

1,9-Dithiophenalenylium Hexafluorophosphate (4a PF₆⁻). 9-Ethoxyphenalenone (7, 4.26 g) was dissolved in 75 mL of carbon disulfide and 8 g of phosphorus pentasulfide (twice recrystallized from carbon disulfide by the Soxhlet method) was added. The mixture was held at reflux for 30 min and then the carbon disulfide removed by evaporation. HCl (4 M, 50 mL) was added to the residue and the mixture was refluxed for 15 min and then filtered. A solution of sodium hexafluorophosphate (4 g in 40 mL of water) was added to the filtrate, and the precipitate isolated by filtration. The solid was dried, dissolved in acetonitrile, and recrystallized by addition of ether to give 1.28 g of orange solid (18%).

4a PF₆⁻: mp 261.3–261.7 °C dec; ¹H NMR (δ, CD₃CN) absorption range 8.1–8.9, AB pattern (intensity 4), δ_A 8.44, δ_B 8.71 (*J*_{AB} = 9 Hz), AB₂ pattern (intensity 3), δ_A 8.23, δ_B 8.74 (*J*_{AB} = 8 Hz); IR (cm⁻¹, CsI) 3060 (w, br), 1611 (s), 1584 (s), 1548 (s), 1474 (m), 1407 (vs), 1354 (w), 1316 (s), 1307 (s), 1289 (s, sh), 1243 (s), 1199 (m), 1172 (s), 1160 (m), 1127 (s), 1087 (vw), 1063 (w), 991 (w), 940 (vw), 900–800 (vs, br), 796 (m, sh), 676 (s), 554 (vs), 497 (w), 478 (m), 387 (vw), 362 (m), 298 (vw); UV [nm (ε), CH₃CN] 213 (32 600), 226 (31 800), 258 (7400, sh), 281 (9400), 343 (5600), 420 (21 600, sh), 439 (30 800). Anal. Calcd for C₁₃H₇S₂PF₆: C, 41.94; H, 1.90; S, 17.23. Found: C, 42.14; H, 1.71; S, 17.42. Semiquantitative X-ray spectrochemical analysis gave an S:P ratio of about 2:1.

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Ion Pairing in Excited States of Carbanions. 2. Emission of Fluorenyl and Fluoradenyl Alkali Salts in Aprotic Media

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Abstract: The UV/visible absorption and emission and excitation spectra of alkali salts of fluorene (FIH) and fluoradene (FdH) were measured in a series of low dielectric constant ethereal solvents in or without the presence of crown ethers. For a series of tight ion pairs the absorption and emission wavelength maximum increased and decreased, respectively, with increasing cation radius. The spectroscopic results for LiF/THP, NaF/THF, and NaFd/THF are consistent with the existence of an equilibrium between contact and solvent-separated ion pairs in the first excited state. The fraction of separated ion pairs in the first excited states was found to increase as THP < THF < DME similar to the ground states. The proportion of separated ion pairs was also invariably found to be higher in the first excited state than in the ground state. It was found that the relative stabilities of the two ion pairs in ground state and first excited states could be quantitatively related through a Förster cycle. Dissociation of contact ion pairs into free ions could be easily observed in emission and excitation spectra of the NaF/THF and NaFd/THP systems. Cation and solvent effects on lifetime of these salts were also examined. Na, K, and Rb contact ion pairs of FI⁻ in THP were shown to have similar lifetimes and emission intensities whereas the Cs ion pair is shorter lived presumably owing to a heavy atom effect. Separated ion pairs and free ions were shown to be longer lived and to emit most intensely.

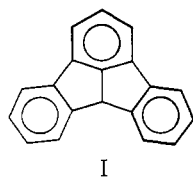
Introduction

Over the last few years there has been a considerable interest in the photochemistry of ionic intermediates.² Much experi-

mental work has been done but not much is known regarding the detailed nature of the postulated ionic intermediates. The behavior of excited-state carbanions has been described by Burley and Young,³ Vander Donckt et al.,⁴ Vos et al.,^{5,6} and

Hogen-Esch and Plodinec,^{7,8} but a systematic investigation of the effect of ion pairing on the emission of excited-state carbanions has only recently begun.^{6,7} In a previous communication we have described several interesting ion-pair effects observed in ethereal solutions of fluorenyl alkali salts.⁷ This carbanion has provided the first direct evidence for the existence of two types of ion pairs in ethereal solutions⁹ and has since been intensively studied by a variety of techniques.^{10,11} Much is now known regarding its ion pairing in the ground state as a function of parameters such as temperature, pressure, concentration, cation, and solvent. Therefore a study of the ion pairing in the excited state of this carbanion has the obvious potential of providing information relating ion-pairing properties of ground- and excited-state carbanions.

The present study deals with the influence of several of the above parameters on ion pairing of the first excited state of the fluorenyl (Fl^-) and fluoradenyl¹² (Fd^-) carbanion (I) and has several objectives: (1) the exploration of the applicability of the ion pair concept to the first excited state of these anions; (2) an examination of the differences between ground and excited states of ion pairs and the role therein of cation and solvent; (3) the investigation of the question whether emission data may reflect in whole or in part the state of ionic association of the ground state. This might, for instance, be the case if the excited state-ground state transition processes were fast compared to excited state relaxation processes such as dissociation or ion solvation. Finally an examination of the effect of ion pairing on the various modes of deexcitation, i.e., quenching and radiative emission, seemed of interest. In the following we wish to report such a study on the emission of the Li, Na, K, and Cs salts of the Fl^- and Fd^- carbanions in low dielectric constant ethereal solvents such as THF, tetrahydropyran (THP), dimethoxyethane (DME), and dioxane in and without the presence of crown ethers.



Experimental Section

Preparation and Purification of Sample System. Tetrahydrofuran (THF), tetrahydropyran (THP), and 1,2-dimethoxyethane (DME) were purified by refluxing over sodium-potassium alloy for about 12 h, then distilled onto fresh alloy. A small amount of benzophenone was added, and the resultant purple dianion solution degassed on a vacuum line.

Dioxane was refluxed over CaH_2 for approximately 12 h, then fractionally distilled and sodium-potassium alloy was added. A small amount of fluorenone was added, and the resultant green solution degassed on the vacuum line.

Toluene and *n*-propylamine (*n*-PrNH₂) were stirred over CaH_2 for 12 h, distilled under vacuum onto fresh CaH_2 , stirred, degassed, then distilled under vacuum and degassed again.

Acetonitrile was stirred over CaH_2 for 12 h, distilled under vacuum onto P_2O_5 , stirred for 12 h, and distilled again under vacuum into an ampule of lithium fluorenyl.

Fluorene was recrystallized from absolute ethanol (mp 115–116 °C, lit. 116 °C), fluoradene from hexane (mp 129–130 °C, lit. 130 °C).

Fluorenyl and fluoradenyl salts were prepared from the corresponding salts of the 1,1,4,4-tetraphenylbutane dianion, usually in THF, which were available in the laboratory. Transfer of the salt to other solvents was achieved by evacuating the THF solution to ultimate vacuum (about 10^{-7} Torr), distilling the desired solvent onto the salt under vacuum, mixing, reevacuating, then adding more of the solvent desired. As an extra precaution, solvents purified by the various means above were usually added to a dry salt sample. If there was any decoloration of the salt, the solvent was repurified. If not, the solvent

was distilled from the solution to the salt sample of interest, under vacuum.

All solutions were stored under vacuum in ampules equipped with break-seals. When not in use, all samples were kept in a freezer at -20 °C, where they usually were stable.

The crown ether used was dicyclohexyl-18-crown-6, obtained from Dr. H. K. Frensdorff of E. I. du Pont de Nemours Elastomers Department, and recrystallized from petroleum ether. Later samples were recrystallized from acetonitrile and stored under vacuum.

Reagent grade sodium tetraphenylboride was purified according to a modification of the method of Skinner and Fuoss,¹³ as follows. The salt was partially dissolved in an 8:1 mixture of methylene dichloride and acetone. The solution was filtered and toluene added until a white precipitate started to appear. The mixture was then immersed in a dry ice-2-propanol bath, and the white precipitate collected on filter paper. The solid was placed in an ampule and dried on the vacuum line for approximately 2 h.

Spectral Measurements. Salt samples were usually prepared at a concentration of about 10^{-2} M, in the following manner. After the apparatus was built (all glass except for the quartz optical cells and the spacer), it was attached to the vacuum line, flamed, evacuated to about 10^{-7} Torr, and sealed from the line. The absorption spectrum of the resulting solution was taken with a Beckman Acta V, in the range 325–600 nm, in the 2-mm cell with or without a 1.8- or 1.9-mm spacer, to determine the concentration.

Dilutions of the sample were accomplished by pouring most of the solution into the side bulb, and distilling solvent back into the cell by application of a cold dauber. Concentrations less than 10^{-2} M could be calculated from the visible and near-ultraviolet spectrum and known extinction coefficients.

Fluorescence emission and excitation spectra were taken on a Perkin-Elmer MPF-2A spectrofluorimeter in the ratio record mode.

In all cases the possible excitation wavelength dependence of the emission spectrum and the emission wavelength dependence of the excitation spectrum were carefully checked. With few exceptions (see Results) no such dependence was found. Lifetimes were measured on a TRW nanosecond decay time fluorometer, using a pulsed nitrogen lamp and a Tektronix 556 dual-beam oscilloscope with two 1A1 plug-in dual-channel amplifiers.

The values given here represent the lifetimes obtained from at least two different concentrations of the same salt (except for cesium fluorenyl, which was anomalous). The accuracy of the lifetimes of the fluorenyl salts is probably much less than that of the fluoradenyl salts for the following reasons. In the systems studied, there was always residual hydrocarbon present, either fluorene or fluoradene. However, there was never any evidence of the formation of an excimer of fluorene, meaning that the output signal of the irradiated solution always contained a component attributable to the hydrocarbon. For the salts of fluorene with lower lifetimes, this was a major source of error. Thus, the data are considered to be no better than 10% and probably no worse than 25%, with the longer lifetime salts being most accurate. For the fluoradene salts, however, the accuracy was probably nearer 10%, since, in the solvents examined, there was very little hydrocarbon monomer emission. The fluoradene hydrocarbon mainly emitted through an excimer state of much lower intensity, relative to the fluoradenyl salt emission.

Relative intensities were obtained either by comparison of peak height to an internal standard, the crown ether separated or solvent-separated ion pair, for instance, or by comparison of peak heights between two different salt solutions at known concentrations. This is a less accurate procedure than the former, since different samples might have different concentrations of quenching impurities. However, results obtained in this manner were reproducible to within 20%.

Implicit in the above work for the fluorenyl ion pairs was the assumption that there was no difference between an solvent-separated ion pair and a crown ether separated ion pair. To check this, a solution of fluorenylsodium in DME (containing predominantly solvent-separated ion pairs) was prepared, and its fluorescence spectrum compared to that of the same solution to which a slight excess of crown ether had been added. There was no difference in terms of peak position (528 and 568 nm for both) or peak heights.

Results and Discussion

Typical emission and absorption spectra of fluorenyl (Fl^-) and fluoradenyl (Fd^-) sodium salts in tetrahydropyran (THP)

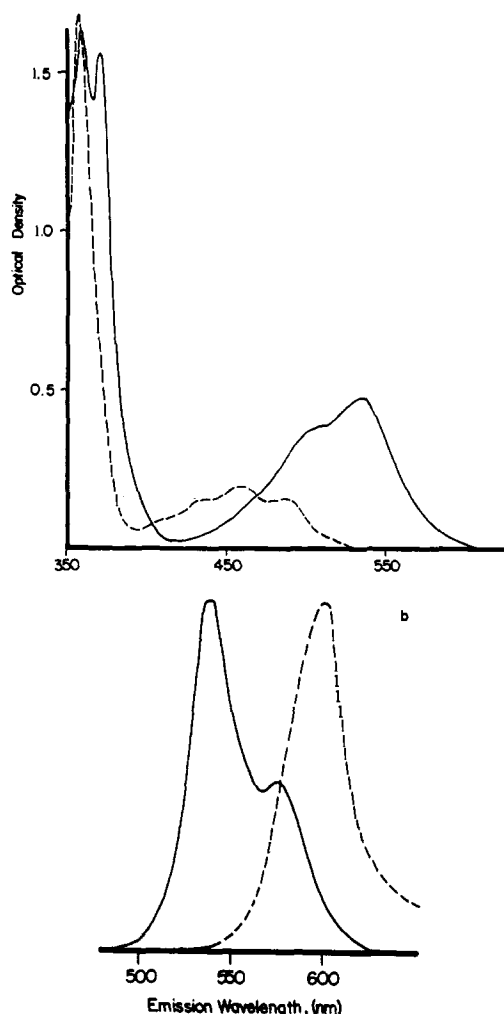


Figure 1 (a). Absorption spectra of fluorenyl- (---) and fluoradenylsodium (—) in THP at about 10^{-4} M. (b) Emission spectra of fluorenyl- (—) and fluoradenyl- (---) sodium salts in THP: $[\text{NaFl}] = 4.10^{-5}$ M, $[\text{NaFd}] = 1.3 \times 10^{-4}$ M.

are shown in Figure 1. The emission spectra of fluorenyl salts in THP and THF display two peaks approximately 30 nm apart while the Fd^- spectra only show a singlet. It is unlikely that the fluorenyl doublet represents two different species since a similar doublet appears for all salts. Moreover, the relative intensity of the two bands is independent of the mode of preparation of the sample, does not depend on the addition of common cation, and is concentration (10^{-4} – 10^{-7} M) and solvent independent. For these reasons it was concluded that the doublet arose from emission from the first excited state into two vibrational levels of the electronic ground state. Additional evidence for this lies in the fact that according to Berlman¹⁴ the parent hydrocarbon fluorene also has two peaks in its fluorescence spectrum. Also the separation of the two peaks (at least below 10^{-3} M) is constant at $1240 \pm 10 \text{ cm}^{-1}$ near where the hydrocarbon¹⁵ and fluorenylcalcium chloride¹⁶ have been reported to have a vibration of appropriate symmetry to couple with the electronic transition (1277 and 1219 cm^{-1} , respectively). At higher concentrations (10^{-4} – 10^{-2} M) regardless of cation both the position and relative intensity of the emission and excitation spectrum are concentration dependent (Figure 2). However, both emission and excitation spectra become concentration independent below 10^{-4} M for Fl^- and below 10^{-5} M for Fd^- .⁴¹ These phenomena can be attributed to reabsorption and inner filter effects for emission and excitation, respectively.¹⁷ For instance, it can be shown,¹⁸ that the change

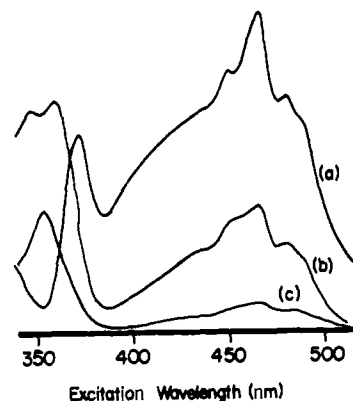


Figure 2. Effect of concentration of excitation spectrum of fluorenylsodium in THP at 25 °C: (a) $[\text{NaFl}] = 1 \times 10^{-3}$ M, (b) $[\text{NaFl}] = 2 \times 10^{-4}$ M, (c) $[\text{NaFl}] = 4 \times 10^{-5}$ M.

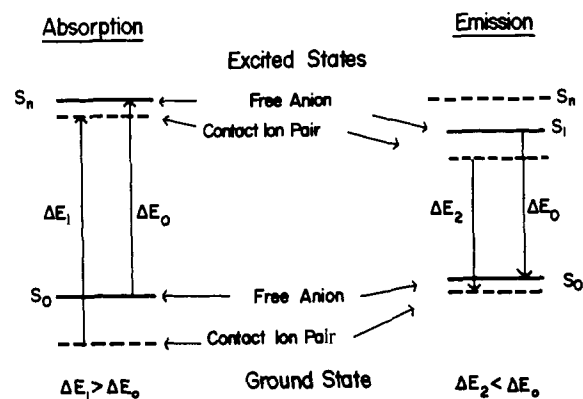


Figure 3. Effect of cation on the absorption and emission spectra of contact ion pairs.

of excitation spectrum with concentration is that expected for the salt assuming this inner filter effect.¹⁹

Effect of Cation. The emission and absorption maxima of the alkali salts of the fluorenyl and fluoradenyl anion in THP are shown in Table I. The Na, K, Rb, and Cs salts in the ground state all have been shown to exist predominantly as contact ion pairs in this solvent and show a regular decrease of absorption wavelength maximum with decreasing cationic radius. These blue shifts have been explained as due to a stabilization of ground state with respect to excited state.^{9,10} This greater ground-state stabilization in turn has been rationalized by greater excited-state charge delocalization and by a Franck-Condon type effect in which the cation is not able to adjust to the changed charge distribution during the very fast ($<10^{-15}$ s) electronic transition (Figure 3).

A reverse effect may be anticipated for emission of a series of first excited state contact ion pairs. Hence greater cation-induced stabilization of the excited state relative to the ground state is possible.²⁰ For the Fl^- and Fd^- type anions the magnitude of the emission shift caused by such an effect may be expected to be smaller than the corresponding shift in absorption maximum since the stabilization of the highly delocalized first excited state of these type anions is probably less than for the more localized ground state. The data are consistent with this description and show moderate emission red shifts of 5 and 10 nm for the Fl^- and Fd^- anion in going from Cs to Na counterion. A plot of reciprocal cation radius vs. wavenumber is seen to be approximately linear for emission of the Fl^- and Fd^- anions (Figure 4). Such a linear relation was also previously found for the absorption of the Fl^- and Fd^- anions.^{10,18} Thus the data clearly show the existence of contact

Table I. Emission and Absorption Maxima and Ion Pairing in Ground and Excited States of Fluorenyl and Fluoradenyl Alkali Salts in Tetrahydropyran at 25 °C

salt	λ_{\max} , nm absorption	ion pairing ^a ground state	λ_{\max} , nm emission	ion pairing excited state
LiFl	349, 373	70% C	528	S
NaFl	356, 373 ^b	C	538	C
KFl	362	C	535	C
RbFl	363	C	534	C
CsFl	364	C	533	C
[Na(K)CE]+Fl ^f	373	S	528	S
LiFd	369, 388	S	580	S
NaFd	359, 371	C	585-600 ^c	C/F
NaFd	359, 371	C/F	580 ^d	F
KFd	361, 374	C	594	C
CsFd	367, 378	C	590	C
[Na(K)CE]+Fd	369, 388	S	580	S
Fd ^{-e}	369, 388	F	580	F

^a C = contact, S = separated ion pair, F = free ion. ^b Shoulder. ^c Concentration and added salt dependent; excited at 359 nm (see text). ^d Excited at 389 nm at concentrations below 8×10^{-5} M. ^e Observed below 10^{-6} M. ^f Slight excess of dicyclohexyl-18-crown-6 added.

Table II. Absorption and Emission Maxima and Ion Pairing in Ground and First Excited State of Fluorenyl-Alkali Salts at 25 °C^a

salt/solvent	λ_{\max} , nm absorption	type ^a ion pair	λ_{\max} , nm emission	type ion pair
LiFl/dioxane	346	C	545	C
LiFl/THP	349, 373	70% C	528	S
LiFl/THF	349, 373	20% C	528	S
LiFl/DME	373	S	528	S
NaFl/dioxane	354	C	540	C
NaFl/THP	356	C	538	C
NaFl/THF	356, 373	95% C	532	40% C
NaFl/THF ^b	373	F	528	F
NaFl/DME	356, 373	20% C	528	S
NaFl/THP/CE	373	S	528	S
KFl/THP	362	C	535	C
KFl/THF	362	C	535	C
RbFl/THP	363	C	534	C
CsFl/dioxane	363	C	534	C
CsFl/THP	364	C	533	C
CsFl/THF	364	C	533	C
CsFl/DME	364	C	532	C

^a Concentrations between 10^{-4} and 10^{-5} M. ^b At concentrations below 10^{-7} M.

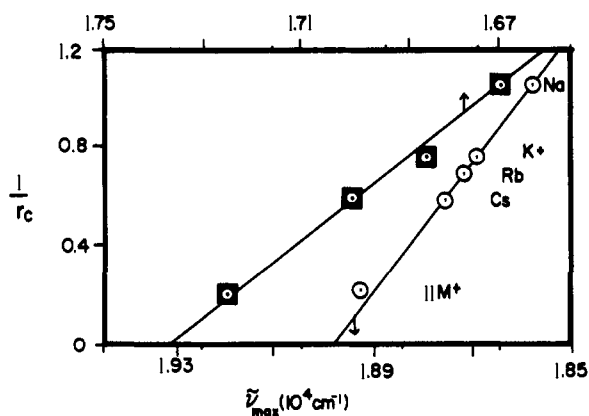


Figure 4. Emission wavenumber as a function of reciprocal cationic radius for fluorenyl (○) and fluoradenyl (■) anions in THP at 25 °C.

ion pairs in the first excited state for the larger cations in THF and THP.

The above rationalization assumes that there is sufficient difference in charge distribution of the ground and first excited state to cause anion-cation reorientation.²¹ As pointed out by

Birks and Dyson the lack of mirror symmetry between absorption and fluorescence spectrum is a sensitive indicator of such a difference.²² A comparison of Figures 1a and 1b would indicate that this is the case.

From Tables I-III, it is obvious that LiFl in THP, NaFl in THF, and NaFd in THF do not conform to the trends outlined above. If ion pairing in the first excited state of LiFl/THP is roughly similar to that in the ground state, emission from predominantly contact ion pairs is expected, leading to an extrapolated emission maximum at about 540 nm (Figure 4). Emission, however, occurs at 528 nm. The position of the maximum was not affected by carbanion concentration in the 10^{-4} - 10^{-5} M concentration range or by the addition of ten times excess of lithium tetraphenylboride so that the possibility of contact ion pair dissociation in the first excited state leading to emission from the free anion seems remote. Moreover, dissociation in these low dielectric constant solvents is generally small. Dissociation constants of these type carbanion salts in THP and THF are generally of the order of $\sim 10^{-9}$ and $\sim 10^{-5}$ M, respectively, or smaller.²³ Assuming a diffusion-controlled ion recombination rate constant of $\sim 10^{11}$ M⁻¹ s⁻¹ the rates of ionization in THP and THF should be equal to or smaller than 100 and 10^5 s⁻¹, respectively. These rates are well below that of radiative emission (10^7 - 10^8 s⁻¹). Moreover, the emission is identical with that of the 18-crown-6 complexed

Table III. Absorption Emission Maxima and Ion Pairing in Ground State and First Excited State of Fluoradenyl Alkali Salts at 25 °C in Various Solvents

cation/solvent	λ_{\max} , nm absorption	type ion pair	λ_{\max} , nm emission	type ion pair
Li ⁺ /THP	369, 388	S	580	S
Li ⁺ /THF	369, 388	S	580	S
Li ⁺ /DME	369, 388	S	581	S
Li ⁺ /CH ₃ CN	370, 389	F	580	F
Na ⁺ /THP ^a	359, 371	C	600	C
Na ⁺ /THF	361, 371, 388	C/S	580	S
Na ⁺ /DME	369, 388	S	580	S
(Na, CE) ⁺ /THP	369, 388	S	580	S
(Na, CE) ⁺ /THF	369, 388	S	580	S

^a In the presence of a large excess of sodium tetraphenylboride.

Na salt in THP and other separated ion pairs of F1⁻ salts so that it seems reasonable to assign the emission at 528 nm to separate ion pairs of LiFl. A similar situation applies to the NaFd/THF system (Table III). Although a mixture of contact and separated ion pairs is present in the ground state,²⁴ the emission signal corresponds to (crown ether) separated ion pairs only. It does not appear probable that these differences are only due to the far greater emittivity of separated ion pairs compared to contact ion pairs. It is observed that separated ion pairs emit only about twice as strong as contact ion pairs in these media (see below). Moreover, the LiFl/THP excitation spectrum at the emission maximum is similar to the absorption spectrum so that evidently the LiFl contact ion pair excited at 349 nm emits at 528 nm. This observation is consistent with a cation-solvent relaxation process occurring in the first excited state converting contact ion pairs to solvent-separated ion pairs followed by emission from the latter species.

The situation appears to be somewhat different for the NaFl/THF system. Again the emission maximum appears at a wavelength (532 nm) that is 6 nm blue shifted compared to that expected for the contact ion pair (538 nm) and slightly red shifted compared to the emission maximum for the separated ion pair (528 nm). This emission is not affected by addition of common salt and again the excitation spectrum closely resembles the absorption spectrum in the 10⁻⁴-10⁻⁵ M range. It appears therefore that in this case the emission at 532 nm results from the emission of both contact and separated ion pairs. Since no separate bands were discernible, the relative proportions of the two ion pairs were estimated by simulation of the emission band through addition of the separate bands of the two ion pairs. The best fit was obtained for an equimolar proportion of the two ion pairs.

The conversion of contact into separated ion pairs in these singlet excited states demands a process which is fast compared to that of radiative emission. Studies on dielectric relaxation of ethereal solvents²⁵ and ESR measurements on cation-glyme relaxation processes in solutions of radical anions^{26,27} indicate that this is indeed the case. Typically cation solvent relaxation rates were found to be ~10⁹-10¹¹ s⁻¹.

The interesting question arises as to why the complete or partial conversion of contact to solvent-separated ion pairs arises in some but not in other cases. Situations such as this appear suitable for a Forster cycle^{30,31} type calculation. The cycle is shown in Figure 7 as it pertains specifically to the equilibrium between contact and separated ion pairs. Denoting the difference in free energy between ground and excited state of a contact and separated ion pair by ΔG_c and ΔG_s , respectively, the free-energy difference for the excited state contact \rightleftharpoons separated ion pair process, G^* , is related to the corresponding ground-state process, ΔG_0 , by

$$\Delta G^* = \Delta G_0 + \Delta G_s - \Delta G_c \quad (1)$$

Now the entropy changes on electronic excitation of either ion pair should be similar and small compared to the contact-separated ion pair equilibrium owing to lack of reorganization of cation and solvent within the very short lifetime of electronic transition so that $\Delta S_c \approx \Delta S_s$ and $\Delta G_s - \Delta G_c \approx \Delta H_s - \Delta H_c$. The enthalpy difference between ground and excited states of both contact and separated ion pairs in solution should be virtually identical with the internal energy differences ΔE_c and ΔE_s . These energies can be approximated by averaging the 0-0 lines of emission and absorption spectra and it can be readily shown that

$$pK^* = pK_0 - \frac{hc(\bar{\nu}_c - \bar{\nu}_s)}{2.3kT} \quad (2)$$

where pK is the negative logarithm of the equilibrium constant, h is Planck's constant, c is the speed of light, k is the Boltzmann constant, and $\bar{\nu}_c$ and $\bar{\nu}_s$ are the average of the 0-0 lines of the absorption and emission spectra for the contact and separated ion pairs, respectively. The results for a number of systems are shown in Table VI. The experimental values of K^* could only be determined for the NaFl/THF system. In all other cases only upper or lower limits could be determined owing to the difficulty in measuring small proportions of either ion pair in the excited state. However, it can be seen that the experimental K^* "values" are just what would be expected on the basis of Forster cycle calculations and that these calculations correctly predict the occurrence of excited state cation/solvent relaxation. Moreover, the agreement between calculated and experimental values for the Na/THF system provides further a posteriori justification for the occurrence of cation/solvent relaxation in the excited state. The data in Table VI indicate that no excited-state Na⁺/THP relaxation is expected to occur in the F1⁻ anion to give solvent-separated ion pairs. Similar calculations yield the same conclusion for the Fd anion. Thus the emission at 580 nm observed for NaFd in THP at lower concentrations at an excitation wavelength of 388 nm must be due to free anions and not to solvent-separated ion pairs.

Effect of Solvent. Tables II and III summarize the emission and absorption maxima of the F1⁻ and Fd⁻ salts in a variety of solvents with and without the presence of crown ethers. The predominant type of ion pair is indicated in each case and in a few instances the proportion of ion pair types is also given. Several observations may be made. First, solvent does not affect the emission of the solvent-separated ion pair or the free anion (observed below 10⁻⁶ M). Thus the emission from solvent-separated ion pairs is the same in THP, THF, and DME with or without the presence of crown ethers, regardless of cation.

For instance, both LiFd and LiFl have an identical emission spectrum in THP, THF, and DME. In these solvents at 10⁻⁴-10⁻⁵ M the emission is due to solvent-separated ion pairs,

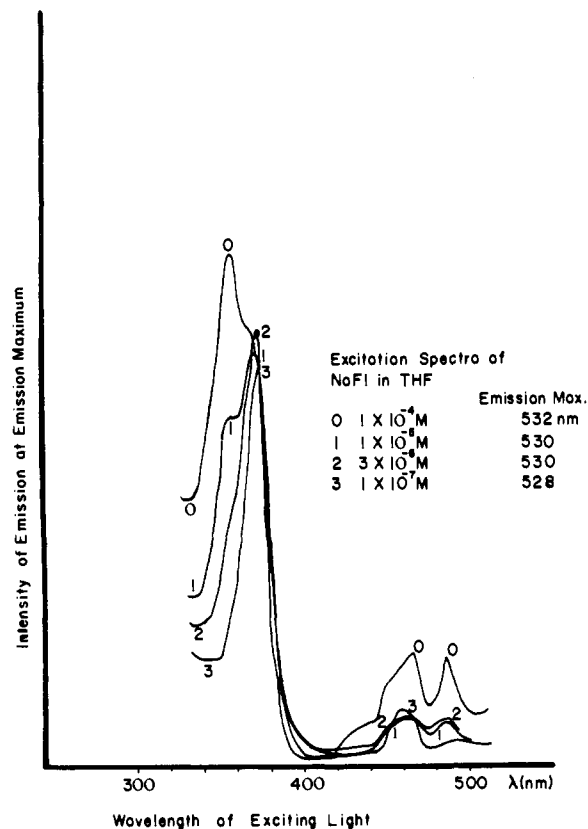


Figure 5. Concentration dependence of excitation spectra of fluorenylsodium in THF in the 10^{-4} – 10^{-7} M range at 25 °C.

and is identical with that of solvent-separated ion pairs of NaFl and NaFd in DME or THF (THP)–crown ether mixtures. Moreover these emission spectra are identical with that due to the free anions observed in THF and THP below 10^{-6} M and in acetonitrile below 10^{-4} M. The lack of effect of solvent on emission parallels a similar lack observed in absorption spectra⁸ and indicates an absence of specific anion solvation in the first excited state as well as in the ground state. A similar lack of effect of solvent may be observed for a given cation in a series of solvents if no specific solvent–cation coordination exists. For instance, the CsFl emission as well as absorption maxima are identical in dioxane, THP, THF, and DME. It is thus apparent that the changes in carbanion emission with solvent are primarily due to specific cation coordination by solvent or coordinating agent and that this cation coordination is most clearly manifested in the shifts in emission maximum due to equilibrium between contact and separated ion pairs. Moreover, it seems that the proportion of separated ion pairs in the first excited state decreases with increasing cationic radius. The same trend is observed in the ground state of these anions.^{8,24} Moreover the effect of the solvent coordinating power on the structure of the excited-state ion pair is similar to that in the ground state, the proportion of excited state separated ion pairs increasing as THF < THF < DME. These similarities are not unexpected since cation–donor solvent interaction is the primary process responsible for the observed spectral changes and specific anion coordination is apparently absent.

Concentration Effects. For a NaFl solution in THF a gradual shift in emission maximum from 532 to 528 nm is observed in diluting the solution from 4×10^{-5} to 10^{-7} M. Excitation spectra at 10^{-4} M show a maximum at 356 nm with a small shoulder at 370 nm that increases on dilution until at $\sim 10^{-7}$ M the excitation spectrum shows a maximum at 373 nm only (Figure 5). These changes must be primarily due to

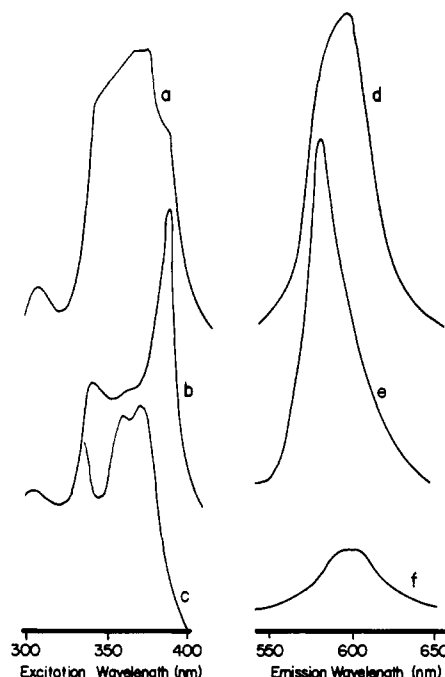


Figure 6. Effect of common ion and excitation and emission wavelength on emission and excitation spectra of NaFd in THP (5×10^{-5} M). (a) $\lambda(\text{emission})$ 600 nm; (b) $\lambda(\text{emission})$ 580 nm; (c) after addition of sodium tetraphenylboride (1 equiv) emission and excitation wavelength independent; (d) $\lambda(\text{excitation})$ 371 nm; (e) $\lambda(\text{excitation})$ 388 nm; (f) see (c).

ground-state ionization since the magnitude of the dissociation constant ($K_d = 6 \times 10^{-7} \text{ M}^{-1}$) predicts ionization over approximately the same concentration span. As pointed out in the Experimental Section, in this case as in most others there was no easily discernible effect of excitation wavelength on emission spectrum or of emission wavelength on excitation spectrum. However, such an effect can be observed for a suitable system such as NaFd in THP (Figure 6). If this system is excited at the contact ion pair absorption maximum (359–371 nm) at higher concentrations, a rather broad band results that has a broad maximum from 585 to 600 nm shifting toward 600 nm as the concentration increases. In the presence of sodium tetraphenylboride the emission of this solution is decreased in intensity and gives a symmetrical absorption at 600 nm. If, however, the solution without sodium tetraphenylboride is excited at 388 nm (corresponding to a free or separated ion pair) carbanion emission occurs at 580 nm with a slight shoulder at around 600 nm. Corresponding changes are seen in the excitation spectra of the three systems (Figure 6). At an emission wavelength of 600 nm the excitation spectrum of NaFd/THP corresponds to a composite of contact and separated ion pairs (or free ion). On addition of sodium tetraphenylboride an excitation spectrum is obtained that is virtually identical with the reported absorption of the contact ion pair of NaFd/THP. At an emission wavelength of 580 nm the resulting excitation spectrum is similar to the separated ion pair spectrum of Fd^- . Moreover, in solutions containing the sodium tetraphenylboride emission and excitation spectra are independent of excitation and emission wavelength, respectively. These results clearly indicate ground-state ionization of the salt in THP, the free Fd^- ion emitting at 580 nm and the Na ion pair at 600 nm:

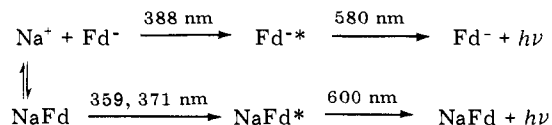


Table IV. Lifetimes and Relative Intensities of Alkali Metal Salts of Fluorenyl at Room Temperature, at 1×10^{-5} M

cation	solvent	emission max, nm	Lifetime, ns	rel intensity
Li ⁺	dioxane	545	24.	10
Na ⁺	THP	538	40.	43
K ⁺	THP	535	41.	41
Rb ⁺	THP	534	40.	43
Cs ⁺	THP	533	15.	18
Cs ⁺	THF	533	15.	18
Na ⁺ (CE)	THP	528	82.	85
free ion ^a	THF	528	96.	92 ^b

^a Obtained in dilute ($c < 10^{-7}$ M) sodium fluorenyl solution. ^b Obtained by extrapolating back to 1×10^{-5} M.

Table V. Effect of Cation on the Lifetime and Relative Fluorescence Intensity of Fluoradenyl Salts

cation	solvent	lifetime, ns	intensity ^a
Cs	THP	4.2	8
Na ^b	THP	11.8	25
free ^{c,d}	acetonitrile	47.8	100

^a Relative intensities. ^b In the presence of sodium tetraphenylboride in order to repress ionization. ^c Lithium as counterion. ^d Similar values have been obtained for separated ion pairs.

It is somewhat surprising that in a low dielectric constant solvent THP (ϵ 5.6, 25 °C) free ion fluorescence should be significant. The dissociation constant for the NaF_d/THP system should be in the order of $\sim 10^{-9}$ M⁻¹.²³ However, the quantum efficiency of the free F_d⁻ ion is substantially higher than that of the ion pairs (see Lifetimes and Relative Intensities) so that ion pair ionization in this system can be more easily observed by fluorescence. It is interesting that no contribution is observed in these media due to solvent-separated ion pairs formed in the first excited state.

Lifetimes and Relative Intensities. Lifetimes and relative intensities for several of the alkali fluorenyl salts at 1×10^{-5} M are listed in Table IV. For all salts examined, except that of cesium, the lifetime at concentrations above 10^{-4} M is considerably lower than the listed value. For example, the lifetime of NaFl in THP at 2×10^{-4} M is 30 ns and at 6×10^{-4} M is 24 ns. However, below 10^{-5} M the measured lifetime was concentration independent. The Cs salt, however, shows a continued decrease of lifetime with increasing concentration throughout the concentration range. The relative intensities at the emission maximum show the same behavior. As Table IV indicates the free ion has the longest lifetime and emits most intensely; the solvent- or crown ether separated ion pair emits about as intensely and has nearly the same lifetime; the sodium, potassium, and rubidium salts all have nearly the same in-

tensity and lifetime, while the Li salt in dioxane and the Cs salt in all solvents are of low relative intensity with the lowest lifetimes. Table V gives lifetime and intensity data of several F_d⁻ salts and shows similar trends.

The strikingly low lifetimes of LiFl and NaFl in dioxane are of interest. For instance, NaFl exists in dioxane and THP as a contact ion pair but has a considerably lower lifetime in dioxane. This lower lifetime is not caused by specific anion-solvent interactions since the Cs ion pair has the same lifetime in dioxane, THP, and THF.³⁰ Also it is unlikely that this significant effect is caused by strong peripheral Na ion solvation by THP since such an interaction is expected to be relatively weak.

It has previously been shown that the low lifetimes and intensities of the Li and Na salts in dioxane may be caused by aggregation of ion pairs.^{30,31} This is consistent with previous results on the pronounced concentration dependence of proton transfer rate constants in these systems that was shown to be due to ion pair aggregation.³² These results also indicate that CsFl is monomeric in THF and dioxane in the 10^{-3} - 10^{-5} M concentration range. Hence the similarity in lifetimes and intensities of CsFl in THF, THP, and dioxane is not surprising given the lack of specific solvation of the Cs⁺ ion pair in all three solvents.^{9,10} The low intensity and lifetime of the Cs salts is most likely due to a heavy atom effect. However, if these were the only effects operative in these contact ion pairs, one might expect to see a gradual increase of lifetime as the cation atomic number decreases from 55 (Cs⁺) to 37 (Rb⁺) to 17 (K⁺) to 11 (Na⁺). The observed invariance of lifetime and relative emission intensity of the Rb, K, and Na salts may be due to the absence of a heavy atom effect for these ions or may be caused by some other effect operating in the opposite direction from the heavy atom effect. The first explanation does not seem reasonable since the Rb cation is isoelectronic to the bromide anion which has been shown to be a more effective quencher than the chloride ion which is isoelectronic with Na⁺.³³⁻³⁵ In fact, evidence presented in ref 35 suggests the occurrence of quenching by all cations. It therefore appears

Table VI. ΔG^* and K^* Calculated According to Equations 1 and 2 Together with Experimentally Determined Values for Fluorenyl and Alkali Salts in Low-Dielectric Constant Ethers at 25 °C

system	K_0	ΔG_0 , kcal	$\Delta E_c - \Delta E_s$, kcal	ΔG^* , kcal	K^*	K_{exp}^*
Li, THP	4.3×10^{-1}	0.50	1.94	-1.43	11.2	≥ 5.0
Na, THP	$\leq 1.0 \times 10^{-2}$	≥ 2.74	1.33	≥ 1.42	≤ 0.093	≤ 0.10
Li, THF	4.0	-0.82	1.94	-2.75	102	≥ 5.0
Na, THF	5×10^{-2}	1.78	1.33	0.45	0.47	~ 1.0
K, THF	1.24×10^{-2a}	2.61	0.81	1.80	0.049	≤ 0.10
Cs, THF	1.1×10^{-3a}	4.05	0.64	3.41	0.003	≤ 0.10
Li, DME	$\geq 1.0 \times 10^1$	1.37	1.94	≤ -3.30	≥ 259	≥ 5.0
Na, DME	4.0	-0.82	1.33	-2.15	37	≥ 5.0
K, DME	3×10^{-1a}	0.72	0.81	-0.092	1.15	≥ 5.0
Cs, DME	1.83×10^{-2a}	2.38	0.64	1.74	0.054	≤ 0.10

^a K_0 calculated from the apparent ion pair dissociation constants (T. Ellington and J. Smid, *J. Phys. Chem.*, **73**, 2712 (1969)).

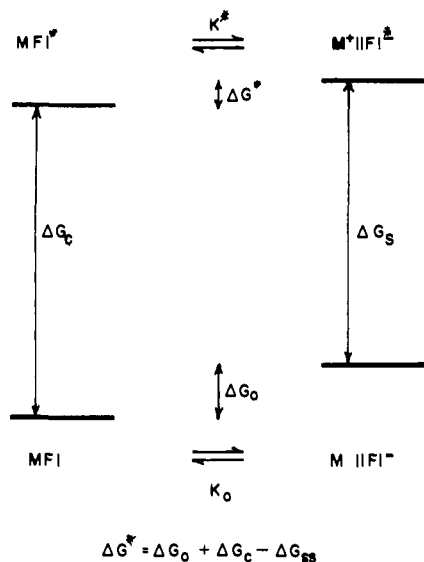


Figure 7. The Förster cycle applied to ion pairing effects in ground and excited state carbanions.

that a "contact ion pair effect" operates that tends to decrease the lifetime with decreasing cation size. Although no firm conclusion can be reached on the basis of the present work, some possibilities are outlined below.

In general, the rate constant for nonradiative deactivation of the excited state is proportional to³⁶

$$\left(\sum_k \langle \phi_1 | \frac{\partial}{\partial Q_k} | \phi_0 \rangle F_k \right)^2$$

where ϕ_0 and ϕ_1 are the ground- and excited-state wave functions, respectively, Q_k is the k th normal vibration mode of the molecule, and F_k is a vibrational term involving the Franck-Condon coupling factor.

The energy of the cation-anion vibration has been shown to increase as the radius of the cation decreases,³⁷ thus requiring fewer vibrational quanta to deactivate the excited state. Thus, the effect of the cation on the purely vibrational part of the above expression, F_k , would be similar in nature to the effects seen in substituting deuterium for hydrogen in aromatic hydrocarbons^{38,39} (deuterated forms have longer lifetimes and higher quantum yields), with this effect greater for sodium than potassium, etc.

Perhaps more significant would be the effect of the cation on the electronic factor, $\langle \phi_1 | \partial / \partial Q_k | \phi_0 \rangle$. As indicated above, charge density is more dispersed into the benzene rings for the excited state free anion, while it is concentrated in the cyclopentadienyl ring in the ground state of the free anion. The cation may reasonably be expected to polarize the π -electron system and draw charge density toward itself. No matter what position the cation occupies relative to the excited anion, this effect should alter the excited-state wave function, and hence the amount of coupling between it and the ground-state wave function via any of the vibrational modes.

Another possible mechanism is one involving electron transfer from the anion to the metal cation (similar to that observed for the quenching of anthracene fluorescence by inorganic anions).³⁵ This would be expected to increase in importance as the cationic radius decreased, or as the electron affinity of the cation (= ionization potential of the metal) increased.

It should be pointed out that other possible explanations for

the dependence of lifetime on cation perturber may be possible.⁴⁰

As is readily apparent, little has been done to quantify the effects of ion pairing on lifetime, quantum yield, or other properties of the excited state. Such a study, coupled with data on the phosphorescence of these compounds, could go far to help explain the storage and transfer of electronic energy in solution, especially since the effect of chemical parameters on the ion pairing has been so extensively studied.

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