Structure–photophysics correlation in a series of 2,6-dimethyl-4-arylpyrylium derivatives [1]

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Abstract

Photophysical properties of a group of closely related pyrylium cations, 1–5, are reported. Our results indicate that these cations have two excited states with similar energies and that the substituent determines which of these has the lowest energy. For cations 1 and 2, the lowest excited state has TICT character. In the case of 3–5, the photophysical properties are better explained by invoking a planar excited state.

1. Introduction

Study of the photophysical properties of pyrylium salts and their derivatives is of considerable interest to Chemists because of their potential applications as photosensitizers in electrophotography or as laser dyes [1–9]. We have been interested in these compounds because of their potential application as electron transfer sensitizers [10–12]. In the course of our studies, we have observed considerable differences in the photophysical properties of structurally very similar pyrylium derivatives. We believe that these differences can be explained by invoking a twisted intramolecular charge transfer (TICT) excited state for some of these derivatives. The concept of TICT was initially advanced by Grabowski and coworkers to account for the dual fluorescence of dimethylaminobenzonitrile (DMABN) [13–16]. In principle, any electron donor–acceptor system connected

by a flexible bond can exhibit the TICT phenomenon [17,18]. Although suitably substituted pyrylium cations are good candidates to study TICT phenomenon, only one of its derivatives, namely, 2,6-diphenyl-4-(p-dimethylaminophenyl)pyrylium tetrafluoroborate, is reported to possess the TICT excited state [19]. In this case, calculations showed the formation of a non-fluorescent TICT state involving the rotation of the dialkylaminophenyl group without energy barrier. In the present paper, we report the photophysical properties of pyrylium salts 1–5 (Fig. 1). Our results suggest that the lowest excited states in 1 and 2 have TICT character, whereas, for compounds 3–5, the photophysical properties are best explained by invoking a planar excited state.

2. Experimental

The pyrylium perchlorates employed in this work were prepared by standard procedures and were thoroughly purified before use [1]. Spectroscopic grade solvents were used throughout.

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1) $R_1 = R_2 = H$

2) $R_1 = CH_3, R_2 = H$

3) $R_1 = H, R_2 = CH_3$

4) $R_1 = H, R_2 = C_{12}H_{25}$
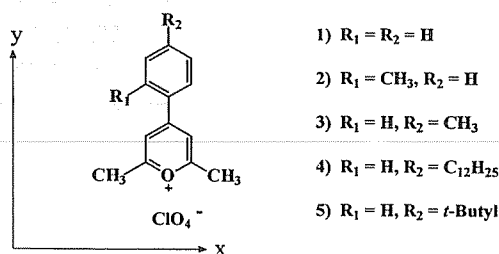
5) $R_1 = H, R_2 = t\text{-Butyl}$

Fig. 1. Structure of pyrylium cations 1–5.

Absorption spectra were recorded on a Shimadzu UV 2100 spectrometer or a GBC double beam UV–Vis spectrophotometer. Fluorescence spectra were recorded on a SPEX Fluorolog F 112-X spectrofluorimeter with a right angled geometry using 1×10^{-5} M solutions. Fluorescence quantum yields were measured using quinine sulfate in 1 N sulfuric acid ($\Phi_f = 0.54$) as reference. Fluorescence lifetimes were measured using a IBH 5000 U single photon counting system.

3. Results and discussion

3.1. Absorption spectra

Compounds 1 and 2 (or 3) differ only by the presence of a methyl group in the ortho (or para) position of the phenyl ring. Yet they exhibit markedly different absorption spectra. Fig. 2 shows the absorption spectra of pyrylium perchlorates 1–3 in dichloromethane solution. The absorption maxima, extinction coefficients and the full width at reciprocal "e" (FWRE) values for the lowest energy absorption band for cations 1–5 are summarized in Table 1. An inspection of Table 1 reveals that introduction of an alkyl group leads to profound changes in the spectral properties. The nature of the alkyl
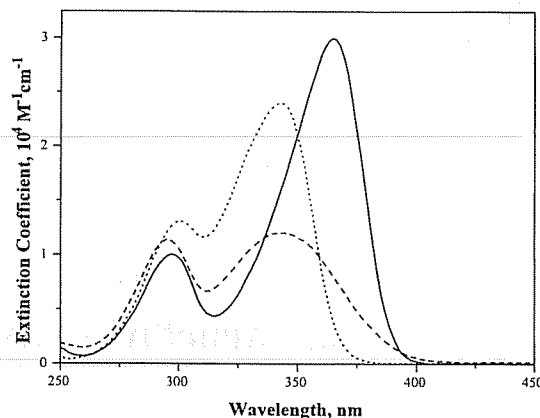
Fig. 2. Absorption spectra of pyrylium perchlorates 1 ($\cdots\cdots$); 2 (– – –) and 3 (——) in dichloromethane.

group (methyl, n-dodecyl or tert-butyl), however, does not have a major role. This is evident from the fact that 3, 4 and 5 have similar absorption and emission properties.

For pyrylium salts, the absorption spectra are normally blue shifted in polar solvents [20–22]. In the present case a blue shift of ~ 20 nm in the absorption maxima was observed for all the substrates in acetonitrile. In the case of 1 and 2, this blue shift leads to an overlap of the two absorption bands and hence the FWRE values could not be determined in this solvent. Slight changes in the extinction coefficients were also noted for all compounds in acetonitrile.

Numerous spectroscopic studies, both experimental and theoretical, have been carried out on pyrylium salts and their structural analogs [19–28]. Rullière et al. suggested that the observed absorption band for 1 in acetonitrile at 326 nm is a superposition of two closely lying bands, namely, the weak $S_0 \rightarrow S_1$ band [calculated $\lambda_{max} = 334$ nm, polarized along the x-

Table 1
Absorption maxima (λ_{max}), extinction coefficients (ϵ_{max}), and full width at reciprocal e (FWRE) values for pyrylium salts 1–5 in dichloromethane. Values in paranthesis are those obtained in acetonitrile

Compound	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}	FWRE, cm^{-1}
1	343 (326)	2.4×10^4 (2.3×10^4)	4585
2	343 (327)	1.2×10^4 (0.97×10^4)	6332
3	365 (347)	3.0×10^4 (2.9×10^4)	3650
4	370 (350)	3.5×10^4 (2.9×10^4)	3575
5	365 (345)	3.4×10^4 (2.9×10^4)	3617

axis, "x"-band (see Fig. 1 for axis convention)] and the strong $S_0 \rightarrow S_2$ band (calculated $\lambda_{max} = 325$ nm, polarized along the y-axis, "y"-band) [9]. The band separation is very small (9 nm, corresponds to $\Delta E = 825$ cm^{-1}) and hence these bands could not be resolved. The FWRE value for 1 (4585 cm^{-1}) indeed suggests that this band is a superposition of two absorption bands. It should be mentioned here that, the existence of two closely lying bands have been confirmed in a few pyrylium salts by fluorescence polarization measurements [19,27].

Substituents affect the absorption spectra of pyrylium cations depending on whether they are in the x-direction or y-direction [1,29–32]. Ortho substitution as in 2, has its major component projected along the x-axis and affect the x-band predominantly. Thus in 2, the $S_0 \rightarrow S_1$ band ($\times$-band) is expected to shift bathochromically relative to the $S_0 \rightarrow S_2$ band leading to increased separation of the bands. This is confirmed by the observation of larger FWRE values and the red shift in the onset of absorption for 2, as seen in Fig. 2. On the other hand, substitution of a methyl group at the para position as in 3, will affect the y-band predominantly. Thus in 3, we expect the $S_0 \rightarrow S_2$ band to shift bathochromically relative to the x-band. If this relative red shift is more than 9 nm, it would lead to a reversal of the energy levels. A methyl group generally induces a bathochromic shift of 20 nm. Hence we believe that the S_1 and S_2 levels of 1 (or 2) are actually reversed in 3. There is very little effect on further increasing the size of the alkyl group. The absorption maxima of 4 and 5 are similar to those observed for 3. Note that in 3–5, the FWRE values are very small. These values are typical of single absorption bands [33]. This suggests that the

$S_0 \rightarrow S_1$ band of 1 (and 2) is extremely weak or even absent in 3–5.

4-Phenylpyrylium cations like 1 are structurally similar to biphenyl and 4-phenylpyridine derivatives, where it is well known that the two aromatic rings are not coplanar [33,34]. Calculations have recently shown that in 2,4,6-triphenylpyrylium cation, the 4-phenyl ring makes an angle (θ_4) of 40° with the plane of the pyrylium ring [27]. The twist angle $\theta_4 = 40°$ for the minimum energy conformation is a result of competition between conjugation (leading to stabilization of planar conformation) and steric hindrance (leading to twisted conformation). The twist angle was found to be reduced to 30° when the para position of the 4-phenyl ring was substituted by an electron donating dimethylamino group (more stabilization of the planar conformation) [19]. The twist angle is expected to increase if the ortho position of the phenyl group is substituted. Thus we expect 2 to be more twisted and 3–5 more planar compared to 1. This argument is supported by the low extinction coefficients of absorption for 1 and 2 compared to other derivatives (Fig. 2).

3.2. Emission properties

Fig. 3 shows the emission spectra of 1–3 in dichloromethane. Compounds 3–5 exhibit very similar emission properties in all solvents. For all these compounds, the emission spectra are red shifted in acetonitrile. The red shifts observed for 1 and 2 are much larger than those observed for 3–5. Table 2 summarizes the emission maxima (λ_{max}), quantum yields (Φ_f), fluorescence lifetimes (τ_f), Stokes shift values (ν_{st}), radiative rate constants (k_R) and the nonradiative rate constants (k_{NR}) for these com-

Table 2
Emission maxima (λ_{max}), Stokes shift (ν_{st}) values, fluorescence quantum yields (Φ_f), fluorescence lifetimes (τ_f), radiative decay rates (k_R) and nonradiative decay rates (k_{NR}) for pyrylium salts 1–5 in dichloromethane. Values in parenthesis are those obtained in acetonitrile

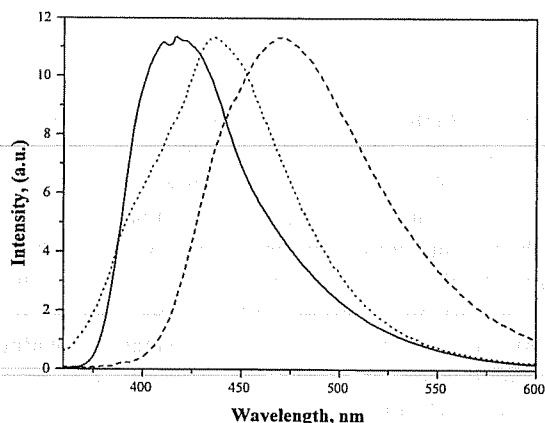| Compound	λ_{max}, nm	ν_{st}, cm^{-1}	Φ_f	τ_f, ns	k_R, 10^6 s^{-1}	k_{NR}, 10^8 s^{-1}
1	434 (462)	6114 (9030)	0.011 (0.10)	0.78 (12.1)	14.1 (8.3)	12.7 (0.74)
2	469 (518)	7833 (11276)	0.05 (0.10)	4.6 (12.2)	10.9 (8.2)	2.1 (0.78)
3	417 (435)	3416 (5830)	0.27 (0.28)	3.3 (8.7)	81.8 (32.2)	2.2 (0.83)
4	418 (435)	3104 (5583)	0.37 (0.36)	3.1 (8.1)	119.4 (44.4)	2.0 (0.79)
5	417 (430)	3416 (5730)	0.25 (0.36)	2.1 (8.0)	119.1 (45.0)	3.6 (0.80)

Fig. 3. Normalized emission spectra of pyrylium perchlorates **1** (· · · · ·); **2** (– – –) and **3** (———) in dichloromethane. The excitation wavelength was 350 nm.

pounds in two solvents. In Table 3, the Stokes shift values (ν_{st})obtained in four solvents for substrates **1–3** are listed. To a first approximation, the Stokes shift is a property of the refractive index (n) and dielectric constant (ϵ) of the solvent and is described by the Lippert equation [35],

$$\nu_{st} = \frac{2(\mu_e - \mu_g)^2 \Delta f}{hca^3} + \text{const.}$$

where μ_e and μ_g are the excited and ground state dipole moments, respectively, $\Delta f = [(\epsilon - 1)/(2\epsilon + 1)] - [(n^2 - 1)/(2n^2 + 1)]$, h is the Planck's constant, c is the speed of light and a is the radius of the cavity in which the fluorophore resides. The slope (m) of a plot of ν_{st} vs. Δf gives the value of $2\Delta\mu^2/hca^3$. Assuming $a = 4$ Å, $\Delta\mu$ values were calculated for substrates **1–3** (Table 3). It can be noted from Tables 2 and 3 that minor changes in the structure lead to profound changes in all the emission properties in this group of compounds.

Substrates **3–5** exhibit slight structure in the emission spectra in dichloromethane. This, coupled with the small Stokes shift (3400 cm^{-1}), higher Φ_f and relatively short τ_f values suggest that these compounds have planar excited states. Their behaviour can be compared with that of biphenyl where $\theta_4 = 23°$ in the ground state and $0°$ in the excited state and a Stokes shift of 3300 cm^{-1} is observed in nonpolar solvents. The fluorescence quantum yields of **3–5** remain relatively unchanged in acetonitrile indicating that the excited state remains the same in this solvent. It has been suggested that the first two singlet transitions of 4-phenylpyrylium cations are charge transfer in nature [25]. As a consequence of this charge transfer, the phenyl ring bears approximately the entire positive charge. The effective change in the positive charge centers (pyrylium → phenyl) is reflected in the large change in dipole moment subsequent to excitation. Assuming planar geometries for ground and excited states, Bigelow calculated $\mu_g = -3.67$ D and $\mu_e = 10.29$ D (polarizations along the y-axis) for 2,6-dimethyl-4-phenylpyrylium cation [25]. The $\Delta\mu$ value we obtained for **3** (13.8 D) is very close to 13.96 D predicted by Bigelow. This again supports our suggestion that **3–5** exhibit planar excited states.

Emission properties of **1** were very different from those of **3–5**. Compound **1** exhibits large Stokes shift value and lower emission quantum yield. The emission quantum yield and lifetime showed a more than 10 fold enhancement in acetonitrile (see Table 2 and Fig. 4). Changing the solvent to acetonitrile increases the Stokes shift to 9030 cm^{-1}. Such large Stokes shift values are normally observed for compounds which exhibit TICT or other adiabatic photoreaction channels [18]. Note that $\Delta\mu$ value obtained for **1** is larger than that predicted for the planar cation [25]. Although we did not observe a precur-

Table 3

Stokes shift values (ν_{st}) in different solvents, solvatochromic slopes (m), and $\Delta\mu$ values for pyrylium salts **1–3**

Compound	Stokes shift, ν_{st}, cm^{-1}				m, cm^{-1}	$\Delta\mu$ [a], D
	CH$_2$Cl$_2$	C$_2$H$_4$Cl$_2$	(CH$_3$)$_2$CHOH	CH$_3$CN		
1	6114	6241	7719	9030	35644	15.1
2	7833	8198	11146	11276	44972	16.9
3	3416	3908	5397	5830	29927	13.8

[a] Calculated assuming $a = 4$ Å.
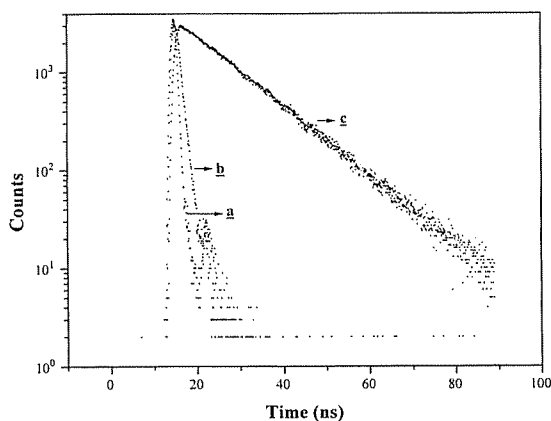
Fig. 4. Fluorescence decay profile of 1. (a) Lamp profile, (b) decay profile in dichloromethane and (c) decay profile in acetonitrile. Excitation wavelength was 350 nm.

sor–successor type dual fluorescence for 1, all evidence suggests that the lowest excited state in 1 has TICT character.

Markovitsi et al. have recently shown that for 2,6-diphenyl-4-(dimethylaminophenyl)pyrylium cation, the S_1 surface has lowest energy at $\theta_4 = 90°$, whereas, the S_2 surface has maximum energy in this conformation [19]. The large Stokes shift observed for 1 suggest that emission occurs from a relaxed excited state. The Franck–Condon (FC) excited state can relax either to a planar excited state ($\theta_4 = 0$) or a TICT state ($\theta_4 = 90$). The twist involved in both the cases is similar and which state is preferentially populated depends on the stabilization of these states in that solvent. Since polar solvents stabilize the TICT state we expect this state to be populated in polar solvents. The higher Φ_f and τ_f values in acetonitrile for 1 are in accordance with the above observations. In dichloromethane solution both these states are populated to some extent and this leads to smaller Φ_f values and short decay times. The higher k_{NR} values obtained for 1 in dichloromethane also support the formation of a TICT state.

Φ_f values obtained for 2 were similar to those for 1 in both the solvents. Fluorescence lifetime for 2 is much higher in dichloromethane compared to 1. The Stokes shift value of ~ 11300 cm^{-1} observed for this compound in acetonitrile is very close to the value observed for DMABN. In acetonitrile solution, 1 and 2 have the same lifetimes indicating that the

emitting states are very similar. All these observations can be explained by considering a TICT model for 2. The methyl group at the ortho position prevents this molecule from attaining a planar conformation in both the ground and excited states. Hence this molecule has only the TICT pathway open to it. Stokes shift of ~ 7800 cm^{-1} in dichloromethane suggests that even in nonpolar solvents, the molecule exhibits TICT emission.

Eventhough both 1 and 2 exhibit similar TICT states, the Stokes shift observed for 2 is much larger. This can be attributed to the different donor groups (phenyl vs. o-tolyl) present in these compounds. The tolyl group stabilizes a positive charge better, leading to a larger red shift in the emission maximum. In this context it should be mentioned that, to the best of our knowledge, TICT states in which an unsubstituted phenyl group is acting as the donor moiety have not been reported so far. In the case of 1, the acceptor strength of the pyrylium moiety coupled with the pre-twisting that existed in the molecule prior to excitation lead to the formation of the TICT state.

Substrates 1–5, thus belong to a group of compounds where small structural changes bring about large variations in the photophysical properties. Introduction of a methyl group at the para position is all that is required to bring about this change. Increasing the length or steric size of the alkyl chain further has very little influence on the observed effect. In the case of 1 and 2, the lowest energy S_1 state has a minimum at a twist angle of 90° in polar solvents leading to the formation of TICT excited states. In the case of 3–5, the lowest excited state (this corresponds to the S_2 state of 1 and 2) has a minimum at the planar geometry. Hence emission occur from the planar state and the TICT state is not observed even in polar solvents. Thus, the differences in the observed photophysical properties can be attributed to a reversal in the ordering of the excited state energy levels induced by alkyl substitution.

4. Conclusions

The present communication describes the photophysical properties of a group of closely related

pyrylium salts 1–5. For the cations 1 and 2, the lowest excited state has TICT character. For cations 3–5, the excited state properties are best explained by invoking a planar excited state. In the case of 1 and 2, the lowest energy absorption band is an envelope of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ bands. Emission occur from the S_1 state and this surface has lowest energy at a twist angle of 90° in polar solvents. The $S_0 \rightarrow S_2$ transition of 1 becomes the lowest energy transition in 3–5. For this excited state, the planar conformation has the lowest energy. In these cases TICT formation is not observed. The reversal of the energy levels observed is attributed to the very small energy difference between the two levels and also to the different directions of polarization of the corresponding transitions.

Acknowledgements

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