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Thermal reversibility and bistability in photochromic diarylethenes

G. Favaro *, U. Mazzucato, F. Ortica, P. Smimmo

Università di Perugia, Dipartimento di Chimica, Laboratorio di Chimica-Fisica, Via Elce di Sotto, 8, 06123 Perugia, Italy

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This paper is dedicated to Professor Vincenzo Balzani.

Abstract

An account is given of the research work in progress in the authors' laboratory on the photochromic behaviour (photocyclization) of diarylethenes structurally constrained to the *cis* geometry. Depending on the aromaticity of the aryl groups, the photoreaction can be thermoreversible, photoreversible or both. Examples of different photochromic behaviours of two series of photochromic diarylethenes (dipyrrolylperfluorocyclopentenes, which are thermally and photochemically reversible, and dithienyldithiolthiones, which are thermally stable and photoreversible) are investigated here by steady state and time-resolved spectroscopy to obtain information about their photochemistry and the competitive relaxation paths of their electronically excited states.

Keywords: Photochromism; Diarylethenes; Photoreaction mechanism; Laser flash photolysis

1. Introduction

The interest in photochromic materials, namely in compounds that undergo a light-induced reversible transformation between species absorbing in different regions, has been widely increased in the last decades because of the real and potential applications of photochromism in optics and optoelectronics [1,2]. Different properties are required for specific applications: thermoreversibility of the photocoloration process is needed for use in ophthalmic lenses whereas thermal stability (only photoreversibility) is required for use in optoelectronics, f.i. as switches and memories [3,4]. Thermal stability of both the starting and the photoproduced compounds, generally uncolored and colored, respectively (bistability), offered by some classes of diarylethenes, is now a subject of intensive experimental and theoretical investigations [3–5].

The research line of our laboratory, which has been addressed until recently to the class of organic photochromes of naphthopyran-type [6], is now focused on both bistable and thermally reversible photochromes of the class of diarylethenes bearing heterocyclic five-membered rings as the aryl groups [7]. Upon stimulation by UV light, these compounds, which are constrained to a *cis* geometry by a pentatomic ring, undergo conrotatory cyclization leading to a closed colored structure, analogous to that of dihydrophenanthrene, the well know photoproduct of *Z*-stilbene [8,9]. Depending on the structure, the photoreaction can be thermoreversible, photoreversible or both. It has been found that the lower is the aromatic stabilization energy of the aryl groups, the higher is the thermal stability of the colored form [3].

This article, which aims to give an account of our recent and new research on the subject, describes the photochemical and photophysical behaviour of some representatives of two series of compounds (see Scheme 1). They are constrained in the original *Z* geometry, needed to avoid competition by the Z → E photoisomerization, by inserting the ethenic bond in five-membered rings, such as cyclopentene, or by [1,3]dithiole-2-thione or -2-one bridging units. The first series is that of dipyrrolyl-perfluoro-cyclopentenes (DPCPs). After UV photocoloration, these compounds

* Corresponding author. Tel.: +39 075 585 5573; fax: +39 075 585 5598.
E-mail address: favaro@unipg.it (G. Favaro).

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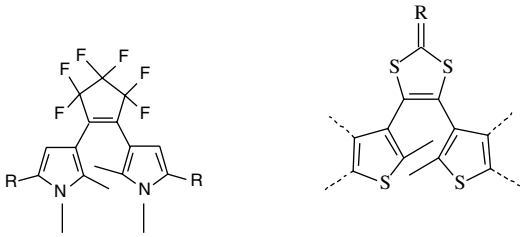


dipyrrolylperfluorocyclopentene (DPCP) dithienyldithiol-one (R=O) or –thione (R=S) (DTDT)

Scheme 1.

return to the initial open form by both thermal and photochemical paths at room temperature, but only photochemically at lower temperature. The second series is that of newly synthesized dithienyldithiolthiones (DTDT) and dithienyldithiolones, which are only photoreversible. All the compounds investigated were synthesized at the University of Marseille [10,11].

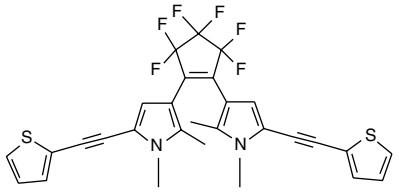
Steady state and time-resolved spectroscopies are used to characterize the photophysics and photochemistry of these compounds and to elucidate the relaxation paths of their electronically excited states. The photochemical and kinetic parameters thus measured allow the photochromic properties to be evaluated under different conditions. Such a quantitative kinetic study of the competitive relaxation processes from the lowest excited states is needed to understand the mechanism of the coloration/decoloration processes and to obtain information of general validity for the characterization of these series of photochromes for potential applications.

2. Results and discussion

2.1. Steady state photochemistry

2.1.1. Dipyrrolylperfluorocyclopentenes (DPCPs)

These compounds exhibit absorption spectra in the UV region; the lowest energy band maxima are in the 300–380 nm range, with absorption coefficients of the order of 10^4 dm^3 mol^{-1} cm^{-1} [7]. Sometimes, they also exhibit weak fluorescence emissions, in the 450 nm region (quantum yields in the range 0.01–0.001). The photoproduced coloration can bleach thermally (with rate constants, k_Δ, strongly dependent on the structure and temperature, ranging from 10^{-5} to 10^{-2} s^{-1} at room temperature) and/or by irradiation with visible light. The photobehaviour of the compound with R = thienylethynyl (**1**) is described in the following as a typical example.



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Intense coloration of toluene solutions of **1** is observed upon UV irradiation at room temperature, the absorption spectra of the colored forms being in the 600–850 nm region. After attainment of the photostationary state, if the UV-irradiation is discontinued, thermal bleaching occurs at rates strongly dependent on temperature (activation energy = 65 kJ mol^{-1}). The spectral evolution upon UV–Vis irradiation and in the dark is shown in Fig. 1 at three different temperatures. Above room temperature ($T = 320$ K), the fastest bleaching is thermal ($k_{\Delta,320\,K} = 2.4 \times 10^{-3}$ s^{-1}), (a); around room temperature, the thermal process is markedly slowed down ($k_{\Delta,290\,K} = 1.6 \times 10^{-4}$ s^{-1}; $k_{\Delta,280\,K} = 8 \times 10^{-5}$ s^{-1}) and the back conversion to the open form can be accelerated by visible irradiation (b); far below room temperature ($T = 200$ K), the photoproduct becomes thermally stable and only Vis irradiation induces cycloreversion to the starting molecular structure (c).

The kinetic equation used to describe the color-forming (open form → closed form) kinetics is:

$$dA_C/dt = \varepsilon_C \times \Phi_{O\to C} I_O - \varepsilon_C \Phi_{C\to O} I_C - k_\Delta A_C \quad (1)$$

where A_C is the absorbance of the closed (colored) form at the analysis wavelength (λ_{an}), I_O and I_C are the intensities absorbed by the open and closed forms, respectively, at the excitation wavelength (λ_{exc}) and ε_C is the molar absorption coefficient of the colored form at λ_{an}. The rate constant of the thermal bleaching is determined in the dark using the first order kinetic equation:

$$-dA_C/dt = k_\Delta A_C \quad (2)$$

The photobleaching quantum yield is determined at 200 K by irradiating the photostationary solution with Vis light, based on the rate equation:

$$-dA_C/dt = \varepsilon_C \times \Phi_{C\to O} I^0 (1 - 10^{-A'_C}) \quad (3)$$

where A'_C is the absorbance of the closed form at λ_{an} and I^0 is the intensity of the irradiating light. Combining Eqs. (1)–(3), the following photochemical and kinetic parameters were obtained:

$\Phi_{O\to C}$	$\Phi_{C\to O}$	ε_C (λ_{max})/dm^3 mol^{-1} cm^{-1}	k_Δ/s^{-1} (290 K)	E_a/kJ mol^{-1}	A/s^{-1}
0.81	0.11	11 100 (698 nm)	0.00016	65 ± 5	7×10^7