The temperature dependence of the fluorescence lifetimes of the ion pairs of α,ω-diphenylpolyenylic carbanions

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Abstract

The alkali metal salts of the α,ω-diphenylpolenylic carbanions exist in ether and amine solutions as mixtures of tight and loose ion pairs which differ in their absorption and emission spectra. Fluorescence lifetimes were determined using pulsed radiation from the Daresbury synchrotron in conjunction with single photon counting and were found to increase towards limiting values on cooling the solutions. Analysis shows that this behaviour is in consonance with a mechanism in which the excited state is deactivated by fluorescence and non-radiative decay in competition with activated skeletal twisting about a polyenylic bond. The Arrhenius parameters have been determined for the loose ion pairs of a variety of systems but those of the tight ion pairs have proved to be less accessible. In certain cases the spectral changes arising from photoisomerisation and the subsequent ground state relaxation could be recorded.

Keywords: Fluorescence lifetime; Ion pairs; Carbanions; Photoisomerization

1. Introduction

Extensive studies of the visible absorption spectra of the α,ω-diphenylpolyenyl carbanions (DP_n^- where $n = 3, 5, 7$ and 9 are the numbers of carbon atoms in the polyenyl chain) have shown [1-3] that they are present in the form of two kinds of ion pair: the tight (contact) ion pair and the loose (solvent-separated) ion pair, in solvents of low permittivity, such as ethers and amines. With every member of the series, the loose ion pair has a larger interionic separation than the tight ion pair and its formation is favoured both by the use of strongly-solvating solvents and by decreasing the size of the counterion. The equilibrium proportion of the loose ion pair is also increased on lowering the temperature. The absorption spectrum of the loose ion pair is indistinguishable from that of the free carbanion formed by its dissociation. In contrast, the absorption spectrum of the tight ion pair is located at shorter wavelength. The small interionic separation of cation and anion in the tight ion pair results in considerable perturbation of the electronic energy levels of the carbanion. The ground state is stabilised by ion association to a greater extent than the excited state and, in consequence, the absorption spectrum is shifted to the blue to an extent that increases with decreasing cation radius [4]. Conductance measurements on ethereal solutions of several alkali metal salts of DP_3^- have shown that there is typically only about 1% dissociation at the concentrations employed for absorption spectroscopy [5]; a somewhat greater value is to be expected at those used for fluorometry.

^{1}H NMR spectroscopy has confirmed the existence of the two kinds of ion pair [6] and has shown that the 1,3-diphenylallyl carbanion (DP_3^-) is a mixture of the trans,trans and cis,trans conformers in about a 93:7 ratio [7,8]. The number of possible conformations increases with increasing chain length of the vinylogues and the equilibrium compositions are less certain. There is general agreement that the all-trans conformations overwhelmingly predominate but opinions vary on the proportion of other conformations. Tolbert and Ogle [9] report that the ^{1}H NMR coupling constants are consistent with all-trans conformations for DP_n^- carbanions where n ranges from 5 to 13. Thiele and Streitwieser [10] examined the ^{1}H NMR spectra of $DP_n^-Cs^+$ in THF and were less certain about the percentage of the all-trans conformation and concluded that it lies between about 70 and 94% for $n = 5$ and 7.

Photolysis of $DP_3^-M^+$ with white light causes trans,trans to cis,trans isomerisation and a photostationary state is established which shifts progressively in favour of the trans,trans conformer as the temperature is decreased [11,12]. The trans,trans conformer is coplanar; however, in the cis,trans conformer, steric interaction between one of the ortho hydrogens of the cis phenyl group with the allylic hydrogen remote
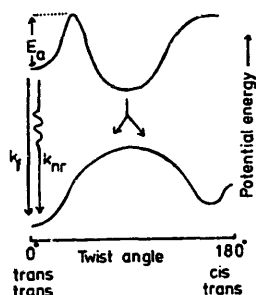
Fig. 1. Energy level diagram for $DP_3^- M^+$.

from it results in distortion of bond angles and/or departure from coplanarity. The attendant 30 nm blue shift of the absorption maximum permits the extent of photoisomerisation to be estimated from the spectrum.

At room temperature, solutions of the trans,trans conformers of both the loose and tight ion pairs of $DP_3^- M^+$ fluoresce weakly but, on cooling, their intensities increase towards limiting values [13,14]. However, no fluorescence attributable to the cis,trans conformer has been detected. Very similar behaviour is shown by stilbene (see, for example Ref. [15]) and adaptation of the scheme established for it provides an explanation of the behaviour of $DP_3^- M^+$ (Fig. 1) [16]. The excited trans,trans ion can deactivate by three paths: (i) fluorescence, (ii) radiationless return to the ground state and (iii) temperature-dependent twisting of the allylic skeleton. Extensive study of fluorescence lifetimes in a wide range of ether and amine solvents has shown [16,17] that they conform to the equation

$$\ln(1/\tau - 1/\tau_o) = \ln A - E/RT \qquad (1)$$

where τ is the lifetime at temperature T and τ_o is the limiting value of the lifetime at such a low temperature that skeletal twisting is reduced to a negligible rate.

The fluorescence intensities of the ion pairs of the longer chain α,ω-diphenylpolyenylic carbanions also increase towards limiting values on cooling. The present work was intended to determine whether the deactivation of their excited states conforms to the same mechanism as $DP_3^- M^+$ and, if so, what the influence of chain lengthening is upon the Arrhenius parameters and upon τ_o. The suggestion has been made [18,19] that $DP_3^- M^+$ might isomerise by the transitory photoejection of an electron to form the 1,3-diphenylallyl radical (which is known to be conformationally very labile) followed by the ultimate recapture of the electron. No evidence was found for this process with $DP_3^- M^+$ but it was thought important to investigate this possibility further in the case of the more highly conjugated ions from which loss of an electron would be expected to require less energy.

2. Experimental details

1,5-diphenyl-penta-1,4-diene was prepared by the reaction of benzaldehyde with the bis-ylide formed from 1,3-bis (triphenylphos; honium)propane dibromide as described [20]. ^{1}H NMR: δ 3.35 (m, 2H), 5.75 (dt, 2H, J = 15.11 Hz), 6.5

(d, 2H, J = 15 Hz) and 7.05–7.5 (m, 10 H). The isomeric 1,5-diphenylpenta-1,3-diene was also isolated: ^{1}H NMR: δ 3.5 (d, 2H, J = 6.5 Hz), 5.95 (dt, 1H, J = 15, 6.5 Hz), 6.25 (q, 1H, J = 15, 9 Hz), 6.85 (dd, 1H, 15, 9 Hz), 6.45 (d, 1H, J = 15 Hz) and 7.1–7.4 (m, 10 H) — in good agreement with the data of Shoppee and Henderson [21]. 1,9-diphenyl-nona-tetra-1,3,6,8-tetraene was prepared analogously using cinnamaldehyde [9]. A mixture of isomers formed by prototropy was obtained which could only be partially resolved. The ^{1}H NMR spectra of these showed resonances in good agreement with those reported by Tolbert and Ogle [9]. Reacting the bis-ylide with the appropriate quantity of an equimolar mixture of benzaldehyde and cinnamaldehyde and separating this triene from the accompanying diene and tetraene by chromatography yielded a mixture of 1,7-diphenylhepta-1,3,6-triene and the isomeric 1,3,5-triene. The ^{1}H NMR spectrum agreed well with that described by Thiele and Streitwieser [10]. 1,1,5,5-tetraphenylpenta-1,3-diene: ^{1}H NMR: δ 3.0 (t, 2H, J = 11 Hz), 6.1 (t, 2H) and 7.1–7.4 (m, 20 H) [22] and 1,5-diphenyl-3-(2-phenylethenyl)-penta-1,4-diene (tristyrylmethanol) [23] were synthesised as described.

The carbanion solutions were prepared under high vacuum conditions from the above weak acids by the abstraction of a proton, using either n-butyl lithium or the dimer dianion of α-methyl styrene. The solvents employed were tetrahydrofuran (THF), 2-methyltetrahydrofuran (MTHF), 2,5-dimethyltetrahydrofuran (DMTHF) (equimolar cis and trans isomers), Trimethylamine (Me_3N), 1,2-dimethylaminoethane (DMEDA) and 1,1,2,2-tetramethyl ethylenediamine (TMEDA). Fluorescence and excitation spectra were determined using a Perkin–Elmer MPF 44 instrument; the data reported here are uncorrected. Photolysis was performed using a 50 W quartz halogen lamp as white light source. The cryostat, the use of visible radiation from the Synchrotron Radiation Source at Daresbury and the method of analysis of fluorescence decay have been described previously [16,17]. Typically, a time range of about 18 ns was used with a resolution of 0.018 ns per channel. Difficulties were sometimes experienced in fitting the very short lifetimes at higher temperatures but usually a reduced χ^2 of < 1.2 could be obtained. The fluorescence was monitored with appropriate filters in front of the photomultiplier. The fluorescence lifetimes of most of the systems reported here were measured at some 9–12 different temperatures in the range from ambient to the freezing point of the solvent employed.

3. Results

Solutions of $DP_5^- Na^+$ in MTHF are red at room temperature and their spectrum (Fig. 2) has its absorption maximum at 548 nm showing that the solute is present almost entirely as the tight ion pair. On cooling, the colour progressively changes to mauve as the tight ion pair is converted into the loose and a new band appears (at the expense of the old) having its maximum at 598 nm; this change is completely
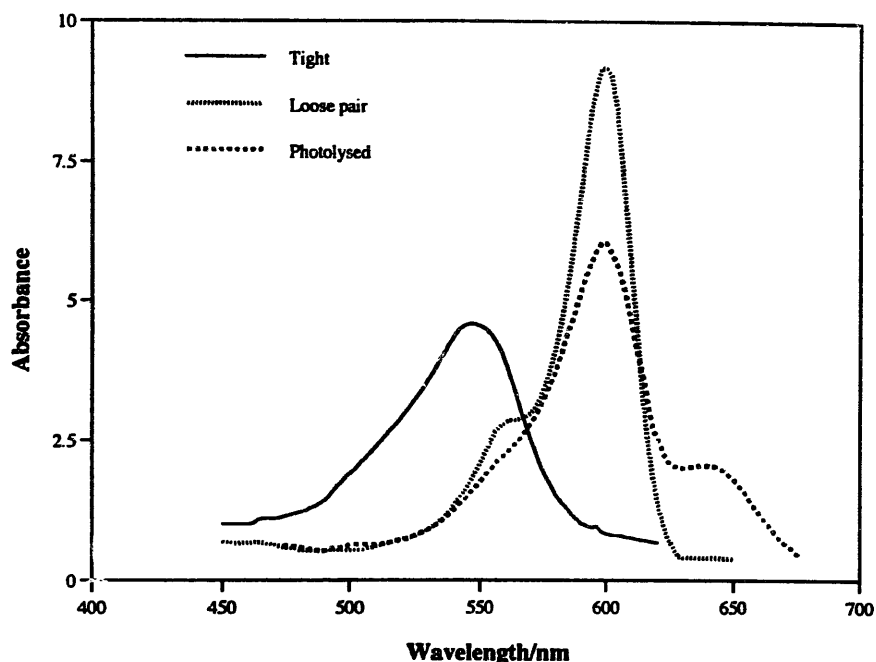
Fig. 2. Absorption spectrum of DP5⁻ Na⁺ in MTHF: ————, at 20 °C (tight ion pair): · · ·, at −120 °C (loose ion pair) before, and - - - after photolysis with white light.

reversible on warming. Similar spectral changes are shown by DP5⁻Li⁺ in MTHF but with the difference that the mole fraction of the tight ion pair is only about 0.35 at room temperature. In addition, the absorption maximum of the tight pair of DP5⁻Li⁺ is located at 535 nm, this blue shift with respect to the spectrum of the Na⁺ counterpart reflecting the smaller interionic separation with the smaller cation.

The fluorescence spectrum of DP5⁻ Na⁺ in MTHF has its maximum at 618 nm. At 25 °C and with excitation wavelengths from about 490 to 550 nm, there is a strong shoulder at about 580 nm; this is very much weaker when exciting at longer wavelengths. On cooling to about 0 °C the shoulder becomes imperceptible and it becomes clear that the emission spectrum is actually the envelope of two heavily overlapped bands. Setting the detector at a wavelength of 620 nm or greater, the excitation spectrum shows two maxima, at 555 and 600 nm, of about equal intensity at room temperature, corresponding respectively to the tight and loose pairs. As expected on the basis of this assignment, the relative intensity of the band at 555 nm is increased by moving the emission monochromator from 618 towards 580 nm; it is decreased by lowering the temperature but is still measurable at −75 °C. This persistent detectability of the tight ion pair is not seen in the emission spectrum because of the much higher fluorescence efficiency of the loose ion pair. This severely limits the scope for the measurement of fluorescence lifetimes of the tight ion pair.

The fluorescence of DP5⁻Na⁺ in MTHF (containing also sodium tetraphenylborate to suppress any tendency of the ion pair to dissociate) was studied using several excitation wavelengths. A bi-exponential decay was observed using a filter cutting off at 580 nm in front of the photomultiplier. Time-resolved excitation spectroscopy (Fig. 3), where separate

measurements were taken early and late in the decay, showed very clearly that the short lived component is due to emission from the tight ion pair and that the long lived component is due to the loose pair. The relative contributions of the two emitters depends upon the excitation wavelength (Fig. 4) in the manner expected from the absorption spectrum. This agreement shows that equilibration between the loose and tight ion pairs is slow relative to the fluorescence decay, so that the observed decay times can be regarded as the excited state lifetimes of the two species. The lifetime of the tight ion pair was too short relative to the width (700 ps) of the instrument response function to permit accurate measurement—a difficulty exacerbated by the more intense emission from the loose pair even when interference from its overlap was minimised by the use of a narrow-bandpass 580 nm filter. The lifetime of the loose ion pair was found to fit Eq. (1) very satisfactorily by taking τ_0 as 3.10 ns; the Arrhenius parameters for skeletal twisting (Table 1) are virtually identical to those for DP5⁻Na⁺.

The absorption spectra of DP5⁻Li⁺ and of DP5⁻K⁺ in DMEDA consist of a single maximum at 584 nm arising from the presence of the loose ion pair. The formation of the latter, even with the K⁺ counterion, can be ascribed to the ready ability of this solvent to chelate these cations. The blue shift of the absorption with respect to that of the loose ion pair in MTHF mirrors an analogous general observation for the spectra of DP5⁻M⁺ in ethers compared with amines. Solutions of DP5⁻Li⁺ in TMEDA and of DP5⁻Na⁺ in MeNH₂ also exist as loose ion pairs, absorbing at 581 and 584 nm respectively. The emission spectra of all these solutions have their maxima in the range 620 to 627 nm except for DP5⁻Li⁺/TMEDA which is at 615 nm. Decay times were determined by exciting at 580 nm and with a filter cutting off light of wavelength
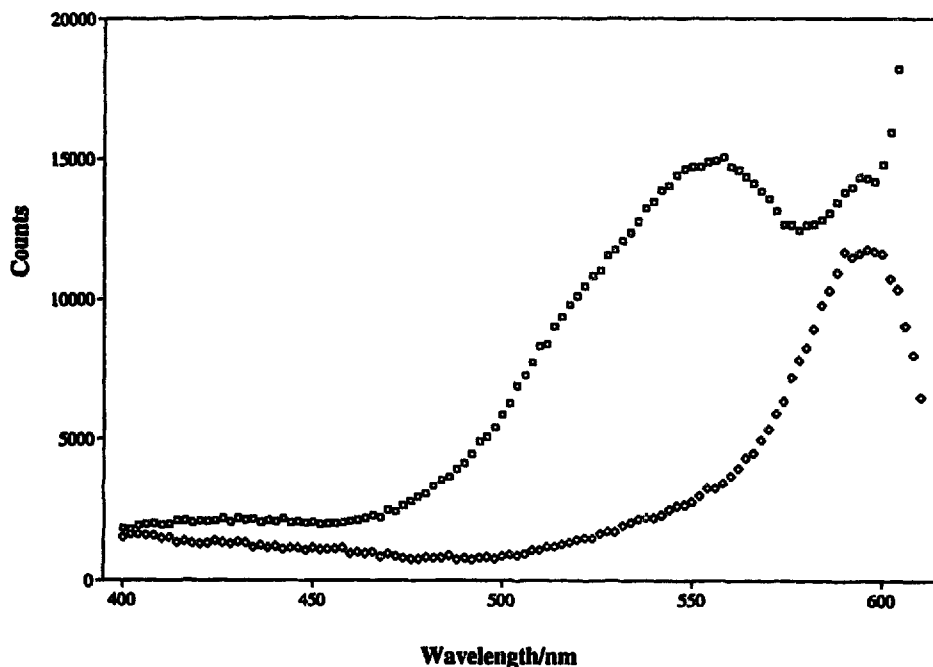
Fig. 3. Time-resolved excitation spectra of $DP_5^-Na^+$ in MTHF at − 10 °C: □, peak of decay; ◇, tail of decay.
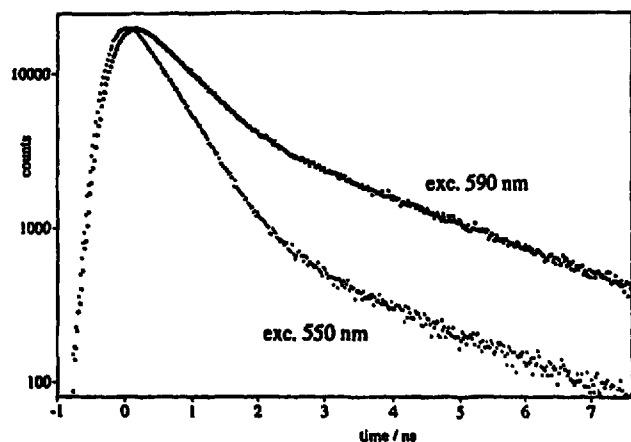

Fig. 4. Fluorescence decays of $DP_5^-Na^+$ in MTHF at − 1 °C showing the effect of excitation wavelength.

shorter than 610 nm in front of the photomultiplier and the results are shown in Fig. 5 as plots of lifetime vs. temperature. Good fits of the fluorescence decays were obtained to single exponentials for all these systems The data for $DP_5^-Li^+$ and $DP_5^-K^+$ in DMEDA lie on a common curve (except at the two lowest temperatures studied) and are systematically slightly greater than those of $DP_5^-Na^+$ in MTHF at any given temperature. The data conform closely to Eq. (1) and the resulting Arrhenius parameters are presented in Table 1. In contrast, the lifetimes for $DP_5^-Na^+$ in MeNH₂ are much smaller but again the data fit Eq. (1) very satisfactorily.

The final diphenylpentadienyl system studied was $DP_5^-Li^+$ in Me₃N. This solvent differs from the others examined in that it has a very small permittivity (2.44 at 25 °C) in comparison with MeNH₂ (11.3) or MTHF (6.9) and, unlike DMEDA and TMEDA, Me₃N is incapable of chelation. At room temperature, solutions of $DP_5^-Li^+$ in Me₃N are

purple–red and the absorption spectrum is a broad envelope with a maximum at about 565 nm. Cooling to − 10 °C causes a marked sharpening of the band, producing a shoulder at about 540 nm and moving the maximum to 570 nm; the colour simultaneously changes to blue. Further cooling to − 110 °C causes a little more sharpening together with a further shift to 574 nm. The emission spectrum has its maximum at 605 nm. The excitation spectrum was found to correspond closely to the absorption spectrum and showed the same dependence upon temperature. Notwithstanding the short wavelength location of the absorption band (which may be a consequence of the low permittivity of the solvent) it seems that, except near room temperature, the solute is most probably present as the loose ion pair. Indeed, the steric hindrance offered by the three methyl groups of Me₃N should not be sufficient to significantly inhibit the coordination of the lithium ion by the lone pair of electrons on the nitrogen atom. Fluorescence excited by light of 560 nm wavelength was monitored with a filter cutting off at 590 nm in front of the photomultiplier. Fitting required the use of two exponentials except at the lowest temperatures studied, where one sufficed. However, the exponential having the longer decay time was very much a minor contributor and was not investigated further. The remaining data could be fitted to Eq. (1) although there was some indication of non-random scatter; the Arrhenius parameters are shown in Table 1.

Abstraction of a proton from 1,1,5,5-tetraphenylpenta-1,4-diene in MTHF by butyllithium yielded turquoise-blue TPP^-Li^+ ($\lambda_{max} = 618$ nm). The fluorescence ($\lambda_{max} = 645$ nm) decays were single exponential and were well fitted by Eq. (1) yielding the Arrhenius parameters in Table 1.

Solutions of $DP_7^-Li^+$ in MTHF are blue. The absorption spectrum has a maximum at 642 nm arising from the presence

of the loose ion pair and a weak shoulder at about 598 nm due to the tight ion pair—representing some 10% of the solute—which disappears on cooling. The emission spectrum has a single maximum at 681 nm and the excitation spectrum shows that the loose ion pair is the sole or overwhelmingly predominant emitter. Very similar results are obtained for $DP_7^-Na^+$ in MTHF containing $NaBPh_4$ to suppress dissociation but the proportion of tight ion pair is greater. The absorption maximum of $DP_7^-Li^+$ in TMEDA is at 633 nm with a shoulder at about 592 nm. The fluorescence of all three salts was excited at 630 nm and monitored with a filter cutting off at 665 nm. Good fits of the decays to a single exponential were generally obtained and close conformity with Eq. (1) was found yielding the parameters shown in Table 1.

At room temperature $DP_7^-Li^+$ exists in DMTHF largely as the tight ion pair, the absorption maximum being located at 556 nm. The emission spectrum is a very broad envelope with a peak at 620 nm and a very broad shoulder at 675 nm. Cooling to −65 °C causes considerable band sharpening and the intensity of the peak at 675 nm relative to that at 620 nm increases markedly, corresponding to the conversion of the tight ion pair into the loose. Attempts were made to observe the fluorescence decay of the tight ion pair while minimising interference from that of the loose pair by exciting at 550 nm and placing an interference filter (620 nm) in front of the photomultiplier. Unfortunately, these were unsuccessful because the lifetimes were too short by comparison with the
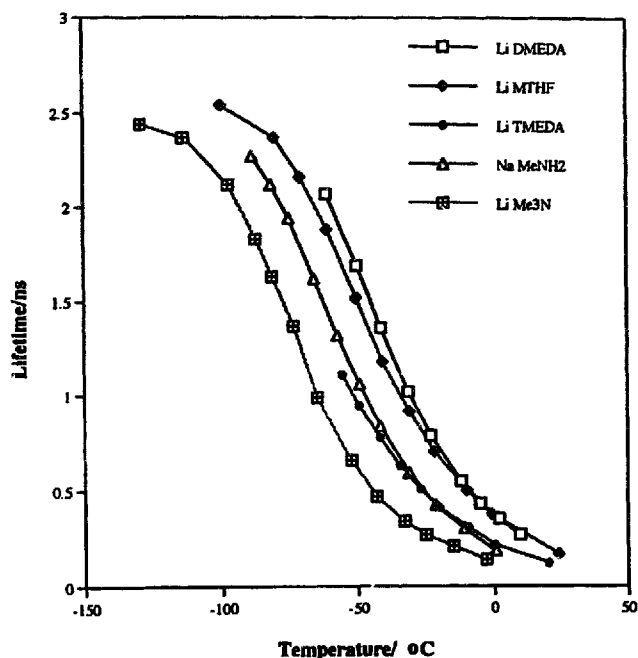

Fig. 5. Temperature dependences of fluorescence lifetimes for: □, $DP_5^-Li^+$ in DMEDA; ◆, $DP_5^-Li^+$ in MTHF; ●, $DP_5^-Li^+$ in TMEDA; △, $DP_5^-Li^+$ in Me_3N; ⊞, $DP_5^-Na^+$ in $MeNH_2$.

width of the instrument response function (700 ps). Measurement of the decay of the fluorescence of the loose ion pair was, however, readily accomplished by exciting at 640 nm;

Table 1
Assignment of absorption and emission maxima and Arrhenius parameters

System	Solvent	Absorption maximum (nm) [a]		Emission maximum (nm)	τ_0 (ns)	$10^{-13}A$ (s⁻¹)	E (kJ mol⁻¹)
		+20°	Low temp.				
DP_3Li^+ [b]	MTHF	428 (t) 565 (l)	565 (l)	582	4.30	2.95	21.7
DP_3Na^+ [b]	MTHF	516 (t)	565 (l)	582	4.59	5.75	21.5
DP_5Na^+	MTHF	548 (t)	598 (l)	568 (t) 618 (l)	3.10	1.68	19.9
DP_5Li^+	MTHF	535 (t)	558 (t) 595 (l)		2.60	4.13	22.1
DP_5Li^+	DMEDA	584 (l)			2.90	4.8	22.5
DP_5K^+	DMEDA	584 (l)	588 (l)	627 (l)	3.30	4.34	22.2
DP_5Li^+	TMEDA	581 (l)		615 (l)	2.50	1.95	19.2
DP_5Na^+	MeNH₂	584 (l)			2.58	4.65	21.0
DP_5Li^+	Me₃N	540 (t)	576 (l)	605 (l)	2.47	4.0	19.4
DP_5Li^+	MTHF	598 (t) 642 (l)	650 (l)	681 (l)	2.22	2.70	23.7
DP_7Na^+	MTHF		650 (l)	683 (l)	1.72	1.53	23.2
DP_7Li^+	TMEDA	592 (t) 633 (l)	635 (l)		2.20	1.45	20.5
DP_7Li^+	DMTHF	556 (t)		620 (t), 680 (l)	2.24	1.39	22.0
DP_7Li^+	Me₃N	610 (t?)	620 (l)	660 (l)			
DP_7Li^+	MTHF			744 (l)	1.62	1.85	24.5
DP_9Na^+	MTHF	648 (t)	708 (l)	735 (l)	1.72	1.53	23.2
DP_9Li^+	Me₃N	615 (t)	664 (l)	703 (l)			
DP_9Na^+	DMTHF	632 (t)	706 (l)		1.00	0.35	15.7
TSM·Li⁺	MTHF	560 (?), 594 (l)	595 (l)	650 (l)	4.40	0.03	15.7
TSM·Li⁺	TMEDA	542, 582 (l)	585 (l)	650 (l)	3.5	0.16	16.6
TSM·Li⁺	DMEDA	546, 590 (l)	590 (l)	648 (l)	6.5	2.58	20.9
TSM·Li⁺	Me₃N	520, 540, 585 (t)	586 (l)	641 (l)	4.85	3.34	18.5
TSM·Cs⁺	DMTHF	510, 562 (t)	573 (t)				
TPP·Li⁺	MTHF	618 (l)	618 (l)	645 (l)	3.84	1.13	12.4

[a] t, tight ion pair; l, loose ion pair.
[b] Ref. [16].
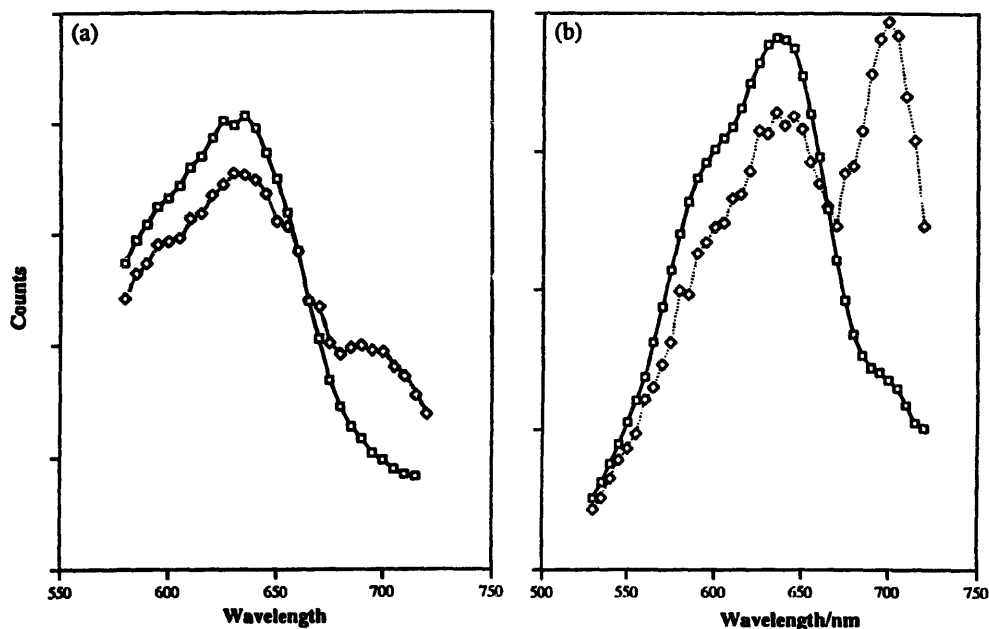
Fig. 6. Time-resolved excitation spectra of $DP_9^- Na^+$ in MTHF: □, peak of decay; ◇, tail of decay: (a) at −7 °C (b) −46 °C.

fits to a single exponential were entirely satisfactory and the temperature dependence of the lifetime was well represented by Eq. (1).

Solutions of $DP_9^- Li^+$ in MTHF are green and the absorption spectrum is insensitive to temperature and consists of a single maximum at 709 nm, showing that only the loose ion pair is present. The emission spectrum consists of a single band ($\lambda_{max} = 750$ nm) and the excitation spectra closely matches the absorption spectrum. In contrast, solutions of $DP_9^- Na^+$ in MTHF are blue at room temperature and the solute is almost entirely present as the tight ion pair which absorbs at 630 nm. On cooling, conversion to the loose ion pair occurs and is substantially complete at −65 °C. On excitation at 700 nm at 20 °C the emission maximum is at 735 nm but suffers a red shift on cooling, reaching 750 nm at −120 °C this progressive change being accompanied by a marked narrowing of the bandwidth—reflecting the changing nature of the ion pairing. Good fits of the fluorescence decays were obtained to a single exponential when the excitation wavelength was at 700 nm with a filter cutting off light of wavelength shorter than 740 nm in front of the photomultiplier. In turn, the temperature dependences of the lifetimes conformed closely to Eq. (1) giving the Arrhenius parameters shown in Table 1.

Time-resolved excitation spectra of solutions of $DP_9^- Na^+$ in MTHF show clearly that the emitters are the tight and loose ion pairs with the former having a much shorter lifetime (Fig. 6). Lowering the temperature from −7 to −46 °C dramatically increases the relative contribution of the loose ion pair in accord with expectation.

Solutions of $DP_9^- Na^+$ in DMTHF contain only the tight ion pair ($\lambda_{max} = 632$ nm) at room temperature. On cooling, the maximum gradually shifts to 650 nm with a loss of intensity and a new band due to the tight ion pair appears at 706

nm. The emission spectrum at ambient temperature is a broad envelope whose shape is dependent upon the excitation wavelength. When the latter is 610 nm the emission has a maximum at about 695 nm and a large broad shoulder at 740 nm; when exciting at 650 nm there are broad overlapping bands with maxima near 695 and 740 nm. Excitation spectra show that these are attributable to the emissions of the tight and loose ion pairs respectively. Lowering the temperature causes very marked sharpening of the emission spectra into bands with maxima near 685 and 750 nm. The large difference between the absorption maxima of the tight and loose ion pairs and also that between their emission bands offers the best opportunity in the $DP_n^- M^+$ series under study of obtaining lifetime data for a tight ion pair system over a reasonable range of temperature. In order to optimise the signals from them, a narrow bandpass filter (IF690) was placed in front of the photomultiplier and excitation at 630 nm was employed. The fluorescence decays required the use of two exponentials to obtain a satisfactory fit. The results of examination of two different preparations of $DP_9^- Na^+$ in DMTHF are shown in Fig. 7. The lifetimes of the tight ion pairs range from about 0.18 to 1.0 ns as the temperature is reduced from 0 to −120 °C and the data for the two solutions are in good agreement with each other. In contrast, the very short lifetimes of the second exponential are in rather poor agreement with each other; it is suspected that they may represent scattered light and deficiencies in fitting. The lifetimes of the loose ion pair of $DP_9^- Na^+$ and for $DP_9^- Li^+$ in MTHF are also shown in Fig. 7 and it can be seen that they are very much longer.

The lithium salt of the "cross-conjugated" 1,5-diphenyl-3-(2'-phenylethenyl)-pentadienyl or "tristyrylmethyl" anion, $TSM^- Li^+$, forms a blue solution in DMEDA. The absorption spectrum is broad and exhibits a maximum at 590
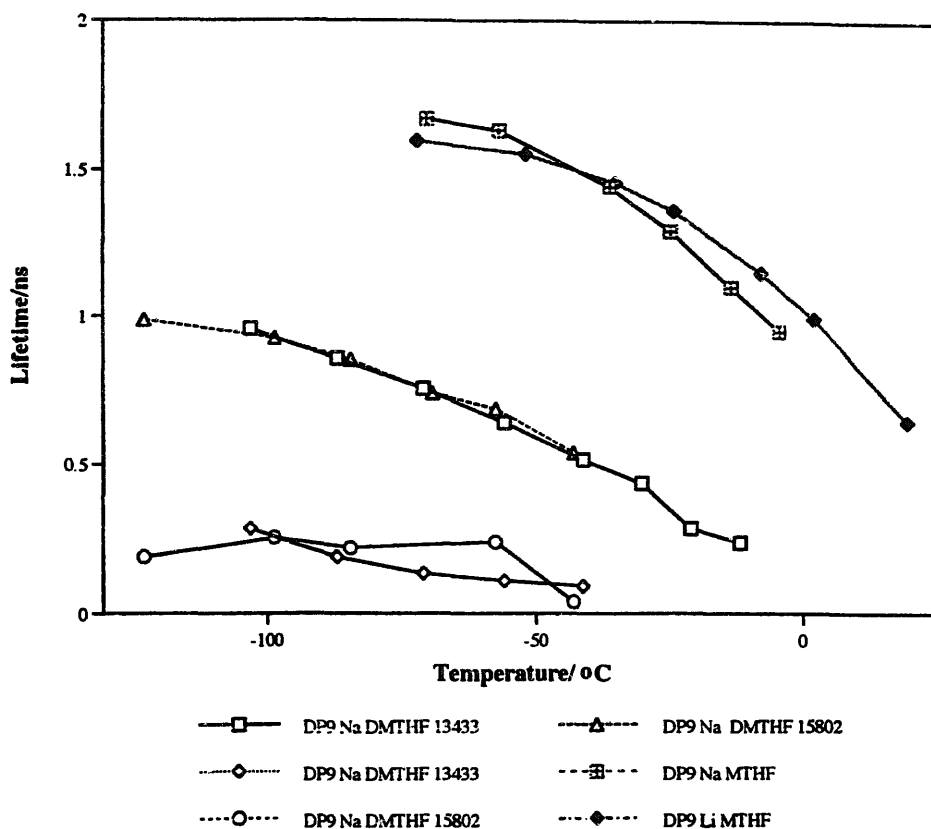
──☐──	DP9 Na DMTHF 13433	────△────	DP9 Na DMTHF 15802
────◇────	DP9 Na DMTHF 13433	───⊞───	DP9 Na MTHF
────O────	DP9 Na DMTHF 15802	───◆────	DP9 Li MTHF

Fig. 7. Temperature dependences of fluorescence lifetimes. DP₉⁻Na⁺ in DMTHF (data set 13433): τ_1, ☐; τ_2, ◇. DP9⁻Na⁺ in DMTHF (data set 15802): τ_1, O; τ_2, △. DP₀⁻Na⁺ in MTHF, ──⊞──. DP₉⁻Li⁺ in MTHF, ──◆──.
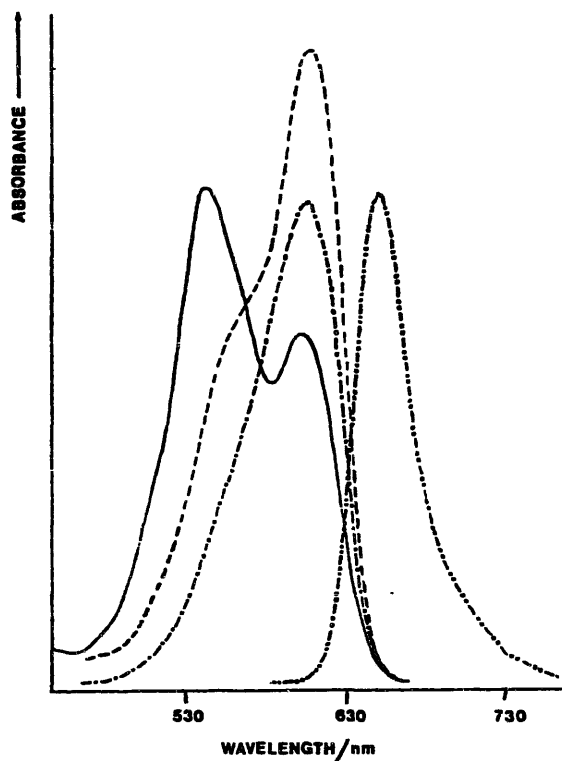
Fig. 8. Tristyrylmethyl lithium in MTHF at − 130 °C: - - -, absorption spectrum; − · · −, emission spectrum; − · − excitation spectrum (for λ_{em} = 550 nm); ───, absorption spectrum following photolysis with white light.

nm with a substantial shoulder at about 540 nm. The predominant species are expected to be loose ion pairs—a view confirmed by the similarity to the spectrum in the powerful solvating medium dimethylsulphoxide. The spectrum of TSM⁻Li⁺ in MTHF is similar but shifted somewhat to longer wavelength (Fig. 8). The emission maximum is at 650 nm with a shoulder on the tail to long wavelength. The excitation spectrum closely matches the absorption spectrum. The decay of fluorescence excited at 600 nm and monitored with a filter cutting off at 630 nm placed in front of the photomultiplier was well fitted by a single exponential. The temperature dependence of the lifetime conformed closely to Eq. (1) and the resulting Arrhenius parameters are given in Table 1. TSM⁻Li⁺ in TMEDA behaved similarly.

At room temperature the absorption spectrum of TSM⁻Li⁺ in Me₃N is a broad envelope but, on cooling, a distinct peak appears at 580 nm with shoulders at about 540 and 520 nm. The excitation spectrum is much less broad, having a maximum at 590 nm and a shoulder at about 540 nm. The emission spectrum is, by comparison, narrow and has its maximum at 637 nm. The decay of fluorescence required two exponentials to achieve a satisfactory fit. The shorter of these had a small weighting and seemed to be largely attributable to scattered light. The major component gave a reasonably linear Arrhenius plot and the parameters are given in Table 1.

3.1. Photolysis of carbanions

Photolysis of TSM^-Li^+ in MTHF with white light at temperatures below $-100\ ^\circ C$ leads to a reduction in the absorbance of the band having its maximum at 598 nm and the formation of a new band at 538 nm (Fig. 8). A photostationary state is rapidly attained—the extent of change increasing with decreasing temperature. When illumination ceases, relaxation to the unphotolysed state ensues. Analysis of data collected over the temperature range of -105 to $-130\ ^\circ C$ showed that this process follows first order kinetics with an activation energy of $47.5\ kJ\ mol^{-1}$ and a pre-exponential factor of $2.7 \times 10^{14}\ s^{-1}$. Experiments conducted at $-130\ ^\circ C$ showed that the shapes of the emission and excitation spectra are unchanged after photolysis. However, their intensities are initially reduced to about 10% of the pre-photolysis values. The original intensities are recovered in a few minutes by first-order processes that mirror the post-photolysis relaxation of the changes in the absorption spectrum. The absorption maximum of TSM^-Cs^+ in DMTHF is at 573 nm—the blue shift relative to TSM^-Li^+ in MTHF showing that this is the tight ion pair, as expected with a large cation in a sterically hindered poor-solvating solvent. Photolysis at temperatures below about $-100\ ^\circ C$ resulted in the formation of a new absorption band ($\lambda_{max} = 515$ nm) at the expense of that at 573 mn. Monitoring the post-photolysis relaxation yielded the approximate Arrhenius parameters $E = 48\ kJ\ mol^{-1}$ and $A = 3.6 \times 10^{14}\ s^{-1}$.

Photolysis of $DP_5^-Li^+$ in THF at $-105\ ^\circ C$ using white light causes a reduction in the absorbance of the loose ion pair and the absorption maximum moves from 595 to 590 nm; these changes are accompanied by the formation of a new absorption band at about 636 nm (Fig. 2). The photolysis appears to have a rather low efficiency and increases in extent with the duration of illumination up to a limit of about 20%—perhaps indicating the establishment of a photostationary state. The new species formed fluoresces ($\lambda_{em} = 678$ nm) and its excitation spectrum matches its absorption spectrum. Very little relaxation is seen in the dark at this temperature, even over several minutes, but warming to near room temperature and recooling to $-130\ ^\circ C$ completely restores the original absorption spectrum. Very similar, but more extensive photolysis (ca. 40%) is seen with solutions of $DP_5^-Li^+$ in Me_3N (λ_{max} moving from 540 to 576 nm on cooling from ambient temperature to $-20\ ^\circ C$)—the new absorption maximum being at 630 nm.

The absorption spectrum of $DP_7^-Li^+$ in Me_3N is a very broad band with a maximum at about 610 nm. Cooling causes dramatic sharpening and a colour change from light blue to dark blue. At $-70\ ^\circ C$ the band maximum is located at 620 nm and exhibits shoulders at ca. 590 and at 672 nm (Fig. 9). The latter shoulder is an artefact due to the presence of $DP_9^-Li^+$ as a contaminant. Photolysis with white light at this temperature causes the absorption maximum to move to 644 nm accompanied by a decrease in absorbance of about 30%. On standing in the dark, first order relaxation to the original
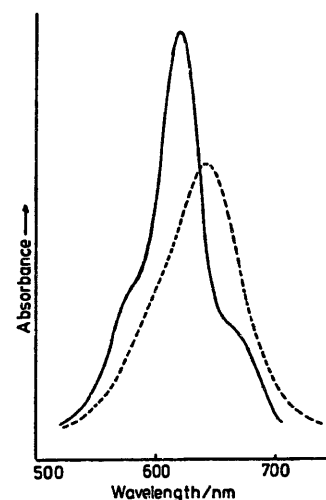

Fig. 9. Spectrum of $DP_7^-Li^+$ in Me_3N before (———) and after (- - -) photolysis at $-70\ ^\circ C$.

spectrum occurs with a rate constant of about $1\ min^{-1}$. Warming to room temperature, followed by cooling in darkness to $-70\ ^\circ C$, removes the effect of photolysis completely. Similarly, the intensity of the emission ($\lambda_{max} = 660$ nm) which is reduced by more than a factor of 10 on brief photolysis at $-70\ ^\circ C$ is completely recovered on warming and re-cooling.

Solutions of $DP_9^-Li^+$ in Me_3N are royal blue at ambient temperature and the absorption spectrum consists of a broad band with its maximum at 615 nm. On cooling to $0\ ^\circ C$ the colour changes to aquamarine and the maximum progressively moves to 656 nm and is accompanied by considerable band sharpening. Cooling to $-100\ ^\circ C$ causes a further red shift to 664 nm. Photolysis with white light over the temperature range studied, from -30 to $-120\ ^\circ C$, caused a small decrease in absorbance (ca. 5%) which was restored on standing in darkness: no new band was observed. The emission maximum is at 703 nm and the excitation maximum is at 667 nm.

3.2. Discussion

The conversion of the tight ion pair to the loose is exothermic and is therefore favoured by lowering the temperature. In addition, the equilibrium at any given temperature shifts in favour of the loose ion pair with increasing length of the conjugated chain. In consequence, the majority of the systems studied in the present work were largely in the form of the loose ion pairs over much of their accessible temperature ranges. In strongly solvating media like MTHF at the low concentrations employed for fluorescence measurements there is the possibility of some dissociation into free ions. In several cases, measurements were made with and without the presence of lithium or sodium (as appropriate) tetraphenylborate to provide common ion suppressant. No differences were detected, suggesting that the loose ion pair and the free anion have the same, or very similar, lifetimes. The formation of tight ion pairs is favoured by weakly solvating media and DMTHF is particularly suitable—especially with sodium.

The heavier alkali cations are even less readily solvated but have the serious disadvantage that the overlap of the absorption spectra of the tight and loose ion pairs increases with increasing cation radius thereby greatly reducing the possibility of selective excitation. Other available solvents considered were rejected because of severely limited liquid ranges or, in the case of, for example, triethylamine because it is suspected that the tight ion pairs are extensively aggregated.

The fluorescence behaviour of the α,ω-diphenylpolyenylic carbanions closely resembles that of DP_3^-. In all cases the temperature dependence of their fluorescence lifetimes fits Eq. (1). This is most easily understood in terms of competition between emission and twisting round one of the polyene bonds (Fig. 1); no evidence was found to suggest the participation of electron photo-ejection as suggested by Tolbert [18,19]. The temperature dependence of the fluorescence lifetimes of the corresponding carbocations, where electron ejection is highly unlikely, also conforms closely to Eq. (1) [24]; the parameters for anions and cations are very similar.

Absolute fluorescence yield measurements have only been attempted for the DP_3^- where it was found that they reached 0.8 at low temperatures [14]. The larger anions are also strong emitters, so the values of τ_o must be dominated by the radiative process which is clearly strongly allowed. Increasing chain length leads to increasing transition dipoles which explains the decrease in τ_o seen in Table 1. However, TSM^- has C_{3h} symmetry: a simple view is that while the electrons are spread over three styryl groups only two can take part in the transition; the transition dipole is therefore less than that of DP_5^- giving a larger value of τ_o as is found.

Low-temperature photolysis partly bleaches the original absorption band and produces new bands; on warming the original spectrum is restored suggesting formation of a less stable isomer as in the case of DP_3^-. (Surprisingly, DP_9^- shows no change). In the following, 'first bond' refers to one of the terminal bonds of the polyenyl chain. It will be assumed that the normal ground state molecules have the all-trans configuration and photolysis leads to trans to cis isomerisation about the first bond; no confirmatory evidence is available. As in DP_3^-, conformers with a cis first bond are destabilised by strong steric interaction, but this is much less true of the central bonds. In principle, ^1H NMR spectroscopy could be used to determine the structures of the photo-isomers but, apart from the existing uncertainty about the equilibrium geometry of the DP_n^- ions [8,21], the high concentrations required would preclude efficient photolysis in practice. However, it may be noted that while central cis isomers are expected to have spectra identical to the trans forms the transition dipoles will be smaller.

The photochemical behaviour of the stilbenes is commonly understood in terms of level crossings between the S_0, S_1 and S_2 states [25,26]. Though the behaviour of ionic species with an odd number of carbons in the central chain closely parallels that of stilbene, the same argument does not apply. Momicchioli et al. [27] tackled this problem for the cyanine dyes— cations which have similar electronic structures to DP_n^-.
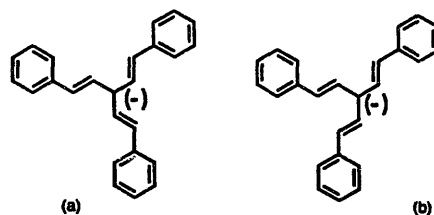

Fig. 10. Conformers of the TSM^- carbanion.

Using CS INDO they showed that a minimum in the potential energy of S_1 occurs at 90 °C for the following reason: in the twisted form of the ground state S_0 charge is localised in one fragment (e.g. benzyl in the case of DP_3^-); in S_1 an electron is transferred to the other (styrene fragment); the orbitals containing the two unpaired electrons do not overlap; there is no electron repulsion so that S_1 and T_1 become degenerate. We have used more modern semi-empirical methods (MOPAC: the AM1 parameterisation) and were able to obtain more satisfactory potential energy curves for the DP_3^- system [28].

Photolysis presumably involves trans to cis isomerisation of the first bond. The observation of a red shift in the larger anions suggests that the steric strain is taken up by twisting of the phenyl–polyenyl bond whereas the first bond is twisted in DP_3^-. Absorption (in the near-planar molecule) involves exciting an electron from the non-bonding orbital to an orbital formed by overlap of the LUMOs of the phenyl group and the polyenyl chain, i.e. one that is bonding for phenyl–polyenyl but anti-bonding for the first bond. The reason for the difference is not clear: attempts to justify it using semi-empirical calculations did not give satisfactory results but it must be borne in mind that these are very large molecules and the energy differences small. In contrast, photolysis of TSM^- leads to a blue shift. Komatsu et al. concluded [23] from ^{13}C NMR measurements that the predominant conformation of TSM^-Li^+ in THF is that with C_{3h} symmetry (Fig. 10(a)) with a small amount of conformer b in dynamic equilibrium; the broadening of the lines due to C_2 and C_3 disappears at temperatures below −45 °C when exchange slows. It seems reasonable to suppose that this is also the photo-isomer and that the strain is taken up in the two first bonds involved. NB it does not follow that twisting round a central bond is the main deactivation pathway; this could involve a first bond but the corresponding isomer would be less stable than b and therefore more labile.

It is now necessary to consider the deactivation process itself. In the larger compounds twisting about any of the polyenyl bonds can lead to deactivation and isomerisation. While isomerisation involves deactivation of the excited state, the reverse is not necessarily true because a limited amount of twisting probably suffices to promote internal conversion: for example it was found previously that DP_3^- derivatives in which the allyl group was contained in a five- or six-membered ring underwent a temperature-dependent deactivation process similar to that of the parent compound [16]. As a guide to the likely site of twisting, Hückel calcu-

lations were carried out on the $DP_n{}^-$ series: if the twist energy is much less in one case, the barrier to twisting may also be smaller. Twisting also changes the charge distribution leading possibly to solvent and counter-ion effects which will be largest for short chain molecules. The calculations show that the twist energy increases with chain length for the first bond: the observed activation energies appear to increase slightly but the effect is small. Twisting the phenyl–polyenyl bond requires less energy in the excited state especially at large n, but the above argument concerning the electron repulsion energy does not apply in this case—no charge transfer is involved in exciting the perpendicular form—so this is not a likely route for deactivation.

The Arrhenius pre-exponential factors for skeletal twisting of $DP_n{}^-$ and TSM^- ions in their excited states are all about 10^{13} s^{-1}—values typical of unimolecular processes. Unfortunately, in many systems the freezing point of the solvent is very much higher than the temperature at which the limiting fluorescence lifetime would be reached. This necessitates the determination of τ_0 through finding the best linear fit to the data which involves a lengthy extrapolation. Often in such cases, the quality of fit is rather insensitive to the choice of τ_0. No clear pattern can be discerned in the values of the Arrhenius activation energies for the $DP_n{}^- M^+$ series. Direct comparison of the τ vs. temperature plots is somewhat more informative. In general, it can be seen that τ_0 decreases as n increases. Interestingly, the temperature dependence of fluorescence lifetimes is similar in amine and ether solvents. This contrasts with earlier work on $DP_3{}^- M^+$ [16] which was found to closely resemble the present $DP_n{}^- M^+$ solutions in ethers but which had anomalously large Arrhenius A and E values in amines such as $MeNH_2$ for which there is no clearcut explanation.

Unequivocal evidence for the fluorescence of the tight ion pairs of $DP_5{}^- Na^+$ in MTHF is provided by the time-resolved excitation spectra (Fig. 3) and by the wavelength dependence of the relative weightings of the two decay exponentials (Fig. 4). Unfortunately, the spectra of the two kinds of ion pair are extensively overlapped thereby severely limiting selective observation of the tight ion pair and adding to the difficulty of measuring short lifetimes with accuracy. The difficulty was compounded by the much greater intensity of the emission from the loose ion pair at lower temperatures. In consequence, it proved impossible even to estimate the Arrhenius parameters. More success was achieved with $DP_9{}^- Na^+$ in DMTHF.

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