIdl$^-$ in MTHF with (a) Li$^+$, (b) Na$^+$, (c) K$^+$, and (d) K$^+$[2.2.2]

positions for the MeIdl$^-$,Na$^+$ and MeIdl$^-$,K$^+$ ion pairs is reversed.

DISCUSSION

(1) Idl$^-$[2.2.2]K$^+$ *in MTHF as a Reference for the Ion Pair Shifts*.—In order to determine the absorption and fluorescence ion-pair shifts it is necessary to have a reference system in which the influence of the counterion on the spectroscopic features of the anion is negligible. The problem is that the anion Idl$^-$ exclusively forms contact ion pairs in ethereal solvents.[1] In principle, it is possible to use the spectra of the Idl$^-$ salts in HMPT as references, as in this solvent free ions are formed.* There are, however, some serious drawbacks. In the first place only spectra at temperatures above +10 °C are accessible. Secondly, the shapes of the emission spectra of Idl$^-$ in HMPT and MTHF are markedly different. In the former solvent the fluorescence band is far weaker and broader indicating that in HMPT the anion in the excited state interacts strongly with the polar HMPT solvent molecules. Therefore, we have used another reference system, Idl$^-$[2.2.2]K$^+$ in MTHF.

The observation that the positions of the maxima in the absorption spectrum of Idl$^-$[2.2.2]K$^+$ in MTHF at room temperature are equal with those of IdlK in HMPT, *i.e.* of the free solvated anion, implies that the *absorption* ion-pair shift of the cryptate in MTHF at room temperature can be neglected (see Figure 1). The same conclusion is justified for the absorption ion-pair shift of the cryptate at low temperatures since the tendency of ion pairs to be solvent-separated increases with decreasing temperature.

Also the *fluorescence* ion-pair shift of Idl$^-$[2.2.2]K$^+$ in MTHF will be zero. This is readily rationalized, since in the excited state in general the interionic interaction is smaller than in the ground state because the negative charge is more delocalized.[4]

(2) *The Stokes Shifts and the Ion-pair Shifts at* -180 °C.—The Stokes shifts and the absorption and fluorescence ion pair shifts at -180 °C are summarized in Table 2. It is found that the Stokes shifts for the three contact ion pairs and the cryptate are equal within experimental accuracy, and that the corresponding absorption and the fluorescence ion-pair shifts don't differ. These results show that the emitting ion pairs at -180 °C have a similar structure to the contact ion pairs in the ground state, which can be argued as follows.

It was concluded in Part 1,[1] partially on the basis of ^{7}Li n.m.r. experiments, that in the ground state the counterion is located in the molecular plane being coordinated with the nitrogen lone-pair electrons thus forming a σ-complex. Immediately after excitation the ion pair is in the Franck–Condon excited state. Thereupon, internal and external relaxation processes towards the ' stable ' excited state take place, in competition with the fluorescence process.† Hence, in order to acquire information about the *structure* of the emitting ion pair, the question has to be answered whether the counterion changes its position within the fluorescence lifetime or not.

If the ion-pair structures are modified before emission of radiation occurs the fluorescence and absorption ion-pair shift will significantly differ, while the magnitude of the difference will depend on the counterion.[4] From the data in Table 2 it follows that the Stokes shifts for the contact ion pairs and the cryptate are the same. Therefore we conclude that the counterions in the Li$^+$, Na$^+$, and K$^+$ ion pairs at -180 °C do not change their position within the fluorescence lifetime. In other words the emission originates from ion pairs with a σ-complex structure.

Of course, at -180 °C there are internal relaxation processes which are rapid on the fluorescence time scale. Furthermore, the reorientation of the surrounding solvent molecules may be partly realized within the fluorescence lifetime (see the following section). These processes may account for the Stokes shift of *ca.* 400 cm^{-1}, observed for the systems under study.

(3) *The Temperature Dependence of the Fluorescence Band Position*.—It is well known from the literature that the fluorescence band position of solutes in fluid solutions changes with temperature, since the difference between solute–solvent interactions in the ground and excited states depends on the dielectric constant of the medium.[10] Additionally, a peculiar influence of the temperature has to be expected if the dielectric relaxation time of the solvent, to which the relaxation time of the solvent-excited solute is related, has the same order of magnitude as the fluorescence lifetime.[11] For ethereal solvents such as MTHF this will only be realized at low temperatures where the viscosity of the solution is high.[11-14] In particular the shifts due to incomplete solvent-excited solute relaxation within the fluorescence lifetime are important for the interpretation of the temperature dependence of the fluorescence bands (see Figure 2).

It has been found that the solvent-excited solute relaxation for neutral solute molecules can be described adequately in terms of one relaxation parameter, provided that solvent quenching is absent.[12-14] Therefore it is appropriate to discuss its effect on the fluorescence band position on the basis of Figure 4, where the energy of the S_1 state is plotted as a function of time. For convenience, internal relaxation is left out of consideration so that $E(\mathrm{FC}) - E(S_1)$ gives the difference in solute–solvent interaction energy for the Franck–Condon state and the stabilized state. After τ_f seconds emission of radiation takes place, at temperature T_1 from energy level E_1, at $T_2 (T_2 > T_1)$ from $E_2 (E_2 < E_1)$, and at T_e-$(T_e > T_2)$ from the stabilized first excited singlet state $E(S_1)$. Thus, with the condition that the solute–solvent

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* Solvent-separated ion pairs and free solvated anions are spectroscopically indistinguishable.[2]

† By internal relaxation we understand the relaxation processes that occur after excitation of the free non-solvated anion in the gas phase, by external relaxation or solvent-excited solute relaxation the processes that involve the interaction of the anion with the counterion and with the surrounding solvent molecules.

relaxation time is comparable with τ_f a red shift of the fluorescence band occurs with increasing temperature, being completed at T_e.* It has been found that the solute–solvent relaxation time and thus T_e mainly depends on the solvent used and not on the solute, whereas the magnitude of the shift is determined by both solute and solvent.[11,12] Within this context it is worthwhile noticing that T_e is also a function of τ_f.

In the present study we are concerned with the solvent-excited solute relaxation of *charged* solute molecules. Each indolyl anion interacts not only with its surrounding solvent molecules but also, specifically, with its counterion. Upon excitation of the anion both interactions will change. Therefore two situations have to be distinguished: (i) only the surrounding solvent molecules reorient themselves in the solvent-excited solute relaxation process and (ii) in addition the counterion migrates to a new position thus changing the structure of the ion pair.

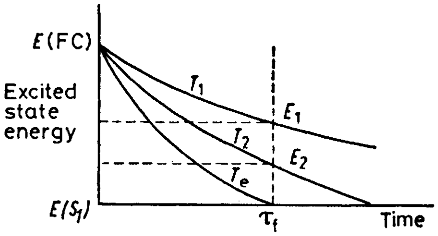

FIGURE 4 Schematic representation of the first excited singlet state energy as a function of time after excitation for different temperatures ($T_1 < T_2 < T_e$). τ_f is the fluorescence lifetime. E(FC) is the energy of the Franck–Condon first excited singlet state. $E(S_1)$ is the energy of the stabilized first excited singlet state

In the first case the description for a neutral solute molecule given in the preceding paragraph applies. In the second case instead of one relaxation time, two relaxation times will be necessary to describe the relaxation process. As a result, the value of T_e will depend not only on the solvent but also on the ion pair under consideration.

Since in MTHF at low temperatures τ_f will have the same order of magnitude as the dielectric relaxation time, the red shifts of the fluorescence bands with increasing temperature reflected by Figure 2 have to be attributed to solvent-excited solute relaxation. At −125 °C the shift for Idl$^-$[2.2.2]K$^+$ is *ca.* 500 cm^{-1} with respect to the position at −180 °C; above −125 °C no further shift is observed (T_e *ca.* −125 °C). In the same temperature region the Idl$^-$,Li$^+$ curve behaves similarly (total shift *ca.* 700 cm^{-1}). The curves of Idl$^-$,Na$^+$ and Idl$^-$,K$^+$, show different behaviour. The red shifts are larger (*ca.* 1 600 and 1 700 cm^{-1}, respectively) and in addition the corresponding T_e values are higher, T_e −50 and −90 °C, respectively. Furthermore, it should be noted that in the region around −125 °C the curvature for Idl$^-$,Na$^+$ is small.

It will be obvious that for Idl$^-$[2.2.2]K$^+$ with T_e *ca.* −125 °C predominantly the redistribution of solvent molecules plays a role. The cation–anion interaction is very small and the cryptand especially interacts with the cation.[2,15-18]

The T_e value found for Idl$^-$,Li$^+$ is also −125 °C. This strongly suggests that for the Li$^+$ ion pair, as for the cryptate, the shift arises from the displacement of solvent molecules, whereas the position of the cation does not change. From the magnitude of the shift (700 cm^{-1}) follows that the extent of solute–solvent interaction is somewhat larger than for Idl$^-$[2.2.2]K$^+$.

For the K$^+$ ion pair the redistribution of solvent molecules cannot be the only cause of the temperature dependence of the fluorescence band position. Both the magnitude of the shift (which is a factor of *ca.* 2.5 larger than for the Li$^+$ ion pair) and the values of T_e (−90 °C), which obviously deviates from −125 °C, indicate that in addition to the displacement of MTHF molecules the counterion migrates towards a position of more favourable cation–anion interaction with the excited anion.

Also for Idl$^-$,Na$^+$ the solvent-excited solute relaxation involves a cation migration process (T_e −50 °C). It is noteworthy that at −125 °C (the T_e value for the cryptate and the Li$^+$ ion pair, systems where counterion migration does not play a role) the slope of the curve (Figure 2b) is small. This suggests that at −125 °C the reorientation of solvent molecules is rapid on the fluorescence time scale whereas the cation migration process is too slow to be effective. Temperatures higher than −125 °C are needed to make the migration rate constant of Na$^+$ similar to the rate constant of fluorescence. At −50 °C also the cation motion is rapid on the fluorescence time scale so that for $T >$ −50 °C the emission originates from the completely relaxed S_1 state.

From the foregoing we conclude that the structure of the fluorescent Li$^+$ ion pair does not change essentially with temperature: as in the ground state, in the excited state a σ-type complex is present. The reverse is true for Idl$^-$,Na$^+$ and Idl,K$^+$. Apparently, for these ion pairs the σ-complex structure, stable in the ground state, is unstable in the excited state.

An alternative explanation for the influence of temperature on the Idl$^-$,Na$^+$ and Idl,K$^+$ fluorescence bands may be the existence of a strongly temperature dependent equilibrium between the σ- and π-type ion pairs.[1] This would mean that at temperatures where the σ- and π-complexes are present in comparable amounts, significant broadening of the fluorescence band is to be expected. However, such broadening has not been observed.

(4) *The Ion-pair Structures in the Excited State.*—From the preceding subsection it is clear that for the systems under study the fluorescence at room temperature originates from ion pairs which are completely stabilized in the excited state before emitting radiation (room temperature $\gg T_e$). The values for the fluorescence ion

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* It should be realized that Figure 4 does not reflect the shift of the fluorescence band position but only the change in excited state energy. For the experimental shift additionally the ground state has to be considered.

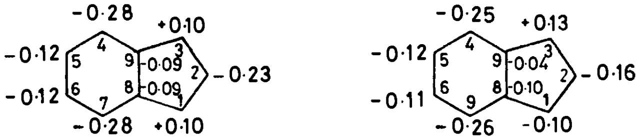
pair shifts at this temperature, taken from Figure 2, are $+1\,350$, -250, and -650 cm^{-1} for Li$^+$, Na$^+$, and K$^+$, respectively. It is interesting to compare these values with those at -180 °C (see Table 2).

The shift found for Idl$^-$,Li$^+$ is similar both in direction and magnitude to the shift at -180 °C. This supports the foregoing conclusion that in the excited state the stable configuration over the whole temperature range is of σ-type.

For the Na$^+$ and K$^+$ ion pairs the fluorescence ion-pair shifts at room temperature (red shifts) are opposite to the fluorescence shifts at -180 °C (see Figure 2). This shows that in the excited state the σ-complex is not stable, as has also been concluded from the solvent-excited solute relaxation process.

It was outlined in Part 1 [1] that the type of complex that an aza-aromatic anion forms is determined by competition between the π-system and the lone-pair dipole in attracting the cation. Apparently in the excited states of Idl$^-$,Na$^+$ and Idl$^-$,K$^+$ the interaction with the π-system outweighs the influence of the lone pair, so that π-complexes are obtained. At first sight it is expected that the location of the counterions in the π-complexes will be the same as in the corresponding excited carbocyclic ion pairs InH$^-$,Na$^+$ and InH$^-$,K$^+$. The experimental results do not support this expectation: the red fluorescence shift for Idl$^-$,K$^+$ is larger than for Idl$^-$,Na$^+$, a finding not in line with the general rule that larger cation effects are observed for smaller counterions.[2]

In order to explain this result, it should be realized, that the charge distributions of Idl$^-$ and InH$^-$ differ significantly. In the first place the π-densities are affected by the heteroatom (see Figure 5). Secondly, the presence of the lone pair electrons in Idl$^-$ may be important for the cation–anion interaction not only in a σ- but also in a π-complex. For Idl$^-$ we expect that, in addition to a position above the six-membered ring (the cation position in indenyl ion pairs) a position somewhere near the centres (C-1, -8, and -7 will also be favourable for a counterion. The last position will be less suitable when a methyl group is substituted at C-7. Therefore we have also determined the fluorescence ion pair shifts of MeIdl$^-$ (see Figure 3).



InH$^-$ Idl$^-$

FIGURE 5 π-electron charge densities of InH$^-$ and Idl$^-$ in the first excited (S_1) state [1,4]

The strong resemblance of Figures 2 and 3 is obvious: apparently the methyl group does not fundamentally affect the interionic interaction so that the MeIdl$^-$ ion pairs can be considered as slightly perturbed Idl$^-$ ion pairs. However, this small perturbation is sufficient to reverse the order of the fluorescence ion-pair shifts of the Na$^+$ and K$^+$ ion pairs at room temperature. For MeIdl$^-$ the Na$^+$ ion-pair shift is larger than the K$^+$ ion-pair shift, -750 and -350 cm^{-1}, respectively. This result supports the interpretation outlined in the preceding paragraph. In the π-type MeIdl$^-$ complex only one position (above the six-membered ring) is available, whereas in the π-complexes Idl$^-$,Na$^+$ and Idl,K$^+$ the counterions are located in different positions. Unfortunately, both the Na$^+$ and the K$^+$ fluorescence ion-pair shifts are influenced by the methyl substitution, so that it is not possible to establish whether in the Idl$^-$ ion pairs Na$^+$ or K$^+$ is located near C-1, -8, and -7. In view of the structure of Idl$^-$,Li$^+$ we suppose that this position will be more favourable for the smaller cation, *i.e.* for Na$^+$.

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