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Photophysics and photochemistry of the 2,4,6-triphenyl-2-benzyl-2H-thiopyran versus 2H-pyran derivatives

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Abstract

The photochemistry and photophysics of one thiopyran (2,4,6-triphenyl-2-benzyl-2H-thiopyran) and two pyran (2,4,6-triphenyl-2H-pyran and 2,4-dimethyl-2,6-diphenyl-2H-pyran) derivatives were investigated by stationary and time resolved techniques. Both theory and experiments indicated a π,π^* character for the lowest singlet states of these molecules, located in the UV region approximately at the same energy. Upon stationary UV irradiation at low temperature, colourless photoproducts were formed from the pyran derivatives, while coloured compound(s) were obtained from the thiopyran. Long-lived transients were observed at room temperature, which were assigned to the photoproducts obtained at low temperature; only in one case (2,4,6-triphenyl-2H-pyran) a triplet precursor was detected.

Keywords: Photophysics; Photochemistry; 2,4,6-Triphenyl-2H-thiopyran; 2H-pyran

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1. Introduction

It is well known that several benzo- and naphtho-pyrans (chromenes) exhibit photochromic behaviour due to the electrocyclic ring-opening at the pyran C–O bond. A review, including practical information on photochromic properties and synthetic methodologies of this class of molecules, has been recently reported by Van Gemert [1].

The photochromism of chromenes was first established and extensively studied by Becker and co-workers [2–9]. These molecules, upon UV irradiation, yield open coloured forms, the structure of which was shown to be an *o*-quinone-allide [3].

The interest in these molecules is two-fold. First, in the activated forms, their colours (yellow to orange) are complementary to those of the better-studied spiroindolino-naphthoxazines (blue to violet). Therefore, they can find alternative practical applications, also because of their rather high fatigue-resistance. Second, many molecules with this structure are naturally occurring compounds. Nature, during evolution, has developed systems, even very complex, to optimize absorption of solar radiation or to protect cells from radiation damage [10]; the photochromic properties of these molecules may have a role in the photoregulation of biological processes in plants.

Generally, the photokinetic behaviour of chromenes is more complicated than that of spiroxazines, since the photoreaction yields two coloured isomers, instead of one, which exhibit different thermal and/or photochemical reactivity [11–14]. Less attention has been devoted to non-annellated pyran derivatives, probably because they do not yield coloured photoproducts and photoreaction cannot be accomplished at room temperature.

This work is aimed at investigating the photochromic properties of the 2,4,6-triphenyl-2-benzyl-2H-thiopyran (TPy) and two pyran derivatives of similar structure, 2,4,6-triphenyl-2H-pyran (Py1) and 2,4-dimethyl-2,6-diphenyl-2H-pyran (Py2), and evaluating the effect of substitution of sulfur for oxygen (Scheme 1).

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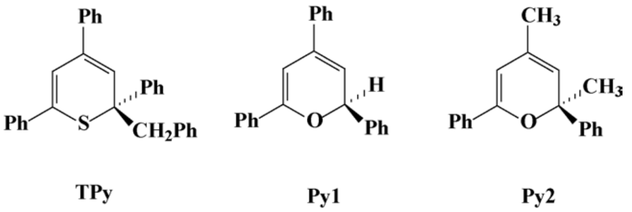
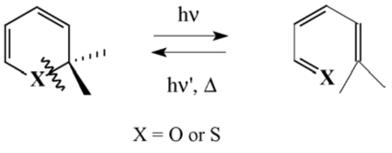


Scheme 1.



Scheme 2.

The photochemistry and spectroscopy of two of the molecules under study, TPy and Py2, were previously investigated by Becker and Kolc in a rigid matrix at 77 K [15]. They found that appreciable photocolouration occurs for TPy, very weak photocolouration is detected for the analogous 2,4,6-triphenyl-2-benzyl-2H-pyran, whilst no colouration is observed for Py2. Based upon analogy with chromenes [3] they established that photochemistry originates from C–O or C–S bond breakage (Scheme 2).

More recently, the same two molecules were investigated at room temperature, using nanosecond flash photolysis techniques [9]; colouration was observed immediately after the laser pulse for TPy, whereas very little photochemistry was seen from Py2. Photophysical and/or -photochemical measurements were never carried out on Py1.

Semiempirical theoretical calculations of the electronic transitions of the photo-coloured forms have been developed for chromenes [16,17] but not for the simple pyran/thiopyran derivatives. Also ab initio calculations of the ring opening reaction in the ground state were recently performed [18].

In this work, absorption and emission spectra of these molecules and their photochemistry upon steady state irradiation and laser flash photolysis were investigated in 3-methylpentane solution. Semiempirical calculations have been carried out on both the closed and open forms of these three molecules, aimed at determining the energy and nature of the spectroscopically accessible excited states.

2. Experimental

2.1. Materials

The molecules investigated were supplied by J. Dreux (Lyon, France) for previous works [3,9,15] and were used without further purification.

The solvent, 3-methylpentane, a Carlo Erba RPE product, was distilled before use. Ethanol and acetonitrile, Uvasol Fluka products, were used without further purification.

2.2. Equipment and experimental conditions

For the spectrophotometric determinations, a Perkin-Elmer Lambda 800 and a Hewlett-Packard 8453 diode array apparatus were used. The emission measurements were carried out on a Spex Fluorolog-2 FL112 spectrofluorimeter controlled by the Spex DM 3000F spectroscopy software. The time resolved unit of this instrument (microsecond time resolution) was used for measuring the phosphorescence lifetime of TPy. An Oxford Instruments cryostat was used for the temperature control.

For laser flash photolysis measurements, the 347 nm line from a ruby laser (J.K. Lasers) was used. The laser energy was less than 10 mJ per pulse; the time resolution was about 20 ns. The expected accuracy in lifetime was within 10%. Transient absorption spectra were recorded in point-by-point fashion. Concentrations were on the order of 10^{-4} mol dm^{-3}, corresponding to absorbance values of 0.6–0.7 at the exciting wavelength.

Spectra at low temperature and in a rigid matrix were taken in 3-methyl-pentane with sample concentrations in the range 10^{-4} to 10^{-5} mol dm^{-3}. The spectra of the metastable form of TPy were obtained from a solution pre-irradiated using a 250 W Hg lamp with an interference filter at 366 nm. The temperature was low enough (160 and 80 K) to exclude the thermal back process.

For the quenching measurements of the room temperature phosphorescence of benzophenone (10^{-3} mol dm^{-3}), acetonitrile was used as solvent to avoid the hydrogen abstraction process by the triplet ketone from the hydrocarbon solvent; the quencher concentrations ranged from 10^{-6} to 10^{-5} mol dm^{-3}.

The photochemistry of the three molecules was investigated under steady irradiation, in 3MP solution, using monochromatic light and following the spectral evolution with time by spectrophotometry up to photostationary state attainment. The irradiation was carried out in the spectrophotometer holder at a right angle to the monitoring beam using a fibre-optic system. A 250 W medium pressure mercury lamp, filtered by an interference filter ($\lambda_{exc} = 366$ nm) or a 125 W Xe lamp coupled with a Jobin-Yvon H10 UV monochromator were used for irradiation. When possible, irradiation was carried out in correspondence of an isosbestic point, in order not to change the total absorbance during the experiment.

In the case of the photochromic TPy, absorbance-time data sets, to be used for the fit procedures, were recorded following the absorbance changes under steady irradiation at the maximum of the colour-band. After achieving the steady state conditions, exposure to the activating radiation was discontinued and the kinetics of bleaching was followed in the temperature range 200–165 K. The rate constants of the bleaching thermal reactions were determined from the disappearance of the coloured form at the wavelength of maximum absorbance (zero time ca. 2–3 s from the end of the irradiation). The kinetics fit a biexponential function well (see below, Eq. (1)) and two bleaching constants could be determined by graphical

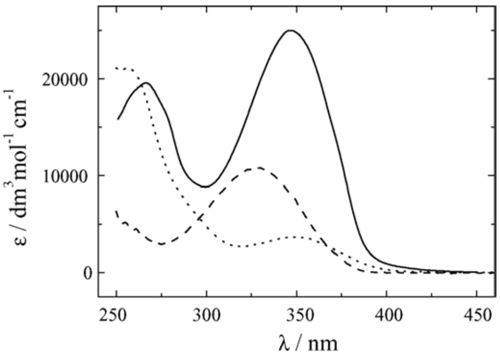


Fig. 1. Absorption spectra of Py1 (full), Py2 (dash) and Tpy (dot) in 3MP.

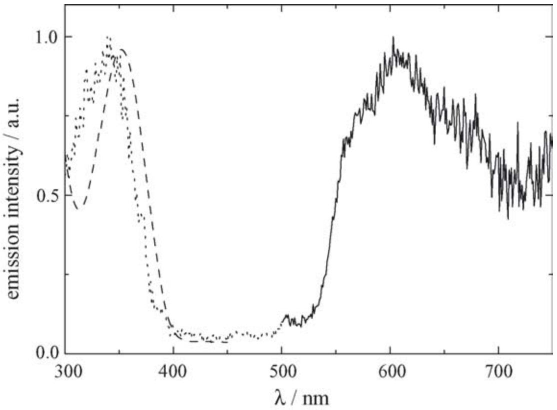


Fig. 2. Phosphorescence emission ($\lambda_{exc} = 350$ nm, full line), phosphorescence excitation ($\lambda_{em} = 610$ nm, dotted line), and absorption (dashed line) spectra of TPy in a 3MP matrix at 80 K.

interpolation of the experimental data. The activation energies of the thermal back reactions, along with the frequency factors, were determined from Arrhenius plots. An uncertainty of about 10% was evaluated for the activation energy, while the frequency factor was presumably affected by more than 50% uncertainty.

Theoretical calculations of singlet excitation energies of the closed and open forms were carried out with the semiempirical INDO/1-C1 program, after optimizing geometries at the MNDO level.

3. Results and discussion

3.1. Absorption and emission spectra of the closed forms

The three molecules studied are colourless and their absorption spectra are characterized by a broad band with maximum around 350 nm. A second transition at higher energy (ca. 250 nm) is only observed for Py1 and TPy. Absorption spectra in 3MP are shown in Fig. 1.

The experimental absorption wavelength maxima and molar absorption coefficients of the three molecules in two solvents (3MP and EtOH) are reported and compared with the calculated values in Table 1. As can be seen, the spectra are scarcely affected by the solvent polarity and the molar absorption coefficients are typical of π,π* transitions. This assignment is supported by calculations, which well reproduce the intensities and positions of the experimental maxima. Calculated bands with oscillator strength smaller than 0.05 are not reported in the table. It can be observed that the lowest energy absorption band of Py1 takes intensity from three fairly strong transitions (oscillator strength ≥0.09), while only one intense transition was calculated for Py2 and TPy, in qualitative agreement with the experimental differences in the molar absorption coefficients. Only one band was calculated for Py2 at wavelengths longer than 250 nm, as found experimentally.

None of the three molecules investigated exhibited detectable emissions at room temperature, in accord with previous findings for TPy and Py2 [9]. However, for TPy, emission was detected ($\lambda_{max} = 610$ nm) in a rigid matrix of 3MP at 80 K. The excitation spectrum satisfactorily reproduces the absorption spectrum of TPy (Fig. 2).

Table 1
Room temperature spectral characteristics (maximum wavelength, λ_{max}, and molar absorption coefficient, ε_{max}) of Py1, Py2 and TPy in a non-polar (3-methyl-pentane, 3MP) and in a polar (ethanol, EtOH) solvent, compared with calculated values of the transition wavelengths and oscillator strengths (π,π* transitions)

Compound	Experimental				Calculated		
	3MP		EtOH		Transition	λ_{max} (nm)	f
	λ_{max} (nm)	ε_{max} (dm^3 mol^{-1} cm^{-1})	λ_{max} (nm)	ε_{max} (dm^3 mol^{-1} cm^{-1})			
Py1	347	25000	348	22000	$S_0 \rightarrow S_1$	355	0.33
					$S_0 \rightarrow S_2$	294	0.23
					$S_0 \rightarrow S_3$	292	0.09
	266	19600	269	21700	$S_0 \rightarrow S_8$	252	0.51
Py2	325	10100	325	10000	$S_0 \rightarrow S_1$	352	0.41
Tpy	349	4200	346	4300	$S_0 \rightarrow S_1$	320	0.56
					$S_0 \rightarrow S_6$	273	0.45
	254	21000	254	21300	$S_0 \rightarrow S_7$	253	0.37

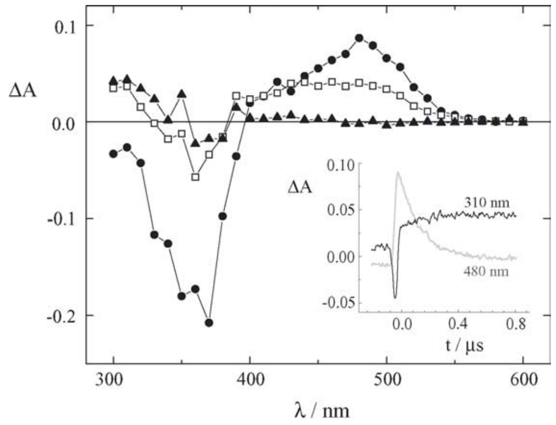


Fig. 3. Time-resolved absorption spectra of the transients obtained from Py1 upon laser excitation (347 nm) in 3MP at room temperature; (●) 0.03 µs; (☐) 0.13 µs; (▲) 0.83 µs after the laser pulse. Inset: decay kinetics of the short-lived transient (480 nm, grey) and rise kinetics of the longer-lived transient (310 nm, black).

The emission lifetime was 20 ms. Based on the spectral position and lifetime, the emission is assigned to phosphorescence. From the 0–0 transition energy, the triplet is estimated to be at 213 kJ mol^{-1}. In a fluid solution, at room temperature, TPy quenched the phosphorescence of benzophenone (E_T = 288 kJ mol^{-1}) at a diffusion controlled rate, $k_q = 5\times10^9$ dm^3 mol^{-1} s^{-1}, as expected based on the triplet energy difference between the donor and acceptor.

3.2. Photobehaviour upon laser flash photolysis

The three compounds were analyzed upon laser excitation (nanosecond time resolution) in order to investigate on possible intermediates of the photochemical processes and on relaxation paths competitive with photochemistry.

3.2.1. Py1

Two transients were detected upon laser excitation (λ_{exc} = 347 nm) of Py1. The short-lived one (λ_{max} = 480 nm, τ = 150 ns) was the precursor of the other (310 nm, $\tau \sim 450$ µs), since both the decay kinetics (480 nm) of the first transient and rise-time (310 nm) of the second transient had the same rate constant (Fig. 3). Only the first transient was quenched by oxygen, $k_{ox} = 2 \times 10^9$ dm^3 mol^{-1} s^{-1}, and therefore it is assigned to a triplet, while the other transient is assigned to a metastable photoproduct, which is formed from the triplet state. In Fig. 3, the negative band around 350 nm, which is in large part due to the bleaching signal of the ground state, is disturbed by both the laser light and the absorption spectra of the two transients, therefore it does not provide kinetically significant information.

3.2.2. Py2

Upon laser excitation, Py2 yielded a long-lived species with the absorption maximum at 320 nm and decay time of 150 µs (Fig. 4). The time resolved spectrum also showed a negative region at 350 nm. The maximum at 320 nm is assigned to the photoproduct (see, below) and the minimum to the ground state bleaching. In this case the decay (320 nm) and rise (350 nm) kinetics match well. The wavelength maximum, however, does not correspond to that previously detected in ethanol (390 nm) [9].

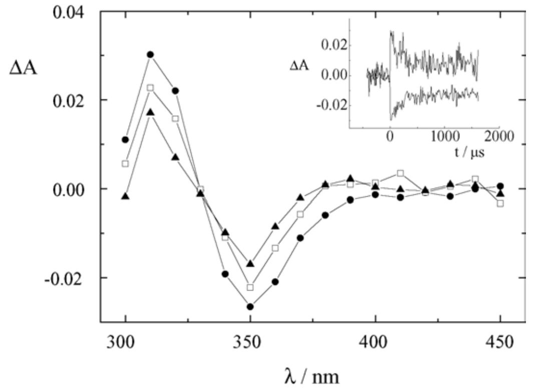


Fig. 4. Time-resolved absorption spectra of the transients obtained from Py2 upon laser excitation (347 nm) in 3MP at room temperature; (●) 8 µs; (☐) 110 µs; (▲) 1600 µs after the laser pulse. Inset: kinetics of the transients decay (310 nm) and ground state recovery (350 nm).

3.2.3. TPy

A long-lived transient was only observed on flashing a TPy solution at room temperature (λ_{max} = 325 and 405 nm, Fig. 5). Its lifetime was rather long (435 µs) and un-sensitive to oxygen. No shorter-lived transients were detected. The results are similar to those previously obtained in ethanol, where the lifetime was somewhat shorter (250 µs). It can be assigned to the metastable photoproduct (open structure).

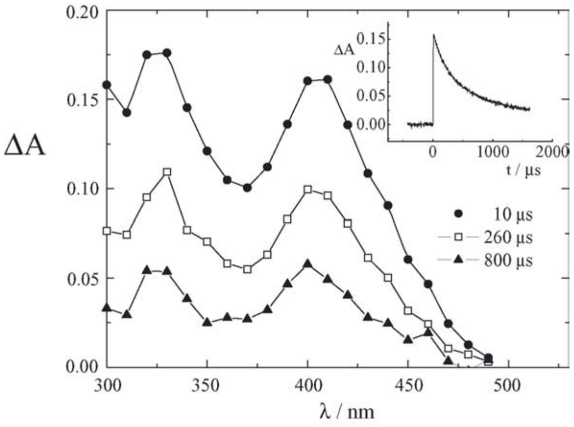


Fig. 5. Time-resolved absorption spectra of the transients obtained from TPy upon laser excitation (347 nm) in 3MP at room temperature; (●) 10 µs; (☐) 260 µs; (▲) 800 µs after the laser pulse. Inset: decay kinetics monitored at 400 nm.

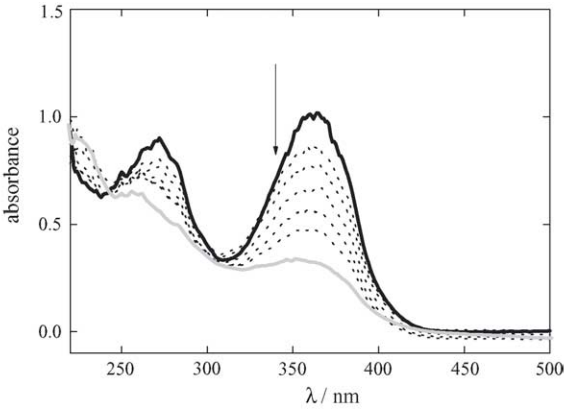


Fig. 6. Spectral evolution of Py1, before irradiation (full, black), during UV irradiation (254 nm, dot) and after 2 h irradiation (full, grey), in a 3MP solution (4.6×10^{-5} mol dm^{-3}) at 140 K.

3.3. Steady state photochemistry

3.3.1. Py1

By irradiating a Py1 solution (3MP) at room temperature no spectral change was observed. At low temperature (140 K), the spectrum changed in the UV region (Fig. 6), but no photocolouration was observed. The photoproduct could correspond to the long-lived transient which was formed from the triplet state in the laser experiments at room temperature, but the assignment is uncertain because the spectra of the starting molecule and of the photoproduct overlap in the 300–400 nm region. The thermal reversibility of the photoreaction was only partial.

In Table 2 the experimental maximum wavelengths of the open form are compared with the results obtained by calculations. Calculations do not well reproduce the experimental spectra, probably because they do not belong to a single molecular species. However, the low *f* value in the near UV region is in agreement with the intensity decrease experimentally observed. The lowest energy transition here located is n,π* in nature and has very low transition probability. A high intensity π,π* transition was calculated at higher energies.

3.3.2. Py2

Steady irradiation of Py2 at room temperature in 3MP did not cause any spectral change. At low temperature (230 K), a very weak photocolouration was observed: the absorbance slightly increased around 400 nm, but the absorption maximum shifted to shorter wavelengths (318 nm). More marked modifications were observed in the UV region, where a new band appeared at 260 nm (Fig. 7). The maximum at 318 nm corresponds well to that observed upon laser excitation at room temperature.

Table 2
Experimental maximum wavelengths, λ_{max}, of Py1 in its open form in 3MP compared with calculated values of the transition wavelength and oscillator strength

Experimental	Calculated		
λ_{max} (nm)	Transition	λ_{max} (nm)	*f*
350	$S_0 \rightarrow S_1$	384	0.0001 (n,π*)
	$S_0 \rightarrow S_2$	277	0.006 (π,π*)
	$S_0 \rightarrow S_3$	273	0.004 (n,π*)
	$S_0 \rightarrow S_4$	273	0.003 (π,π*)
	$S_0 \rightarrow S_5$	265	0.004 (n,π*)
259	$S_0 \rightarrow S_6$	260	1.0 (π,π*)

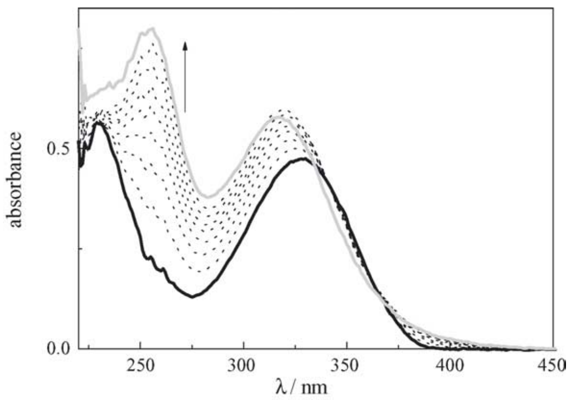


Fig. 7. Spectral evolution of Py2: before irradiation (full, black), during UV irradiation (350 nm, dot) and after 1 h irradiation (full, grey), in a 3MP solution (4.4×10^{-5} mol dm^{-3}) at 230 K.

In Table 3 the experimental and calculated transitions of the open form are compared. Even for this compound the lowest energy transition is located in the near UV region and is n,π* in nature. A higher intensity π,π* transition is calculated and was experimentally found at higher energies.

3.3.3. TPy

Photochromism of TPy was observed in a 3MP fluid solution at low temperature ($T < 220$ K); accordingly with previous experiments carried out in a matrix [3], the solution became yellow-orange upon UV irradiation. Initially, a new maximum appeared at 425 nm, which shifted to higher energy (412 nm) under prolonged irradiation. A global intensity enhancement was observed in the UV region (λ_{max} = 288 and 337 nm). The initial spectral pattern is close to that observed on flashing a TPy solution at room temperature. The photoproduct underwent thermal bleaching in the dark, but the initial spectrum was not restored.

Photo-bleaching was observed by irradiating the solution with 435 nm light, at a temperature, 140 K, at which the thermal processes were inefficient. However, the decolouration

Table 3
Experimental maximum wavelengths, λ_{max}, of Py2 open form in 3MP compared with calculated values of the transition wavelength and oscillator strength

Experimental	Calculated		
λ_{max} (nm)	Transition	λ_{max} (nm)	*f*
	$S_0 \rightarrow S_1$	382	0.0001 (n,π*)
318	$S_0 \rightarrow S_2$	275	0.006 (π,π*)
	$S_0 \rightarrow S_3$	273	0.006 (n,π*)
256	$S_0 \rightarrow S_4$	270	1.0 (π,π*)

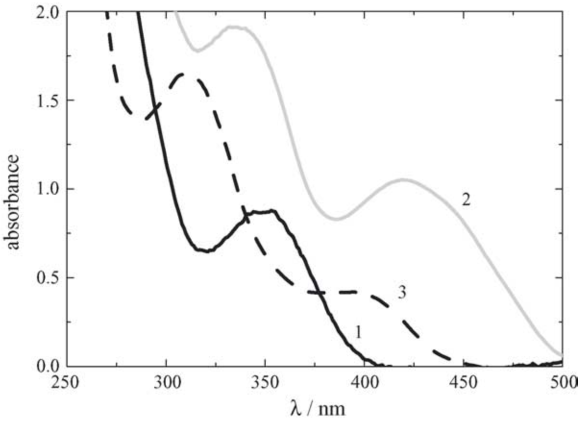
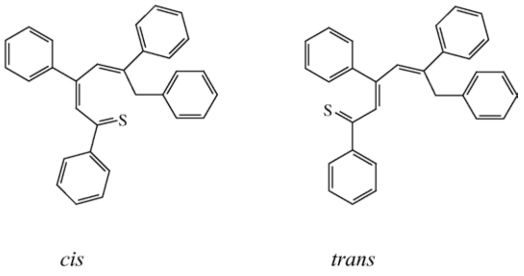


Fig. 8. Spectral changes of TPy in a 3MP solution (4.3×10^{-5} mol dm^{-3}) at 140 K: (1) before irradiation; (2) upon UV irradiation and (3) upon visible light (435 nm) irradiation of the coloured solution.



Scheme 3.

was not complete (Fig. 8); even when the temperature was increased in the dark, the initial spectrum was not restored.

Calculations were carried out for both the *trans* and *cis* isomers of the open form (Scheme 3, Table 4) with the aim to determine the nature of the excited states and understand which geometries are involved in the low temperature transformations. From the comparison of the experimental results with the values in the table, it can be argued that the first coloured photoproduct is the *cis* isomer which converts at least partially to the *trans* isomer upon visible irradiation.

Table 4
Experimental maximum wavelengths, λ_{max}, of TPy, in its open form in 3MP compared with calculated values (for both the *cis* and *trans* forms) of the transition wavelength and oscillator strength (π,π^* transitions, unless otherwise indicated)

Isomer	Experimental	Calculated		
	λ_{max} (nm)	Transition	λ_{max} (nm)	*f*
Tpy *cis*		$S_0 \rightarrow S_1$	745	0.006
		$S_0 \rightarrow S_2$	689	0.008
	425	$S_0 \rightarrow S_3$	424	0.04
		$S_0 \rightarrow S_4$	398	0.30
		$S_0 \rightarrow S_5$	384	0.14
	340	$S_0 \rightarrow S_6$	376	0.014
		$S_0 \rightarrow S_7$	354	0.024
	256	$S_0 \rightarrow S_{14}$	276	0.13
Tpy *trans*		$S_0 \rightarrow S_1$	639	0.0000 (n,π^*)
	310 (after visible irradiation)	$S_0 \rightarrow S_2$	328	0.96
		$S_0 \rightarrow S_3$	302	0.001
		$S_0 \rightarrow S_4$	287	0.007 (n,π^*)
	288	$S_0 \rightarrow S_5$	285	0.005 (n,π^*)
		$S_0 \rightarrow S_6$	277	0.007 (n,π^*)

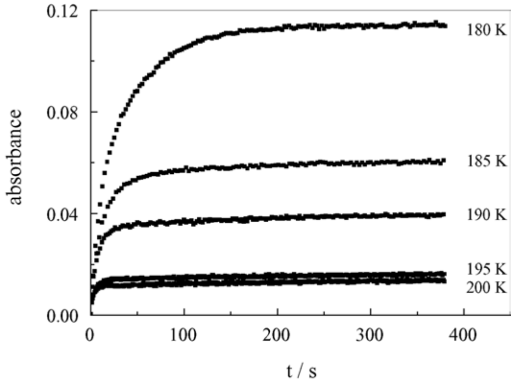


Fig. 9. Colour-forming kinetics of TPy at various temperatures.

To determine the quantum yield of the photoreaction and the kinetic constant and activation energy of the thermal back reaction, colour-forming and colour-bleaching kinetics were followed in the 165–200 K temperature range. However, because of the complexity of the system, kinetic parameters were determined for the thermal back processes, whereas a qualitative description of the photocolouration processes could be only obtained.

The colour-forming kinetics, which were followed under steady irradiation (366 nm), are described by a bi-exponential function at every temperature. This behaviour indicates that at least two molecular species are formed upon irradiation. As can be seen in Fig. 9, where the absorbance of the colour maximum is plotted against time at various temperatures, the colourability, that is the maximum colour intensity attainable under specific experimental conditions, greatly increased with decreasing temperature, due to decrease of the thermal bleaching rate. Methods previously developed [19–21] to determine the molar absorption coefficient of the metastable photoproduct(s) and the quantum yield of photocolouration did not give reliable results in the present case.

Colour bleaching kinetics were also described by a bi-exponential function at each temperature, Eq. (1),

$$A_{\mathrm{P}}^{\infty} = A_{\mathrm{P1}}^{\infty} \mathrm{e}^{-k_{1\Delta} t} + A_{\mathrm{P2}}^{\infty} \mathrm{e}^{-k_{2\Delta} t} + R \qquad (1)$$

where A_{P1}^{∞} and A_{P2}^{∞} are the amplitudes of the rapid ($k_{1\Delta}$) and slow ($k_{2\Delta}$) parts of the bi-exponential bleaching kinetics, respectively. In the temperature interval explored, the kinetic rate constant of the fast process was in the 2.6×10^{-1} (200 K) to 6.2×10^{-3} (165 K) s^{-1} range and that of the slower one in the 5.9×10^{-2} (200 K) to 6.6×10^{-4} (165 K) s^{-1} range. By applying Arrhenius treatment (Fig. 10), activation energies of 32 ± 3 kJ mol^{-1} and 34 ± 2 kJ mol^{-1} and frequency factors around 10^8 s^{-1} (lower than the typical 10^{12} s^{-1} value

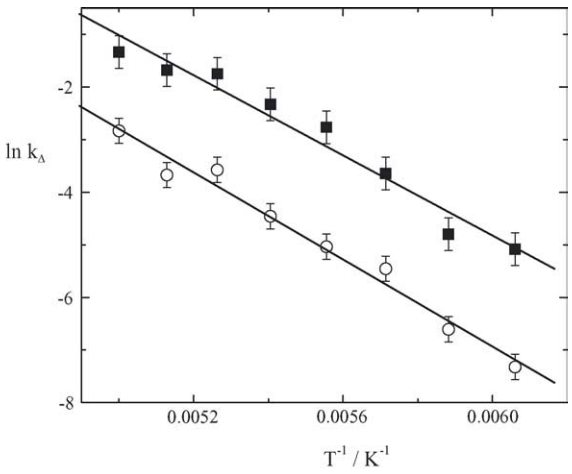


Fig. 10. Arrhenius plot of the thermal bleaching of TPy in MCH ((■) correlation coefficient = 0.980; (○) correlation coefficient = 0.989).

for a mono-molecular process) were determined for the fast and the slow components of the thermal bleaching, respectively. The residual absorption, *R*, increased with decreasing temperature (from 0.0006 at 200 K to 0.0962 at 165 K) and disappeared after one day in the dark at room temperature. However, the initial spectrum was not completely restored.

Additional qualitative information about the number of photoproducts could be obtained from their fluorescence and fluorescence excitation spectra. The emission of the coloured form was investigated in a rigid matrix (80 K) to minimize thermal bleaching. Different results were obtained when the solution was photocoloured in a matrix or in a fluid solution at low temperature (160 K) and than brought down at 80 K. Under the first experimental condition, the spectral distribution of the emission changed markedly with the excitation wavelength (Fig. 11a). This confirms that at least two species are formed during irradiation, one with emission maximum at 490 nm ($\lambda_{exc} = 400$ nm), the other with maximum at 540 nm ($\lambda_{exc} = 435$–450 nm). When the solution was irradiated at 160 K and than cooled at 80 K, the excitation wavelength effect was less marked and the ipsochromic emission prevailed (Fig. 11b). This behaviour indicates that various isomers are formed in different relative amounts when the experimental conditions change. It seems reasonable that different conformations are present in a rigid matrix, while the molecule relaxes at the minimum energy conformation when it finds itself in a fluid solution.

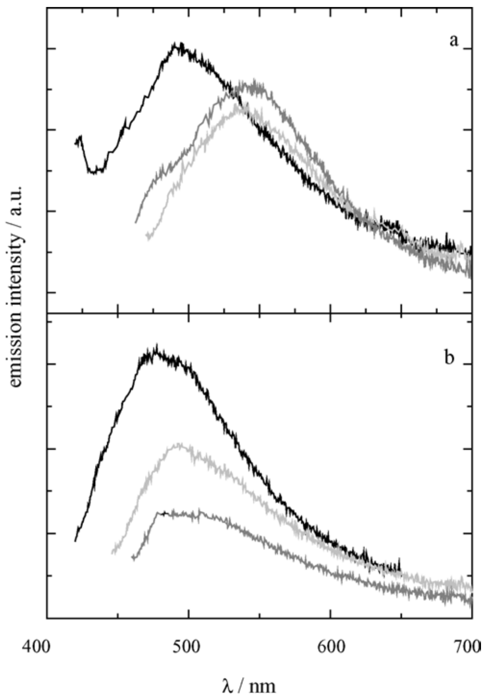
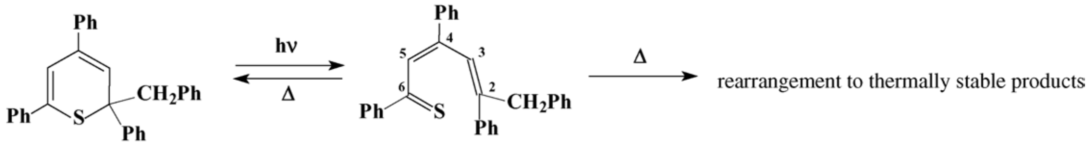


Fig. 11. Fluorescence emission spectra of the coloured form of TPy in 3MP at 80 K, excited at 400 nm (black); 435 nm (light grey) and 450 nm (grey): (a) after photocolouration at 80 K; (b) after photocolouration at 160 K and freezing at 80 K.

4. Concluding remarks

The three molecules investigated exhibit absorption spectra in the same wavelength region. Photochemistry can only be observed at low temperature, but the spectra of the photoproducts for the thiopyran derivative only are in the visible region. At room temperature, transients are produced upon laser excitation which are tentatively assigned to the low temperature photoproducts; a triplet precursor could only be detected for Py1.

The two pyran derivatives show poor reversibility and no colouration. Therefore, only TPy can be considered a photochromic compound, because the photoproduced thioketone is coloured, even though it only partially reconverts to the closed colourless form by thermal bleaching. It has been proposed that the red-shift of the thioketone band is due to a π,π^* transition, based on its structureless character [3]; the value of molar absorption coefficient, here



Scheme 4.

determined, supports this hypothesis. As can be seen in Tables 2 and 3, the lowest transitions of Py1 and Py2 in their open forms are located in the near UV region; they are n,π^* in nature and have very low transition probabilities. The experimentally observed bands of the photoproducts correspond to the π,π^* transitions calculated at higher energies.

Based on the calculations, the lowest transition for TPy may be n,π^* or π,π^*, depending on the assumed geometry (*cis* or *trans*); however, fairly intense π,π^* transitions ($S_0 \rightarrow S_4$ and $S_0 \rightarrow S_5$, $f > 0.1$) were calculated for the *cis* geometry in the 400 nm wavelength region. These transitions may well correspond to the observed colour band. For this molecule, the photoinduced breaking of the S–C_2 bond (Scheme 4) in a fluid solution, is followed by very fast thermal processes that stabilize the molecule to give isomers which are spectrophotometrically detectable, by both steady state and pulsed techniques. At room temperature, the thermal bleaching is so fast that the formation of the coloured form cannot be detected by stationary techniques, but only by laser flash photolysis. The rate of photoproduct formation is faster than the time resolution of our laser apparatus (∼20 ns) and the precursor excited state cannot be revealed. As temperature decreases, the barrier to thermal bleaching is high enough (about 30 kJ mol^{-1}) that photocolouration was observed under steady irradiation and the thermal bleaching rate constants, $k_{1\Delta}$ and $k_{2\Delta}$, could be measured from the absorbance fading in the dark in the temperature range explored (200–165 K). Compared with other photochromic molecules, the activation energies (32 and 34 kJ mol^{-1} versus 60–80 kJ mol^{-1} [12,19]) are rather small, which explains the fastness of the reaction at room temperature. A further temperature decrease (140 K) causes the barrier of the back reaction to be insurmountable and the open molecule stabilizes through paths with lower activation energy. Under these experimental conditions, several metastable species (isomers) can be qualitatively evidenced from both absorption and, much more, emission spectra. We have to consider that the open thio-ketone form, where rotation around double bonds (C_2–C_3; C_4–C_5) as well single bonds (C_3–C_4; C_5–C_6) may occur, might be represented by four geometric isomers, and each of them by four conformers. Even though some of these conformations can be excluded based on simple sterical considerations, several possibilities remain open.

The photobleaching reaction, observed at low temperature, probably involves the conversion of a *trans* species to a *cis* one, which thermally converts to the starting molecule when temperature is enhanced.

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