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FLUORESCENCE IN ALKALI-METAL SALTS OF SOME ACYCLIC, RESONANCE-STABILIZED CARBANIONS

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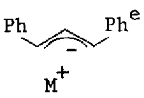
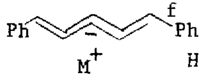
Abstract: While fluorescence can be clearly observed in resonance-stabilized acyclic anions, its occurrence is insufficient for unambiguous assignment of either ion-pairing type or anion geometry. As in cyclic, aromatic anions, the requirement for contact ion-pairing is less severe in the excited state than in the ground state. The fluorescence lifetimes of acyclic anions are affected more by the associated cation than by the type of ion-pairing.

Studies which report emission from hydrocarbon anions are relatively rare, most examples having been discovered within the last decade.[1] This paucity of information makes generalization risky, but one recurrent observation in several types of anions is a dramatic effect of carbanion-alkali metal ion-pairing on observed fluorescence efficiency. For example, the cyclooctatetraenyl monoanion associated with two cations (M^+ COT^- M^+) fluoresceces strongly if $M=Cs^+$, Rb^+ or K^+ but no emission is observed if $M^+=Na^+$ or Li^+ or in simple ion pairs M^+ COT^-.[2] In closed shell acyclic anions, similar extremes have been noted: the occurrence of fluorescence in 1,3-diphenylpropenyl anions seems to depend on temperature (ion-pairing)[3] and on geometry.[4] Several factors have been suggested as possible explanations of this behavior[2]: (1) decreased rigidity or non-planarity in some ion pair forms, (2) the dependence of the relative positions of excited states of different multiplicity on ion-pairing and/or geometry and (3) the energy ordering of charge-transfer states in ion-paired excited state manifolds.

The assignment of ion-pairing type to a given alkalai metal-carbanion pair is easy if well-resolved absorption bands for contact, solvent-separated, and/or free ion pairs can be seen in the ultraviolet or visible spectrum. If only a single band is present, however, this assignment is difficult. If the fluorescence properties of acyclic carbanions could be related accurately to a single ion-pairing type, fluorescence spectroscopy might provide a valuable adjunct to absorption spectroscopy for the delineation of ion-pairing. We report in this note a comparison of fluorescence maxima and lifetimes in lithium and potassium salts of 1,3-diphenylpropene (1) and 1,5-diphenylpentadiene (2) in ether solvents at room temperature, conditions under which the balance between contact and solvent separated ion pairing can be manipulated experimentally.[5]

Lithium salts of 1 and 2 were prepared by treating dilute, degassed solutions of the hydrocarbons in dry[6] tetrahydrofuran (THF) under Ar with 1.1 equivalents of n-butyllithium. Potassium salts were obtained by treating the lithium salts with 1 equiv. of potassium menthoxide, by treating the hydrocarbon with complex base,[7] or by treating 1 with trimethylsilyl potassium, all reactions having been conducted under an argon blanket. Diglyme (DME) or spectral grade hexane was added to the resulting solutions to make a 1:2-5 dilution with THF.

Table 1. Fluorescence of 1,3-Diphenylpropenyl and 1,5-Diphenylpentadienyl Anions

	M^+	Solvent[a]	Type of Ion-Pairing[b]	λ_{max} (absorption),[c] nm	λ_{max} (excitation),[c] nm	λ_{max} (emission),[c] nm	τ,psec[d]
	H (neutral hydrocarbon)	Hex	-		296	310,320	2100
	Li^+	THF	SS	528 (c,t)	- (c,t)	-	
				560 (t,t)	562 (t,t)	582	185
	Li^+	THF/DME	SS	515 (c,t)	-	-	
				565 (c,t)	565	583	188
	Li^+	THF/Hex	C	510 (c,t)	- (c,t)	-	
				520 (t,t)	525 (t,t)	560	178
	K^+	THF	C	515 (c,t)	-	-	
			C	530 (t,t)	525	560	85
	H (neutral hydrocarbon)	Hex	-		312	331,345	<1000
	Li^+	THF	SS	596	594	617	107
	Li^+	THF/DME	SS	593	593	626	98
	Li^+	THF/Hex	C	560	558	617	108
	K^+	THF	C,SS	570	572	595	73
	K^+	THF/DME	SS	590	588	612	84

a) THF = tetrahydrofuran ; Hex = Hexane; DME = diglyme

b) C = contact; SS = solvent separated. Ion-pairing type was assigned by shifts in absorption spectra.

c) All wavelengths ± 3 nm.

d) Fluorescence lifetimes are accurate to ± 10% of the cited lifetimes.[8]

e) The predominance of E,E geometry was assigned by nmr spectroscopy.[9,10]

f) W (E,E,E,E) geometry was assigned by nmr spectroscopy.[11]

Fluorescence spectra were recorded on a Spex Fluorolog instrument. Identical spectra were obtained in the front face or normal 90° modes. Fluorescence lifetimes were measured with a Hamamatsu streak camera with a mode-locked Nd-Yag laser (pico-second resolution).[8] Absorption spectra were recorded on a Cary-14 UV-visible spectrophotometer against a solvent blank. The results are summarized in Table I.

It is clear that in these acyclic anions, as in related aromatic anions,[12] fluorescence at room temperature occurs both from contact and solvent-separated pairs. Thus, the observation of fluorescence is insufficient for assigning ion-pairing. A number of interesting structural features do evolve from the fluorescence study, however.

In these acyclic conjugated ions, the trends in absorption maxima and fluorescence excitation and emission exactly parallel those observed in cyclic, aromatic carbanions[12,13]. Namely, contact ion pairing shifts the absorption and excitation maxima to shorter wavelengths, the shift being most dramatic for association with cations of smaller radius.

Since the excited states of these salts are sufficiently long-lived for solvent and cation relaxation to have ocurred before emission, application of the Born-Oppenheimer approximation predicts a larger Stokes shift for the ion-paired species than for the free ion (preferential excited state stabilization) if comparable ion-pairing is obtained in the ground and excited states. Often this effect gives rise to a red-shifted fluorescence band. Such red shifts are not observed here. Furthermore, the separation of absorption and emission maxima in the contact ion pairs tends to be somewhat larger than that found in analogous solvent separated pairs. We conclude therefore that there probably exists less electron delocalization in these acyclic anions than in related aromatic anions and that, as has been shown before, the preference for contact pairing can be diminished in the excited state. These same trends were observed in comparing the fluorescence spectra of cyclic, aromatic carbanions with aromatic nitranions.[12]

Ion-pairing seems to have a smaller effect on excited state lifetime than does the identity of the associated cation. That is, the similar lifetimes observed in lithium salts irrespective of pairing are significantly longer than those of the corresponding contact or solvent-separated ion paired potassium salts. Since the shorter lifetimes are encountered in salts which are oxidized more readily at platinum electrodes,[14] we suggest that these lifetime differences can be attributed to rapid excited state decay by electron transfer to the cation or to cation-dependent excited state rotational barriers. The product of electron transfer, a radical-metal atom pair, may be analogous to the interceptible species involved in intermolecular electron transfer in anion photochemistry.[1] A parallel trend was observed, but not discussed, in the fluorescence lifetimes of metal-fluorenyl salts.[15] No anomalous emission bands attributable to geometric isomers of the excited ions could be detected in these room temperature experiments.

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