The Fluorescence of Alkali-metal Salts of 1,3-Diphenylbut-1-ene in Ether Solutions

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Summary The solvent-separated ion pairs, but not the contact ion pairs, of the alkali-metal salts of 1,3-diphenylbut-1-ene fluoresce in certain ethers at low temperature.

SPECTROSCOPIC studies in the visible region have shown that the alkali-metal salts of 1,3-diphenylbut-1-ene ($DPB^- M^+$) exist in ether solutions as mixtures of contact and solvent-separated ion pairs, the fraction of the latter increasing as the temperature is lowered.[1] We now report that in addition to this change, solutions in certain ethers—notably s-butyl ether (SBE), 2-methyltetrahydrofuran (MTHF), and 2,5-dimethyltetrahydrofuran also become fluorescent when the temperature is lowered sufficiently. Although there is no theoretical reason why many carbanions should not fluoresce, we believe that the present instance is the first recorded example.

Figure 1 shows the excitation and emission spectra of $DPB^- Li^+$ in SBE at 77 K, recorded using an Aminco–Bowman Spectrophotofluorimeter. In accordance with expectation for an alternant species, these spectra exhibit near complementarity. When the sample was allowed to warm up, little change was observed until the glass temperature of SBE (*ca.* 146 K) was reached. Further raising of the sample temperature caused a progressive decrease in the intensity of the emission and excitation spectra without changing their spectral characters. At temperatures higher than about 10° above the glass temperature no fluorescence was detectable.

The absorption spectrum of $DPB^- Li^+$ in SBE is shown in Figure 2. At 293 K the spectrum consists of a single peak at 468 nm corresponding to a contact ion pair. At 146 K the contact ion pair absorption band is centred at 522 nm and there is a new band at 561 nm corresponding to the solvent-separated ion pair. At intermediate temperature the absorption due to the contact ion pair is very broad and is best interpreted as indicative of the presence of two species—a "non solvated" contact ion pair ($\lambda_{max} \leqslant 468$ nm) and a "solvated" contact ion pair (λ_{max} *ca.* 522 nm). As the temperature is lowered the formation of the latter is favoured, resulting in the observed bathochromic shift.[2]

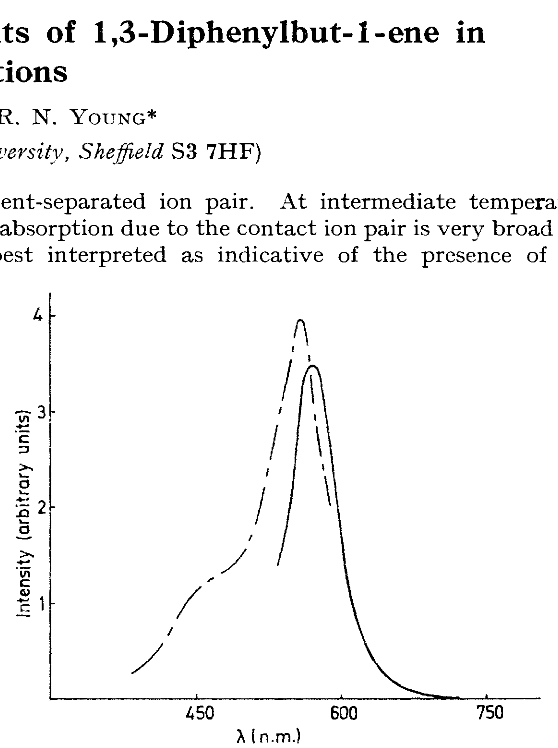

FIGURE 1. *Emission and excitation spectra of* $DPB^- Li^+$ *in* SBE *at* 77 K. *Emission spectrum* (*excitation wavelength* 500 nm) ———; *Excitation spectrum* (*emission wavelength* 650 nm) - - - -.

Since the maximum of the excitation band is at the same wavelength as that of the absorption band of the solvent-separated ion pair we must conclude that the fluorescence arises from an excited state of the solvent separated ion pair, or, rather less probably of the free anion which also absorbs at this wavelength.[3] Solutions of DPB$^-$ Cs$^+$ in MTHF, where the presence of free ions is very unlikely, behave in an entirely analogous fashion (Table). More conclusively, the addition of Ph$_4$B$^-$ Na$^+$ to the system DPB$^-$ Na$^+$—MTHF (which should suppress dissociation to the free carbanion in the liquid phase) left the intensity of the emission spectrum unaffected.

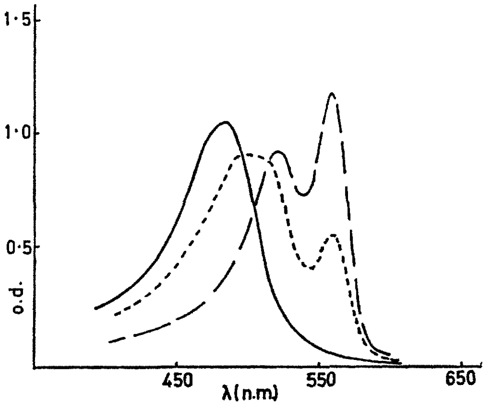

FIGURE 2. *The visible absorption spectrum of* DPB$^-$ Li$^+$ *in* SBE. ——— 293 K; ------ 215 K; — — — 147 K.

The excitation spectrum also exhibits a weak shoulder at about 470 nm which is not present in the emission spectrum. We believe that this absorption represents conversion of the solvent separated ion pair to a higher excited state. The location of the absorption band of the contact ion pair near this wavelength must be regarded as coincidental, since increasing the sample temperature caused a large increase in the fraction of contact ion pairs but did not change the relative intensities of the excitation shoulder and maximum.

Excitation, emission and absorption spectra of DPB$^-$ M$^+$ *in ether solutions*

M$^+$	Solvent	Excitation maximum (nm)[a]	Emission maximum (nm)[a]	Absorption maximum for solvent separated ion pair[b]
Li$^+$	SBE	561	572	560
Li$^+$	MTHF	560	575	562
Na$^+$	MTHF	562	572	563
Cs$^+$	MTHF	560	568	562

[a] Accurate within ±3 nm.
[b] Accurate within ±2 nm.

That the presence of solvent-separated ion pairs is not in itself sufficient to produce fluorescence is verified by a study of DPB$^-$ Li$^+$ in MTHF. This solution contains mainly solvent-separated ion pairs (with small amounts of contact ion pairs and of free ions) even at 293 K but the solution exhibits no fluorescence until cooled to 102 K.[4] Since the contact ion pair does not fluoresce it seems probable that, except at very low temperatures, the rapid interconversion of the contact and solvent-separated ion pairs will effectively quench the fluorescence.

(*Received, October* 19*th*, 1970; *Com.* 1794.)

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[3] H. V. Carter, B. J. McClelland, and E. Warhurst, *Trans. Faraday Soc.*, 1960, **56**, 455.
[4] H. Greenspan and E. Fischer, *J. Phys. Chem.*, 1965, **69**, 2466.