Fluorescence Properties of Pyrylium and Thiopyrylium Salts

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Due to their very substantial fluorescence emission, pyrylium and thiopyrylium salts are widely used as laser dyes and photosensitizers. This paper deals with the fluorescence properties (quantum yields and wavelengths of the fluorescence maxima as well as the lifetimes of the singlet excited states) of eight pyrylium and ten thiopyrylium salts, with special emphasis on the effect of α and γ substitutions of the heterocycle.

The pyrylium and thiopyrylium salts make up a class of cationic heterocycles consisting of 5 carbon atoms which exhibit sp^2 hybridization and an atom of the sixth group: O for pyrylium and S for thiopyrylium salts. Their molecular structure is as follows (Chart 1):

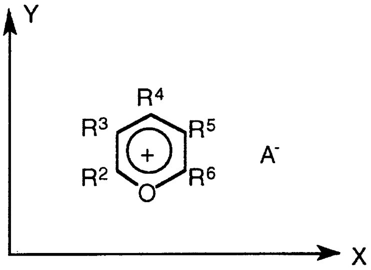


Chart 1.

These compounds occur as natural products in pigments called "anthocyanins", which are responsible for the blue or red color of many fruits and flowers. Research performed by Balaban et al.[1] amply covers the chemistry of the pyrylium salts: Their various methods of synthesis, their chemical reactivities, their physical properties and their practical uses. As for the thiopyrylium salts, they have been much less extensively studied than their isoelectronic counterparts, the pyrylium salts. However, their methods of synthesis and their reactivities have been described by Karchenko et al.[2]

The pyrylium and thiopyrylium salts display substantial absorption in the wavelength range from 400 to 700 nm. They can be considered to be a two-dimensional chromophoric system. Among the two lowest-lying absorption bands, the former is polarized along the X-axis (x band or chromophore) and the latter along the Y-axis (y band or chromophore). The wavelengths of the absorption maxima of these two bands are dependent on the nature of the substituents placed at positions 2, 4, and 6 of the heterocycle. Owing to these attractive properties, the salts were used as the photosensitizers of many polymerizations in the visible range in order to develop resins for artificial fingernails,[3] an acrylic dental resin,[4] polymers in the field of laser imaging[5] or still compositions for printing plates.[6] Pyrylium and thiopyrylium salts can also be used as anticorrosive agents, intermediates in the synthesis of many carbocyclic or heterocyclic organic compounds, or still as bactericides or fungicides in the biological field.

It must, however, be noted that the very substantial fluorescence emission of the pyrylium salts has received special attention, which has resulted in their use as laser dyes. Schäfer et al.[7,8] have observed a laser effect for some pyrylium salts when the excitation source is a pulsed nitrogen laser delivering a pulse of ca. 1 MW of peak power within 2.5 ns. No definite specification has been given concerning the range and effectiveness of the laser effect. More recently, Rulliere et al.[9] and later Tripathi et al.[10] investigated the laser emission properties of pyrylium and thiopyrylium salts. Their studies stressed the role played by the fluorescence quantum yield in the laser effect. More recently, Miranda and Garcia published a large review concerning the role of an electron-transfer photosensitizer played by 2,4,6-triphenylpyrylium tetrafluorobrorate.[11]

We also investigated the behavior of this compound as a photosensitizer in the photoisomerization of the cinnamates derivatives reaction[12)] or the spin-orbit coupling-induced triplet formation of the triphenylpyrylium ion.[13)]

On the other hand, thiopyrylium salts are well suited to play the role of photosensitizers in the visible photoinduced polymerization reaction, rather than pyrylium salts, due to their relatively high intersystem crossing quantum yields. One example of this photoinitiating system was studied by our group.[14)]

In the present paper attention is focused on the fluorescence quantum yields, the dependence of the shifts of the fluorescence maximum on the substituents of the heterocycle, and the lifetime of the singlet excited states of eight pyrylium and ten thiopyrylium salts.

Experimental

Reagents. The solvents required for the spectroscopic measurements were acetonitrile (spectral grade, supplied by Fluka Corp.) and denatured alcohol (purchased from Aldrich Chemical Co.), both of which were used without prior purification.

The chemical formulas of the various compounds that were investigated are shown in Table 1. Compounds TMP, TPC1, and TPC2 were supplied by Prof. Xavier Coqueret from the Université des Sciences et Techniques de Lille (France). All of the other salts have been synthesized according to the literature: from the corresponding acetophenones and chalcones for pyrylium salts;[15)] from the corresponding pyrylium salts for TP4, 7, and 8;[16,17)] and for TP1, 10, 11, 12, 13.[18)] The purity was checked by ^{1}H NMR. Some impurities (starting materials and non-identified products) can exist at a very low level. The percentage of purity could not be evaluated in this work and was not mentioned in other reports e.g.[10,15,17,19)]

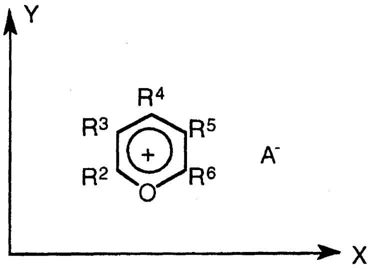
Emission. The fluorescence-emission spectra of the various products were recorded using a Perkin–Elmer LS5B spectrophotometer connected to a Perkin–Elmer R100A plotter. The excitation source was a pulsed xenon lamp. All of the experiments were performed at 25 °C.

The quantum yields of the investigated salts were determined by measuring the relative quantum yield of fluorescence. This method consists of comparing ϕ_f of the salts with that of a reference compound (ϕ_R), which was measured under the same conditions. The relationship between these two quantum yields of fluorescence is:

$$\frac{\phi_f}{\phi_R} = \frac{(1-10^{-OD})_R}{(1-10^{-OD})_f} \times \frac{S_f}{S_R} \times \left(\frac{n_f}{n_R} \right)^2, \qquad (1)$$

where OD is the optical density at the different excitation wavelengths; S_f and S_R are the areas of the emission bands of the salt and the reference, respectively; and n_f and n_R

Table 1. Chemical Formulas of Investigated Pyrylium and Thiopyrylium Salts



Compound	R^2=R^6	R^4	R^3=R^5	A^-
Pyrylium salts				
TMP	p-$OMeC_6H_4$	p-$OMeC_6H_4$	H	ClO_4^-
P1	C_6H_5	C_6H_5	H	BF_4^-
P4	p-ClC_6H_4	C_6H_5	H	BF_4^-
P7	p-BrC_6H_4	C_6H_5	H	BF_4^-
P8	C_6H_5	p-$N(CH_3)_2C_6H_4$	H	BF_4^-
P10	p-$OMeC_6H_4$	C_6H_5	H	BF_4^-
P11	p-$OMeC_6H_4$	p-$OMeC_6H_4$	H	BF_4^-
P12	p-$OMeC_6H_4$	p-$OC_4H_9C_6H_4$	H	BF_4^-
Thiopyrylium salts				
TPC1	C_6H_5	C_6H_5	H	ClO_4^-
TPC2	p-$OMeC_6H_4$	p-$OMeC_6H_4$	H	ClO_4^-
TP1	C_6H_5	C_6H_5	H	BF_4^-
TP4	p-ClC_6H_4	C_6H_5	H	BF_4^-
TP7	p-BrC_6H_4	C_6H_5	H	BF_4^-
TP8	C_6H_5	p-$N(CH_3)_2C_6H_4$	H	BF_4^-
TP10	p-$OMeC_6H_4$	C_6H_5	H	BF_4^-
TP11	p-$OMeC_6H_4$	p-$OMeC_6H_4$	H	BF_4^-
TP12	p-$OMeC_6H_4$	p-$OC_4H_9C_6H_4$	H	BF_4^-
TP13	p-$OMeC_6H_4$	H	H	BF_4^-

are the refractive indexes of the solvents used for preparing the salt solution and the reference, respectively.

Rhodamine 6G (CI 45160 Merck for microscopy) dissolved in ethanol was used as a reference (ϕ_f=0.95).[20] It was essential to correct the emission spectrum by storing the response of the detecting system before measuring the relative quantum yield. The LS5B spectrofluorometer was designed with this end in view. The internal filter effect was ruled out by using solutions whose optical densities did not exceed 0.05 at the excitation wavelength. The excitation wavelength must be the same for the salt and the reference, in order to avoid a possible correction defect resulting from the apparatus, both when measuring the absorption and when carrying out the internal correction of the excitation beam of the fluorometer. Correcting the refractive index is essential to rule out any differences in refraction when luminous radiation passes from the solution into the air. It is more advisable, however, to use media having close refractive indexes in order to minimize this effect. The measurements were performed with freshly prepared solutions in order to avoid any problem concerning the chemical or photochemical stability.

The fluorescence lifetimes were measured using a streak camera (ARP-RGM-SC1) operating in the repetitive mode as a detecting system. The excitation source was a mode-locked Q-switched and cavity dumped Nd-YAG laser emitting at 355 nm after the third-harmonic generation of the fundamental emission (1064 nm). The temporal width of the pulse was 100 ps. The repetition rate of the laser pulses and of the synchronized triggering system of the camera was 800 Hz. The acquisition system connected to the streak camera was a 512 diode-array multichannel analyzer. The time scales that were used ranged from 2.4 ps/channel to 24 ps/channel. The optical densities of the solutions were between 0.2 and 0.6 at the excitation wavelength.

Results and Discussion

The pyrylium and thiopyrylium salts exhibit attractive fluorescence properties in the spectrum range from 420 to 600 nm.[21] Just as in the case of UV-visible light absorption, the cation is responsible for the emission; the anion which associates with it only slightly affects the fluorescence properties.[21] The purity of the solvent used is still more important for emission than for absorption, since trace amounts of electron donors (and especially of amines) in the acetonitrile may result in fluorescence quenching.[22]

The wavelengths of the fluorescence maxima, the fluorescence quantum yields and the lifetimes of the S_1 states of the investigated salts are given in Table 2. The ca. 10% uncertainty in the ϕ_1 values that were measured through the comparative method arises, among others, from unavoidable inaccuracies of the dilution when preparing the solutions, or to the approximations that were made when measuring the area of the spectra through the method of tangents.

The fluorescence quantum yields determined for the pyrylium salts are in agreement with those reported,[10] where the obtained values were 0.52, 0.50, and 0.60 for salts P1, P10, P11, respectively. A substantial difference, however, should be noted between the ϕ_f value measured for TP1 in the present study (ϕ_f=0.05) and that reported by these workers (ϕ_f=0.35). It is also worth noting that the ϕ_f values published by different authors are not always in agreement: e.g. 0.82 and 0.97 in acetonitrile for P10 and P11, respectively.[19]

The introduction of bromine atoms at the para position of α-positioned phenyls caused the fluorescence quantum yield to decrease sharply from 0.60 for P1 to

Table 2. Values Measured in Acetonitrile at 25 °C of Wavelengths of Fluorescence Maxima, Fluorescence Quantum Yields at Mentioned Excitation Wavelength, and Lifetimes of State S_1 of the Various Salts

Compound	λ_{ex}	λ^{max} (nm)	ϕ_f	τ_s (ns)
TMP	475	545	0.49	—
P1	415	470	0.60	4.3
P4	420	489	0.43	3.9
P7	420	496	0.08	1.9
P8		No fluorescence		
P10	470	558	0.58	5.6
P11	460	541	0.59	—
P12	475	542	0.59	—
TPC1	360	483	0.12	—
TPC2	460	600	0.14	—
TP1	420	502	0.05	0.25
TP4	380	520	0.04	—
TP7	380	528	0.03	0.23
TP8		No fluorescence		
TP10	460	605	0.10	—
TP11	420	600	0.10	—
TP12	420	603	0.10	—
TP13	460	602	0.10	—

0.08 for P7.

An inspection of the results for compounds P1 and TP1 or P11, for instance, shows that the substitution of sulfur for oxygen redshifts the fluorescence spectrum by 30 to 60 nm. In addition, the fluorescence quantum yields of thiopyrylium salts are distinctly lower than those of pyrylium salts, due to a higher efficiency of the forbidden singlet-triplet transition, because the intersystem crossing of the latter ones in not an efficient process (less than 10%), in contrast with the former ones, whose quantum yields of intersystem crossing may reach 50%.[10)]

Judging from the wavelengths of the fluorescence maxima of the investigated salts, it seems that the introduction of electron-donating mesomeric substituents redshifts the emission band by ca. 20 nm for Cl and Br (P4 and P7), and 90 nm for OMe (P10 and TP 10). According to other results,[19)] this redshift is all the more pronounced such that the mesomeric effect of the substituent is greater. These workers thus observed a 21 nm shift (in solution in dichloromethane) if the substituents were methyl groups, 76 nm for methoxy groups and 223 nm for dimethylamino groups.[19)] These authors have also stated that the highest fluorescence quantum yield is obtained when the previously mentioned substituents are moderately electron-donating groups, such as OMe.

It would appear that a detectable fluorescence quantum yield can be obtained only if the fluorescence transition is due to chromophore x. The formation of a TICT (twisted intramolecular charge transfer) may be responsible for this phenomenon.[19)] The pyrylium part of chromophore y would be more strongly electron attracting than that of chromophore x. Accordingly, the formation of a nonradiative TICT might be favored in the case of a y chromophore.[23)] Therefore, this would explain why it was not possible to observe fluorescence emission in acetonitrile for salts P8 and TP8. The results obtained by Haucke et al.[19)] show that for P8 no fluorescence has been detected in dichloromethane either, although this solvent is less polar than acetonitrile, and adversely affects the formation of the TICT.[24)] Recently, Markovitsi et al.[25)] studied the excited-state properties of P8 salts in various solvents of increased viscosities. The experimental and theoretical results showed the formation of nonfluorescent TICT, corroborated by the influence of the rotor size and solvent viscosities.[25)] However, for a pyrylium salt having a methoxy group at the para position to the γ-phenyl,[19)] fluorescence emission has been observed in dichloromethane (ϕ_f=0.28), but not in acetonitrile. The authors of Ref. 19 have also demonstrated the formation of a nonradiative TICT through the rotation of the α-substituents: introduction of dialkylamino substituents at the para position to α-phenyls decreases the fluorescence quantum yield, both in dichloromethane and acetonitrile. The introduction of a third dialkylamino group at the γ-phenyl produces an increase in ϕ_f by decreasing the electron-accepting character of the pyrylium part.

The fluorescence lifetimes of the salts were measured in an acetonitrile solution with a temporal window of 24 ps/channel. For the pyrylium salts, values from 1.9 to 5.6 ns were obtained (Table 2). These figures are in agreement with those reported by Tripathi et al.[10)] For the thiopyrylium salts, the fluorescence lifetimes are tenfold shorter than those of their pyrylium counterparts. In addition, two emitting forms seem to exist. The determination of the lifetimes of these compounds, therefore, becomes very difficult and requires a deconvolution-type mathematical processing. In the case of salt TP1 (Fig. 1), this method makes it possible to assign to the predominating species (96% of population) a fluorescence lifetime of 250 ps and, for the longer species, a lifetime (τ_f) of 1.9 ns (a value of 3.1 ns was reported for TP1 in Ref. 10). For TP7 these values are 230 ps (85%) and 510 ps. In the case of salt TP4, the mathematical processing did not allow for the separation of the relative contributions of the two species (their spectral overlapping is too extensive). An average fluorescence lifetime of 530 ps, however, was determined.

Conclusion

The pyrylium salts display a very strong fluorescence emission, hence their use as laser dyes. The fluorescence quantum yields measured in acetone at 25 °C are on the order of 0.5, expect when the fluorescence transition is due to chromophore y; Thus no fluorescence is detectable, which could be accounted for by the formation of a TICT. Owing to a higher efficiency of the forbidden singlet–triplet transition, the fluorescence of the thiopyrylium salts is much lower than that of the

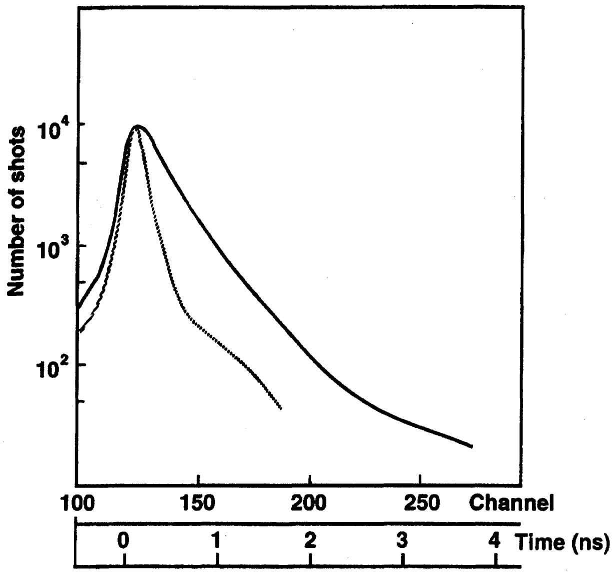


Fig. 1. Decay curves (analysis system 24 ps/channel): ····: response function of the system, ——: thiopyrylium salt TP1 in acetonitrile.

corresponding pyrylium salts because their yields of intersystem crossing may reach 50%. Their fluorescence quantum yields are, then, on the order of 0.1.

An increased fluorescence intensity of Rhodamine 101 has been observed due to a locking of the diethylamino substituents, whose rotation is suppressed through insertion into a polycyclic structure.[26] Taking there results as a basis, Tripathi et al.[10,27,28] had set out to prepare pyrylium salts exhibiting higher fluorescence yields by locking the rotation of the α-and γ-positioned aromatic subtituents through bridge linkages consisting of methylene groups. Their studies have demonstrated that preventing the rotation of the aromatic substituents at positions 2, 4, and 6 of the pyrylium nucleus causes a marked increase of the fluorescence, except in the case where the locking of the phenyl substituents is ensured by a trimethylenic chain. In this case, a sharp decrease in fluorescence has been observed with regard to molecules where the locking is ensured by one or two methylene groups, to higher degrees of deformation freedom around the cation that vibrationally increases nonradiative inhibitions.[28]

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