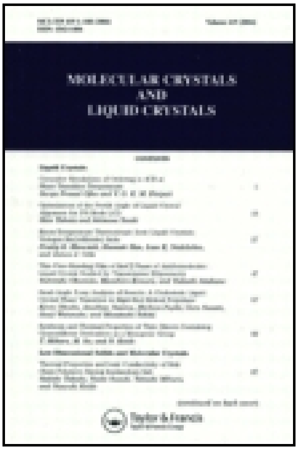

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Photophysics and Photochemistry of some Dipyrrolylperfluorocyclopentenes

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Photophysics and Photochemistry of some Dipyrrolylperfluorocyclopentenes

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The relaxation properties of the lowest excited states of singlet and triplet multiplicity of some photochromes with dipyrrolylperfluorocyclopentene structure have been investigated by conventional and time-resolved spectrometric techniques. These compounds can be photocoloured with a fairly high quantum yield ($\Phi_{PC} \geq 0.5$). The bleaching is thermal and photochemical. The fluorescence emission is scarceor undetectable. No triplet absorption was observed by laser flash photolysis, whereas transients unaffected by oxygen (lifetimes in the range 60 ns–10 μs) were detected beside the metastable closed form.

Keywords: bleaching; dipyrrolylcyclopentenes; photophysics; photochromism

INTRODUCTION

The photochromic properties of diarylethenes structurally constrained to a single (*cis*) geometry by a perfluoro-pentatomic ring at the double

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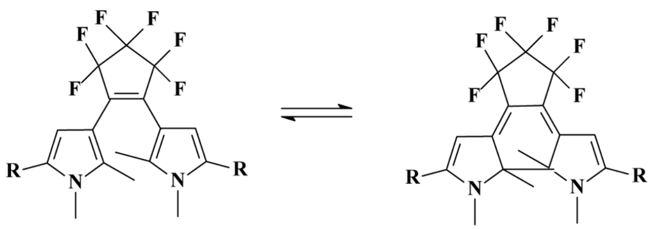
bond, and their potential applications in optoelectronics (e.g., for optical memories and switching devices), have received much attention in the last few years [1]. The aryl groups are generally pentatomic heterocycles (thienyl, furyl, pyrrolyl) bearing different substituents, which can affect the absorption coefficient and photostability of the coloured forms [1,2]. The colouration reaction is the well known conrotatory photocyclization of the 1,3,5-hexatriene moiety of *cis*-stilbene [3], which leads reversibly to a photoproduct with an extended conjugation, the coloured dihydrophenanthrene. The latter is relatively stable in the absence of oxygen (lifetime of about 2 hours) [3]. Replacement of phenyl rings by thienyl rings increases the lifetime of the dihydro-type intermediate up to several hours or days [1,4]. Therefore, dithienylethenes have been deeply investigated as thermally irreversible photochromic compounds because the thermal stability of the coloured forms makes them particularly suitable for specific applications. The pyrrolyl analogues have been reported to display an intermediate behaviour [1,5].

In this work, the photochemistry and photophysics of some photochromes with dipyrrolyl-perfluorocyclopentene structure, have been investigated by conventional and time-resolved spectrometric techniques. All the compounds studied can be photocoloured with a fairly high quantum yield. The bleaching is thermal and photochemical. Qualitative information about their photochromic behavior has already been reported by some of us in a previous work mainly concerned with their synthesis [6]. The present preliminary work has been focused on the characterization of their lowest excited states by fluorimetry and laser flash photolysis and on the colouration/decolouration kinetics.

EXPERIMENTAL

The compounds investigated are shown in Scheme 1.



R = CN (**1**), CO_2CH_3 (**2**), Phenyl (**3**), Thienyl (**4**), Thienylethynyl (**5**)

SCHEME 1

They were prepared for a previous work [6] and purified (>98%) by HPLC when necessary. Measurements were carried out in toluene (Uvasol Fluka), unless otherwise specified. Compound **1**, bearing 2-cyanopyrrole rings, has been already studied in ethyl acetate solutions [5,6] and is here revisited to complete the available information and make a comparison with the other four analogues (**2–5**) in the same solvent.

The absorption spectra were recorded with a HP 8453 diode-array spectrophotometer. The quantum yields of photocolouration (Φ_{PC}) and photobleaching (Φ_{PB}) were measured spectrophotometrically at low sample concentrations ($\sim 10^{-5}\,\text{mol}\,\text{dm}^{-3}$). The experimental set-up is described elsewhere [7]. The uncertainty in the yields was about 15%. The kinetics of the thermal ring-opening reaction was recorded following the colour-bleaching of the irradiated solution immediately after removal of the UV source. An Oxford Instruments cryostat was used for the temperature control.

Corrected fluorescence spectra and quantum yields were determined at room temperature using a Spex Fluorolog-2 1680/1 spectrofluorimeter. The uncertainty on the fluorescence quantum yields was within 15%. For laser flash photolysis measurements, the third harmonic ($\lambda = 355\,\text{nm}$) from a Continuum Surelite Nd-YAG laser was used with energy less than 5 mJ per pulse and time resolution of about 20 ns. Details are reported elsewhere [7].

RESULTS AND DISCUSSION

The absorption spectra of the compounds investigated recorded in toluene are in agreement with those in ethyl acetate reported

TABLE 1 Fluorescence Quantum Yields (Φ_F), Spectral (λ_{max}^{Tr}) and Dynamic (τ_{Tr}) Properties of the Transient (Tr) Produced by Laser Flash Photolysis, Photocolouration (Φ_{PC}) and Photobleaching (Φ_{PB}) Quantum Yields, Molar Absorption Coefficient of the Coloured Form (ε_{max}) and Thermal Bleaching Rate Constants (k_Δ) for Some Dipyrrolylperfluorocyclopentenes in Toluene

Compound	Φ_F (10^{-3})	λ_{max}^{Tr} (nm)	τ_{Tr} (μs)	Φ_{PC}	ε_{max} ($10^3\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}$)	Φ_{PB}	k_Δ ($10^{-4}\,\text{s}^{-1}$)
1	7.5	420	13	0.58	8.1		1.8 (260 K)
2	2.8	430	0.0067	0.71	8.1		29 (260 K)
3	Not detected	410	13	0.32	13.1	0.39	0.3 (290 K)
4	1.9	430	0.43	0.55	9.5	0.17	1.5 (290 K)
5	7.0	450	11	0.61	13.7	0.21	1.6 (290 K)

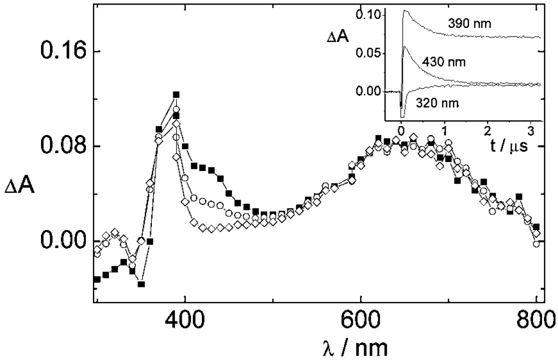


FIGURE 1 Time resolved spectra of a 1.3×10^{-4} mol dm^{-3} solution of **4** in toluene: ■ 0.1 μs; ○ 0.4 μs; ◇ 3.2 μs after the laser pulse ($\lambda_{exc} = 355$ nm). Inset: kinetics monitored at different wavelengths.

in previous papers. The fluorescence emissions (Table 1), in the 450 nm region, are weak (quantum yields ~0.01–0.001) and undetectable for **3**.

The laser measurements (Fig. 1 and Table 1) showed, in addition to the formation of the coloured forms, the presence of transients which were unaffected by oxygen and therefore did not correspond to the triplets. These transients exhibited similar spectral patterns ($\lambda_{max} \sim$ 410–450 nm) and lifetimes ranging in a wide time interval (0.07–13 μs). There is no evidence that they are precursors of the coloured forms.

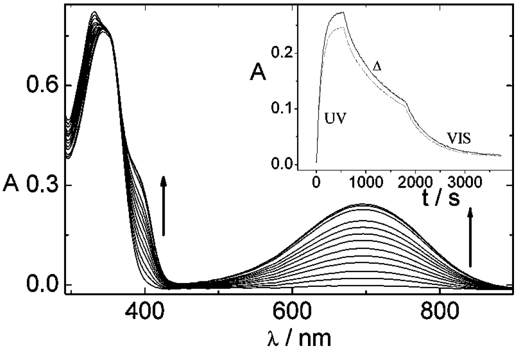


FIGURE 2 Time evolution of a 7.5×10^{-5} mol dm^{-3} solution of **5** in toluene at room temperature. Inset: colour forming, thermal bleaching and photochemical bleaching kinetics at 398 and 698 nm (dash).

The photocolouration and thermal bleaching kinetics follow mono-exponential trends. An experimental run of photocolouration-decolouration at 290 K is illustrated in Figure 2 for **5**. The inset shows that, after attainment of the photostationary state by UV light, the thermal bleaching process ($k_\Delta = 0.0015 \pm 0.0001\,s^{-1}$ for **5**) is further accelerated by visible-light irradiation. This behaviour was exhibited by three (**3–5**) of the molecules investigated. The kinetic treatment for the photocolouration process leads to Eq. (1).

$$dA/dt = \varepsilon \times \Phi_{PC} I^0 F A^0 - A\,[I^0 F \varepsilon_{iso}\,(\Phi_{PC} + \Phi_{PB}) + k_\Delta] \qquad (1)$$

(A: absorbance at the analysis wavelength; ε: molar absorption coefficient of the coloured form at the analysis wavelength; ε_{iso}: molar absorption coefficient at the irradiation wavelength (isosbestic point), I^0: intensity of the incident light; F (photokinetic factor) = $(1 - 10^{-A^0})/A^0)$; A^0: initial absorbance at the irradiation wavelength. From Eq. (1), $(\Phi_{PC} + \Phi_{PB})$ and $\varepsilon \times \Phi_{PC}$ can be determined by integral or differential methods [8]. To determine Φ_{PB} separately, the reaction was studied at a lower temperature (200 K), where the thermal back process becomes inefficient, by irradiating the photostationary solution with visible light and following the colour fading up to 30% transformation. Based on Eq. (2) (A': absorbance of the coloured form at the irradiation wavelength), Φ_{PB} was obtained from the plot of dA/dt vs. $10^{-A'}$.

$$-dA/dt = \varepsilon \times \Phi_{PB} I^0 (1 - 10^{-A'}) \qquad (2)$$

Combining the results from Eqs. (1) and (2), all kinetic and spectral parameters were determined and are reported in Table 1.

CONCLUSIONS

All the molecules studied showed reversible photochromic behaviour. Those bearing aromatic substituents (**3–5**) underwent slower thermal bleaching processes and therefore exhibited better colourability at room temperature. The coloured products from **3–5** were also photobleacheable under visible light irradiation. Since this process is activated by UV light too, it impedes total conversion of the colourless to the coloured form. A photokinetic method was developed to determine the quantum yields for the formation and bleaching of the coloured form and its molar absorption coefficient. No reaction intermediate was detected by laser flash photolysis. The assignments of the transients formed are still under investigation.

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