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Journal of Photochemistry and Photobiology A: Chemistry 102 (1997) 203–206

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A:CHEMISTRY

A study of the photophysical properties of 2,4,6-triphenyl pyrylium salts with rigid and non-rigid structures

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Received 21 November 1995; accepted 28 May 1996

Abstract

The photophysical properties of 2,4,6-triphenyl pyrylium salts with rigid and non-rigid structures were investigated. It was found that the polarizability of compound **2** (with a rigid structure) was stronger than that of compound **1** (with a non-rigid structure) in the excited state. The fluorescence quantum yield of compound **1** increased slightly with increasing viscosity of the solvent, while the fluorescence quantum yield of compound **2** decreased dramatically in the same conditions. It was also discovered that the hindered rotation of the 4-phenyl group in the molecules of 2,4,6-triphenyl pyrylium salts inhibits the fluorescence emission of these compounds.

Keywords: Fluorescence emission; Hindered rotation; Intramolecular charge transfer; Pyrylium salt

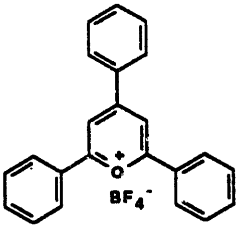
1. Introduction

Pyrylium salts are a type of heterocyclic system with a positive charge. They can function as intermediates for a large variety of organic syntheses [1]. In recent years, the luminescence behaviour and spectral properties of pyrylium salts have attracted increasing interest due to their strong fluorescence emission. Some have been used as laser dyes, *Q*-switch dyes and photosensitizers [2–12] in electrophotography. The photoinduced luminescence of pyrylium salts is of considerable interest. 2,4,6-Triphenyl pyrylium salts exhibit two perpendicular transitions in their molecular structure, similar to triphenylmethane dye. Thus there is dual excitation and two singlet excited states: $(S_0\text{–}Sx_1^*)$ and $(S_0\text{–}Sy_1^*)$. The former is the electronic transition along the *XX'* axis and the latter along the *YY'* axis. It has been reported [13] that, during the process of excitation decay, the rotation of the phenyl group at position 4 of 2,4,6-triaryl pyrylium salts may be an important pathway for non-radiative decay due to twisted intramolecular charge transfer (TICT) state formation resulting from strong intramolecular charge transfer. Therefore considerable influence may be exerted on the fluorescence emission of pyrylium salts by fixing the 4-phenyl group to be coplanar with the pyrylium ring by a bridge bond.

In this work, two pyrylium salts with different structures were synthesized, and their spectral properties and photophysical behaviour were studied, with the purpose of gaining a clearer understanding of the influence of the molecular structure on the photophysical behaviour of pyrylium salts.

2. Experimental details

The compounds studied in this work are shown below.



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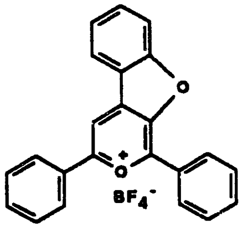

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Compound **1** was synthesized by a literature method [13]. Compound **2** was prepared by the following procedure.

1. Preparation of α-benzoyl benzofuran. A 10% NaOH solution (10 ml) was added to a mixture of 1.99 g (0.01 mol) of 2-bromo-acetophenone and 1.22 g (0.01 mol) of 3-hydroxybenzaldehyde in 100 ml of ethanol (95%) at 25 °C with stirring. The reaction mixture was stirred at the same temperature for 24 h. The resultant white precipitate was collected by filtration, washed with cold water (3 × 15 ml) and recrystallized from 95% ethanol to give white

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PII S1010-6030(96)04410-3

prisms in 75% yield. Melting point (m.p.), 132–134 °C. Mass spectrum (MS): 222 (M^+, 100).

2. Synthesis of compound 2. A mixture of 2.22 g (0.01 mol) of α-benzoyl benzofuran, 1.44 g (0.01 mol) of acetophenone and 2.84 g (0.02 mol) of boron trifluoride–ether was stirred at 100 °C for 4 h. After the reaction mixture had cooled to room temperature, 300 ml of ether was added and stirred for 10 min. The product was filtered and washed with ether (3 × 15 ml), and then purified by column chromatography on a silica gel column (eluent, acetone–ethyl acetate (2 : 1, v/v)) to afford 2 as a dark brown solid in 10% yield. M.p., 248–250 °C. IR (KBr): 1623, 1593, 1511, 1465, 1375, 1268, 1078, 1026, 976, 780 cm^{-1}. ^{1}H-NMR δ: 7.23–8.56 (m, 14H), 8.86 (s, 1H). MS: 323 (M^+).

All solvents used in this work were purified by the methods described by Perrin et al. [14].

The absorption and fluorescence spectra were recorded on a Hitachi 330 UV–visible spectrophotometer and a Hitachi MPF-4 fluorescence spectrophotometer respectively. The fluorescence quantum yields were determined using fluorescein in 0.1 N sodium hydroxide as a standard ($\Phi_f = 0.93$) [15].

3. Results and discussion

Fig. 1 and Fig. 2 show the absorption and fluorescence spectra of the pyrylium compounds in acetonitrile. The spectral data of the pyrylium salts are listed in Table 1.

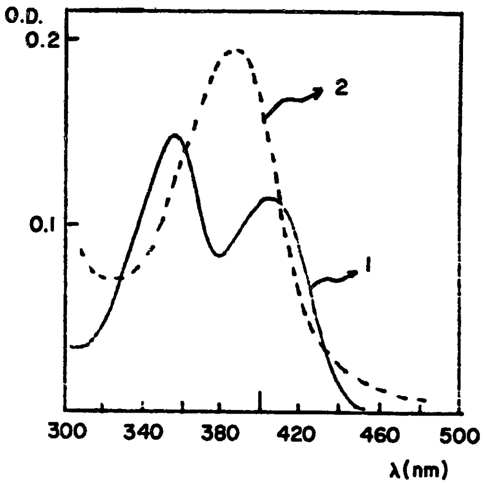

Fig. 1. Absorption spectra of compounds 1 and 2 in acetonitrile ($C_1 = 2 \times 10^{-6}$ mol dm^{-3}, $C_2 = 2 \times 10^{-5}$ mol dm^{-3}).

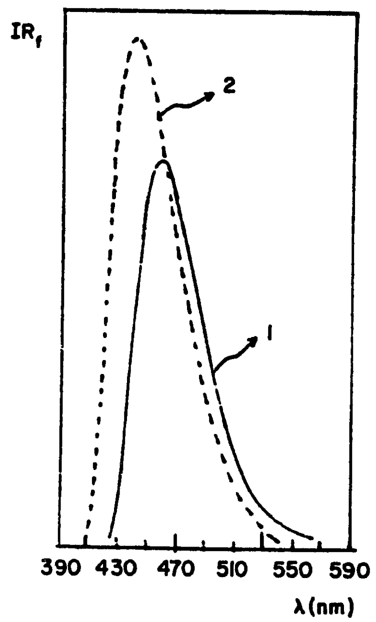

Fig. 2. Fluorescence spectra of compounds 1 and 2 in acetonitrile ($C_1 = 2 \times 10^{-6}$ mol dm^{-3}, $C_2 = 2 \times 10^{-5}$ mol dm^{-3}, $\lambda_{em1} = 420$ nm, $\lambda_{em2} = 400$ nm).

It is generally considered that, typically, there are two absorption bands in the visible region for 2,4,6-triaryl pyrylium salts, the longer wavelength band corresponding to the *XX'* axis and the other band to the *YY'* axis. Fig. 1 shows that compound 1 has two absorption maxima at 403 and 355 nm, whereas compound 2 has only one absorption maximum at 385 nm. Comparing the absorption band of compound 2 with those of compound 1, it can be seen that the long-wavelength absorption of 1 (403 nm) is bathochromically shifted compared with that of 2 (385 nm), but the short-wavelength absorption of 1 (355 nm) is hypsochromically shifted compared with that of 2 (385 nm). This result suggests that the coplanarity of 2 is not as good as that of 1 along the *XX'* axis in the ground state, but is better than that of 1 along the *YY'* axis due to the hindered rotation of the single bond in position 4; this results in the observation of only one band in the absorption spectrum of 2. Fig. 2 demonstrates that the fluorescence emission bands of compounds 1 and 2 are at 465 nm and 450 nm respectively, with Stokes shifts of $\Delta\lambda_1 = 62$ nm and $\Delta\lambda_2 = 65$ nm. This indicates that the intramolecular charge transfer of 2 is stronger than that of 1 in the excited state. In addition, from Table 1, it is clear that the quantum yield (Φ_f) of 2 is much lower than that of 1 in the same

Table 1

Spectral data of pyrylium salts 1 and 2 in two solvents ($c = 2 \times 10^{-6}$ mol dm^{-3}): λ_a, peak wavelength in absorption spectrum; λ_f, peak wavelength in fluorescence spectrum; Φ_f, fluorescence quantum yield; ε, molar absorption coefficient of the longest wavelength band (l mol^{-1} cm^{-1})

Compound	Solvent	λ_a (nm)	λ_f (nm)	Stokes shift (nm)	Φ_f	ε
1	Acetonitrile	403, 355	465	62	0.40	19400
	1,2-Dichloroethane	420, 370	463	43	0.28	27000
2	Acetonitrile	385	450	65	0.18	14950
	1,2-Dichloroethane	390	451	61	0.10	15850

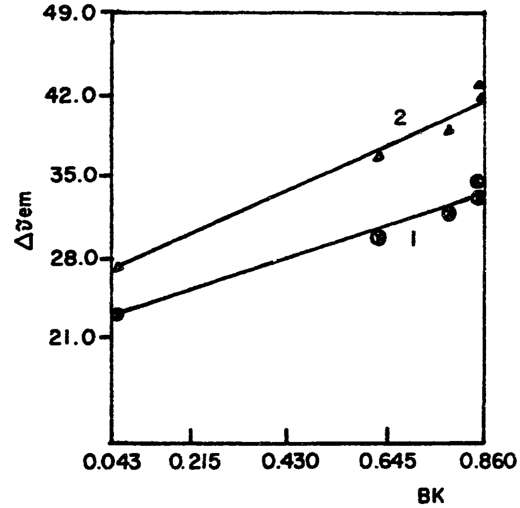

Fig. 3. Plot of the Stokes shifts of compounds 1 and 2 vs. the BK values.

solvent, which indicates that hindered rotation of the single bond at position 4 inhibits the fluorescence emission of 2,4,6-triphenyl pyrylium salts.

Recent calculations reported by Markovitsi et al. [16] depict the molecular conformation of 2,4,6-triaryl pyrylium salts in the ground state; the two phenyl groups in positions 2 and 6 are in one plane coplanar with the pyrylium moiety, while the 4-phenyl group is twisted from this plane by an angle of 40°. This calculation of the equilibrium conformation in the ground state was based on the competition between intramolecular conjugation (leading to a stable planar conformation) and steric hindrance (leading to a stable twisted conformation). Therefore it can be expected that one of the phenyl groups in position 2 or 6 along the *XX'* axis may be in the twisted conformation when the rotation of the 4-phenyl group in position 4 is hindered, i.e. the 4-phenyl group is coplanar with the pyrylium moiety, and this leads to the absorption spectrum observed for compound 2.

Fig. 3 shows plots of the Stokes shift vs. the solvent polarity parameter BK for compounds 1 and 2. Both show a good linear relationship according to the Bilot–Kawski formula [17–20]

$$\Delta\nu_{cm} = \nu_a - \nu_f = 2(\mu_e - \mu_g)^2/hca^3\mathrm{BK} + \mathrm{constant}$$

where $\nu_a - \nu_f$ is the Stokes shift, μ_g and μ_e are the dipole moments in the ground and excited states respectively, *h* is Planck's constant, *c* is the velocity of light and *a* is the radius of the molecule. Table 2 shows the Stokes shifts and BK values of compounds 1 and 2.

The slope of the straight line in plots of the BK value vs. $\Delta\nu_{cm}$ is $2(\mu_e - \mu_g)/hca^3$. Thus $\Delta\mu_1$ and $\Delta\mu_2$ are calculated from the slopes as 2.8 D and 3.1 D respectively; this indicates that the polarizability of compound **2** is stronger than that of compound **1** after excitation. It is known that the polarity of the Sy_1^* state (along the *YY'* axis) is much larger than that of the Sx_1^* state (along the *XX'* axis) in the excited state. Therefore this suggests that the larger $\Delta\mu$ value for compound **2** results from the participation of the Sy_1^* state in its photophysical behaviour.

It is noteworthy from Table 1 that the fluorescence quantum yields of **2** are smaller than those of **1**, and that both **1** and **2** show a negative solvatochromic effect, i.e. the fluorescence quantum yield increases with increasing solvent polarity. The existence of a negative solvatochromic effect illustrates that strong intramolecular charge transfer does not occur in the excited state in 2,4,6-triphenyl pyrylium salts with unsubstituted phenyl groups and, consequently, strong non-radiative decay does not take place. It also illustrates that an n–π^* electronic transition with a similar energy to the π–π^* transition, the so-called proximity effect, may occur together with the π–π^* transition.

The fact that the fluorescence quantum yield of **2** is smaller than that of **1** may be explained in terms of their molecular conformations. The fluorescence emission of **1** results mainly from Sx_1^* along the *XX'* axis. The function of Sy_1^* along the *YY'* axis is twofold. Firstly, when a strong electron-donating group, such as *N,N*-dimethylaminophenyl, is introduced into position 4, a TICT state may be formed in the excited state and becomes the main pathway of non-radiative decay leading to fluorescence quenching. Secondly, if a strong electron-donating group is not present in position 4 of the pyrylium molecule, energy transfer may take place from the Sy_1^* state to the Sx_1^* state, inducing molecular luminescence in addition to partial charge transfer. In the excited molecules of these compounds, the formation of an Sx_1^* state favours molecular fluorescence emission, whereas the formation of an Sy_1^* state inhibits molecular fluorescence emission. This explains the results obtained.

In order to verify further the assumption that the Sx_1^* state in the *XX'* axis is the luminescence state and that excitation in the *YY'* axis (Sy_1^*) acts only as an energy loss or energy transfer pathway, the fluorescence quantum yields of the two compounds were measured in solvents with similar polarity and different viscosity (mixture of methanol and glycerol with different ratios) and the results are listed in Table 3. An

Table 2
Stokes shifts ($\times 10^2$ cm^{-1}) and BK values of compounds 1 and 2

Parameter	Acetonitrile	1,2-Dichloroethane	Acetone	Toluene	Methanol
$\Delta\nu_{em1}$	33.1	29.5	31.8	23.0	34.9
$\Delta\nu_{em2}$	42.3	36.7	38.6	27.8	44.8
BK	2.861	0.630	0.794	0.044	0.859

BK value was calculated on the basis of the formula: $\mathrm{BK} = \{[(\epsilon-1)/(2\epsilon+1)] - [(n^2-1)/(2n^2+1)]\}/\{[1-(n^2-1)/(2n^2+1)]^2 \times [1-(\epsilon-1)/(2\epsilon+1)]\}$.

Table 3
Fluorescence quantum yields (Φ_{f1} and Φ_{f2}) of compounds 1 and 2 in solvents of different viscosity (η)

Φ	Viscosity η											
	0.55	1.60	2.61	3.25	3.60	4.90	7.51	9.10	10.21	12.90	13.40	15.10
Φ_{f1}	0.171	0.171	0.172	0.172	0.175	0.176	0.178	0.179	0.178	0.178	0.177	0.178
Φ_{f2}	0.136	0.125	0.117	0.109	0.099	0.100	0.099	0.100	0.094	0.087	0.081	0.076

inspection of Table 3 shows that the fluorescence quantum yield of compound 1 increases with increasing viscosity; this is consistent with the general pattern whereby, with an increase in the viscosity of the medium, rotation or vibration energy loss in the molecule is decreased leading to an increase in the fluorescence quantum yield. It is intriguing to note that the fluorescence quantum yield of 2 decreases with increasing viscosity of the solvent. The fluorescence quantum yield in the solvent with the largest viscosity is almost half the original Φ_f value. This interesting result is in accordance with the existence of different molecular conformations in the ground state for these two compounds.

According to the results calculated by the molecular orbital method by Markovitsi et al. [16], it can be considered that, in the ground state, two of the three phenyl groups in 2,4,6-triphenyl pyrylium are in a plane coplanar with the pyrylium moiety and the third is twisted from this plane by an angle of 40°, i.e. this conformation possesses the lowest energy and is the most stable in the ground state. However, the conformation of lowest energy in the excited state is when the whole molecule is in a single plane [16]. Thus the twisted phenyl group may adjust to the conformation in which the whole molecule is coplanar by rotation during the relaxation process in the excited state of the compound. The relaxation process in the excited state involves the rotation of the 4-phenyl group for compound 1, and the rotation of the 2- or 6-phenyl groups for compound 2. Because the Sx_1^* state of compound 1 is the normal fluorescence emission state, i.e. the two phenyl groups in positions 2 and 6 form an angle of 0° with the pyrylium ring, the rotation pattern, fast or slow, of the 4-phenyl group will not exert an obvious influence on the fluorescence emission. Therefore the fluorescence quantum yield of compound 1 changes only slightly with changing viscosity of the solvent. However, in the case of compound 2, because the 2- or 6-phenyl group is twisted from the plane of the pyrylium ring, which inhibits fluorescence emission, it is only when one of these two phenyl groups rotates to a position in which it is coplanar with the pyrylium ring can fluorescence emission occur, leading to a decrease in the fluorescence quantum yield of compound 2. Thus we have explained the unusual phenomenon of the decrease in the fluorescence quantum yield of compound 2 with increasing solvent viscosity, which is contrary to that of compound 1, and have provided evidence for the viewpoint that the 2- and 6-phenyl groups are not coplanar with the pyrylium ring in the molecular conformation of 2,4,6-triphenyl pyrylium salts with a rotation-hindered 4-phenyl group in the ground state. This work also illustrates that the rotation hindrance of the 4-phenyl group inhibits the fluorescence emission of 2,4,6-triphenyl pyrylium salts.

4. Conclusions

Phenyl groups in the 2 and 6 positions are not coplanar with the pyrylium ring in the molecular conformation of 2,4,6-triphenyl pyrylium salts when 4-phenyl group rotation is hindered in the ground state. Moreover, the hindered rotation of the 4-phenyl group inhibits the fluorescence emission of 2,4,6-triphenyl pyrylium salts.

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