

Photobehaviour of diarylethenes with thiophenes as aryl groups and dithiole-2-thione and dithiole-2-one at the ethenic bond

F. Ortica^a, P. Smimmo^a, C. Zuccaccia^a, U. Mazzucato^a, G. Favaro^{a,*},
N. Impagnatiello^b, A. Heynderickx^b, C. Moustrou^b

^a *Università di Perugia, Dipartimento di Chimica, 06123 Perugia, Italy*

^b *Université de la Méditerranée, Faculté des Sciences de Luminy, UMR CNRS 6114, 13288 Marseille Cedex 9, France*

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Abstract

Four diarylethenes, which were expected to be thermally irreversible photochromic compounds, containing thiophene groups as aryls and dithiole-2-thione or dithiole-2-one at the ethenic bond, were investigated by steady state and time-resolved spectroscopy to obtain information about their photochemistry and the competitive relaxation paths of their electronically excited states. Only for the 4,5-bis(2-methyl-1-benzothien-3-yl)-1,3-dithiole-2-thione (BTDT), a good photochromic response was observed. The photocoloration reaction was undetectable for the 4,5-bis(2,5-dimethylthien-3-yl)-1,3-dithiole-2-thione (TDT), whereas for the two analogous compounds with oxygen (-ones) the occurrence of side reactions reduced their photochromic properties. For the photoreactive compounds, the quantum yields of the UV-photoinduced ring-closing reaction and the visible-stimulated cycloreversion reaction were determined. Nanosecond time-resolved experiments showed the formation of transients which were assigned to n, π^* triplets for thiones and π, π^* triplets for ones, respectively. ^1H NMR measurements allowed the equilibrium ratio between parallel and antiparallel conformations for the benzo-annellated compounds to be determined.

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1. Introduction

The light induced processes of diarylethenes bearing heterocyclic aryl groups have been a subject of intensive experimental and theoretical investigations during the last decade due to their potential for applications as optical switches and non-linear optical devices [1–3].

The molecules investigated in this paper are two thienyldithiols and two thienyldithiolones whose synthesis is described elsewhere [4]. Their formulas are shown in Scheme 1.

The presence of the pentatomic ring at the double bond inhibits *Z–E* isomerization constraining the molecules to *Z*-geometry. Electronic excitation is then expected to result in a cyclization reaction leading to a coloured compound which can cyclorevert to the starting molecule, thermally or by visible-light irradiation, thus displaying photochromic behaviour. In this series of molecules, due to the low aromatic stabilization energy

of the thiophene groups, the coloured forms are expected to be thermally stable [2,5].

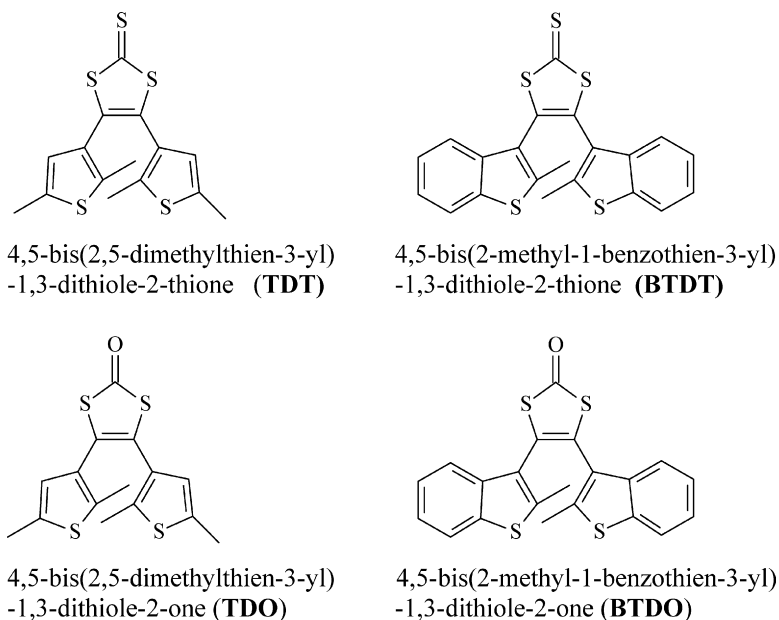
Steady state and time-resolved spectroscopy was used to characterize the photophysics and photochemistry of these compounds and to elucidate the relaxation paths of their electronically excited states. The results obtained indicate that, despite of the structural similarity, not all of the molecules investigated have suitable properties to be used as thermally irreversible photochromic systems. The NMR technique was used to determine the ratio of parallel and antiparallel conformers.

2. Experimental

2.1. Materials

The synthesis of the compounds investigated was previously described [4]. Their purity (>98%) was checked by HPLC. Photokinetic measurements were carried out in 3-methyl-pentane (3MP, BDH), acetonitrile (ACN, Fluka) and/or toluene (TOL, Fluka), unless otherwise specified. Other solvents used in

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



Scheme 1.

the solvatochromic study were cyclohexane (CHX, Fluka), diethylether (DE, Fluka), ethanol (ETOH, Carlo Erba), methanol (MeOH, Fluka), ethylacetate (ETAC, Fluka), acetone (ACE, Carlo Erba), chloroform (CHF, Carlo Erba), tetrahydrofuran (THF, Carlo Erba), 1,4-dioxane (DIOX, Fluka) and dimethylsulfoxide (DMS, Fluka). When necessary, the solvents were purified. Benzophenone, from Aldrich, used as a triplet sensitizer, was crystallized before using.

2.2. Apparatus

The absorption spectra were recorded using a HP 8453 diode-array spectrophotometer. Irradiation of the samples was carried out in a 1 cm cell-path in the spectrophotometer holder, at a right angle to the monitoring beam, using a fibre-optic system. A 125 W Xe lamp, coupled with a Jobin-Yvon H10 UV monochromator, was used for irradiation and an Oxford Instruments cryostat for the temperature control. A grey filter (10% transmittance) was inserted between the sample cell and the spectrophotometer source, to avoid that a fraction of the UV light intensity might reach the sample, thus inducing photochemistry.

The emission spectrum of BTDT closed form was taken using a Spex Fluorolog-2 1680/1 spectrofluorimeter; the quantum yield was determined using 9,10-diphenylanthracene in cyclohexane as a standard and the fluorescence lifetime was measured using the Spex Fluorolog-τ2 apparatus, based on the phase modulation technique (excitation wavelength modulated in the 1–300 MHz range; time resolution ca. 20 ps). An uncertainty of 15 and 10% is estimated for the fluorescence quantum yield and lifetime, respectively.

For laser flash photolysis measurements, the third harmonic ($\lambda = 355$ nm) from a Continuum Surelite Nd–YAG laser was used with fluence less than $10^6 \text{ J cm}^{-2} \text{ s}^{-1}$ per pulse and time resolution of about 30 ns. Q-switch delays were used to reduce the laser intensity. For the spectrophotometric analysis, a 150 W Xenon

source, a Baird-Tatlock monochromator blazed at 500 nm, a Hamamatsu R928 photomultiplier and a Tektronix DSA 602 digitized analyzer were used. The data were processed by a Tektronix PEP 301 computer.

NMR experiments were carried out on a Bruker Avance DRX 400 spectrometer in CDCl_3 at 298 K. Chemical shifts for ^1H spectra were referenced to the residual resonance of the deuterated solvent ($\delta = 7.27$) and are reported as parts per million relative to tetramethylsilane. Standard integration of signals in a single-scan experiment was used to calculate the relative percentage of the p (parallel) and a-p (anti-parallel) conformations. Experimental error was determined by random integration on regions of the spectrum without signals and was estimated to be $\pm 2\%$. 2D NOESY spectra were acquired with a mixing time of 800 ms. ^1H NMR data (coupling constants (J) are given in Hz): BTDT a-p conformer: $\delta = 7.84$ (d, $^3J_{\text{HH}} = 8.0$, 1H), 7.74 (d, $^3J_{\text{HH}} = 7.9$, 1H), 7.43 (dd, $^3J_{\text{HH}} = 8.0$, $^3J_{\text{HH}} = 7.0$, 1H), 7.35 (dd, $^3J_{\text{HH}} = 7.9$, $^3J_{\text{HH}} = 7.0$, 1H), 2.01 (s, 3H); BTDT p conformer: $\delta = 7.63$ (d, $^3J_{\text{HH}} = 8.0$, 1H), 7.57 (d, $^3J_{\text{HH}} = 8.1$, 1H), 7.22 (dd, $^3J_{\text{HH}} = 8.0$, $^3J_{\text{HH}} = 7.0$, 1H), 7.13 (dd, $^3J_{\text{HH}} = 8.1$, $^3J_{\text{HH}} = 7.0$, 1H), 2.47 (s, 3H); BTDO a-p conformer: $\delta = 7.86$ (d, $^3J_{\text{HH}} = 8.0$, 1H), 7.73 (d, $^3J_{\text{HH}} = 8.0$, 1H), 7.43 (dd, $^3J_{\text{HH}} = 8.0$, $^3J_{\text{HH}} = 7.0$, 1H), 7.34 (dd, $^3J_{\text{HH}} = 8.0$, $^3J_{\text{HH}} = 7.0$, 1H), 2.00 (s, 3H); BTDO p conformer: $\delta = 7.62$ (d, $^3J_{\text{HH}} = 8.0$, 1H), 7.60 (d, $^3J_{\text{HH}} = 8.0$, 1H), 7.20 (dd, $^3J_{\text{HH}} = 8.0$, $^3J_{\text{HH}} = 7.0$, 1H), 7.13 (dd, $^3J_{\text{HH}} = 8.1$, $^3J_{\text{HH}} = 7.0$, 1H), 2.47 (s, 3H).

A Waters HPLC system, equipped with 600 pump and controller, 2487 dual λ absorbance and 996 photodiode array detector, was used for the separation of the compounds at the photostationary state.

2.3. Methods

The quantum yields of the open \rightarrow closed photocoloration ($\Phi_{\text{O} \rightarrow \text{C}}$) and the back photobleaching ($\Phi_{\text{C} \rightarrow \text{O}}$) were determined

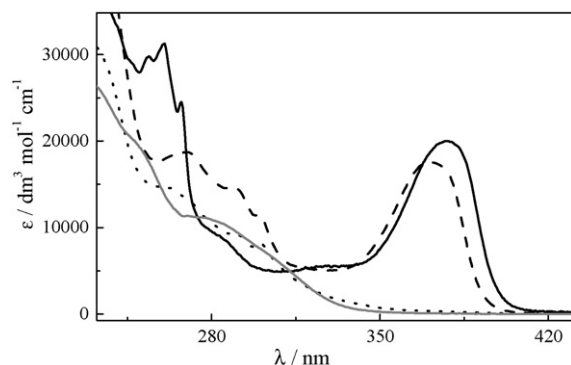


Fig. 1. Absorption spectra of the investigated compounds in 3-methylpentane at ambient temperature: TDT (solid); BTDT (dash); TDO (grey); BTDO (dot).

by spectrophotometry, using potassium ferrioxalate actinometry to measure the radiation intensity, typically on the order of $(2\text{--}3) \times 10^{-7}$ Einstein $\text{dm}^{-3} \text{s}^{-1}$. The uncertainty in the quantum yield determination was about 10%.

The heats of formation were calculated by the AM1 program of Hyperchem Pro 6.0 on geometries optimized with Amber.

3. Results

3.1. Steady state photochemistry

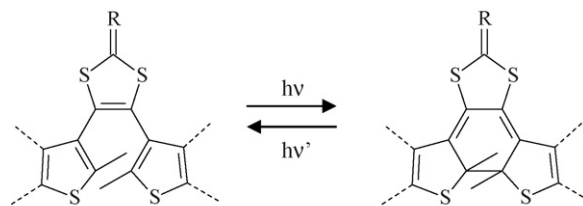
The four molecules investigated exhibit absorption spectra in the UV region, Fig. 1; the lowest energy band maxima and absorption coefficients are reported in Table 1. No fluorescence emission was detected from the colourless forms.

Photocolouration was observed for three of the molecules investigated; the TDT could not be photocoloured by continuous UV irradiation from room temperature down to 200 K. For the other compounds, the photoproducts were thermally stable and bleached upon visible irradiation only. The photochromic reaction is shown in Scheme 2 ($R = S, O$).

The colour-forming kinetics is described by Eq. (1) [6]:

$$\frac{dA_C}{dt} = \varepsilon_C \times \Phi_{O \rightarrow C} I_O - \varepsilon_C \times \Phi_{C \rightarrow O} I_C \quad (1)$$

where A_C is the absorbance of the closed (coloured) form at the analysis wavelength, I_O and I_C the intensities absorbed by the



Scheme 2.

open and closed form, respectively, at the irradiation wavelength and ε_C is the molar absorption coefficient of the coloured form at the analysis wavelength. It can be rearranged to:

$$\frac{dA_C}{dt} = \varepsilon_C \times \Phi_{O \rightarrow C} I^0 F A^0 - A_C [I^0 F \varepsilon_{\text{iso}} (\Phi_{O \rightarrow C} + \Phi_{C \rightarrow O})] \quad (2)$$

where ε_{iso} is the molar absorption coefficient at the irradiation wavelength (isosbestic point), $F = A_{\text{total}} / (1 - 10^{-A_{\text{total}}})$ is the photokinetic factor [7], I^0 the intensity of the incident light and A^0 is the initial absorbance at the irradiation wavelength. From Eq. (2) and absorbance-time data sets, $(\Phi_{O \rightarrow C} + \Phi_{C \rightarrow O})$ and $\varepsilon_C \times \Phi_{O \rightarrow C}$ were obtained. The photobleaching quantum yield was determined by irradiating the photostationary solution with visible light and following the colour fading, based on the rate equation [8]:

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

where A'_C is the absorbance of the coloured form at the irradiation wavelength. Both A_C and A'_C are time dependent variables. Eq. (3) provided the $\varepsilon_C \times \Phi_{C \rightarrow O}$ value from the linear plot of $-dA_C/dt$ versus $10^{-A'_C}$. Combining the results from Eqs. (2) and (3), all kinetic and spectral parameters were obtained. The photocyclization and cycloreversion quantum yields and the molar absorption coefficients of the coloured forms of the three photoreactive molecules are reported in Table 1.

The spectral evolution of BTDT in acetonitrile upon UV irradiation is shown in Fig. 2 along with the kinetics of photocolouration and photobleaching (inset). The photoreaction appears to be clean because isosbestic points were conserved up to the photostationary state. Despite of the low $\Phi_{O \rightarrow C}$

Table 1
Spectral characteristics (λ_{max} and molar absorption coefficient, ε_{max}) of the open (colourless) and closed (coloured) forms together with the photocolouration ($\Phi_{O \rightarrow C}$) and photobleaching ($\Phi_{C \rightarrow O}$) quantum yields of the molecules investigated at 280 K in 3MP

Compound	Colourless		Coloured		$\Phi_{O \rightarrow C}$	$\Phi_{C \rightarrow O}$
	λ_{max} (nm)	ε_{max} ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)	λ_{max} (nm)	ε_{max} ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)		
TDT	378	20000	No photocolouration observed			
BTDT	372	17500	520	14800	0.10	0.20
	377 ^a	12700 ^a	527 ^a	12400	0.09	0.23 ^a
TDO	277	11100	~362	3800	0.29	0.03
				9100 ^b	0.27 ^b	0.03 ^b
BTDO	300	8300	476	3700 ^c	0.18 ^c	0.02 ^c

^a Values in acetonitrile.

^b At 250 K.

^c At 200 K.

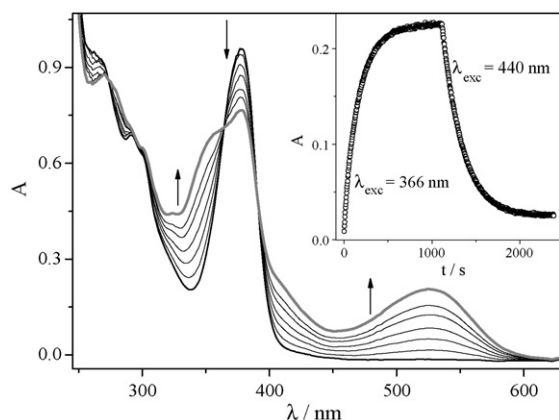


Fig. 2. Spectral evolution upon UV irradiation of $6.5 \times 10^{-5} \text{ mol dm}^{-3}$ BTDT in acetonitrile at 280 K. Inset: Photocolouration ($\lambda_{\text{exc}} = 366 \text{ nm}$) and photobleaching ($\lambda_{\text{exc}} = 440 \text{ nm}$) kinetics monitored at 527 nm.

value (0.09), the colourability of BTDT was good due to the compensating effect of the high molar absorption coefficient of the colour band. At the photostationary state, reached by irradiating at an isosbestic point (366 nm), photoconversion occurred up to 27%. Looking at the absorption spectra of the pure isomers (Figs. 1 and 3), the photocolouration percentage can be predicted to significantly increase if the irradiation is carried out at 378 nm, a wavelength which is close to the maximum absorbance of the open colourless form. The closed form exhibited the rather unusual property of fluorescing ($\lambda_{\text{max}} = 640 \text{ nm}$, Fig. 3) with non-negligible quantum yield ($\Phi_F = 0.036$) and lifetime of 0.16 ns, therefore, the radiative rate constant is $k_F = \Phi_F/\tau_F = 2.2 \times 10^8 \text{ s}^{-1}$. Unusual [9] emission from the coloured form has been also observed for an analogous compound [10]. The fluorescence excitation spectrum showed a good matching with the absorption spectrum of the closed form, obtained from the photostationary mixture after HPLC separation (Fig. 3).

The photocolouration and photobleaching reactions of BTDT were investigated in different solvents. Generally, the ring-closure quantum yield decreased with increasing the solvent polarity, while the ring-opening quantum yield was scarcely affected. This behaviour is related to the relative amounts of parallel and anti-parallel conformations equilibrated in the open

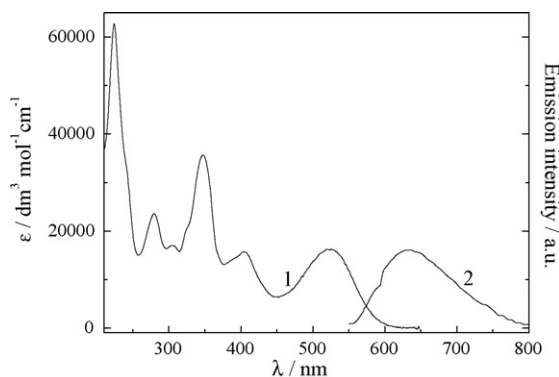


Fig. 3. Absorption (1) and normalized emission (2) spectra of BTDT coloured form in acetonitrile, after HPLC separation from the photostationary mixture.

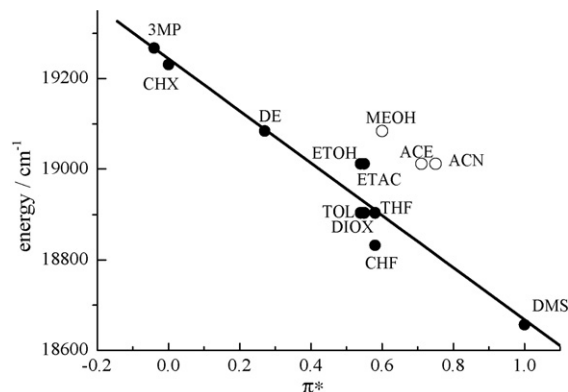


Fig. 4. Correlation diagram of the energy of the colour band of BTDT with the solvent parameter π^* .

form. The non-reactive parallel conformation is more stable and prevails in polar solvents, thus explaining the lower quantum yield found in these media [11]. The results obtained for BTDT in two solvents (acetonitrile and 3-methylpentane), reported as an example in Table 1, do not show appreciable difference in the ring-closure quantum yield and only a slight difference in the quantum yield of the back ring-opening reaction. This behaviour suggests a lower stabilization of the parallel form of this compound in polar solvents with respect to the maleic anhydride diarylethene derivatives, where a solvent effect was observed [11]. Particularly interesting was the unusual finding that the photobleaching quantum yield was significantly greater than the photocolouration quantum yield. By changing the solvent, negative solvatochromic effect was observed in the absorption of the coloured form. This effect is adequately described in terms of the solvent parameter π^* (Fig. 4), which accounts for the solvent polarity and polarizability [12]. This correlation excludes donor–acceptor hydrogen-bonding solvents, such as alcohols, acetonitrile, ethyl acetate and acetone. This means that the solute–solvent interaction, which stabilizes the excited state more than the ground state, is a dipole–dipole interaction.

The photocolourability of TDO and BTDO was poorer than that of BTDT. The maximum absorbance of the closed form appeared in the 350–400 nm region, but the spectrum was broadened up to 550 nm. The colourability at ambient temperature was almost undetectable or very weak for TDO and BTDO, mainly due to the low molar absorption coefficient of the coloured form.

The photocycloreversion of these two dithiole-2-one derivatives was not clean, leaving a spectrum with consistent residual absorptions in the visible. Compared with the absorbance at the photostationary state, the residue was about 37% for BTDO and 75% for TDO, whereas in the case of BTDT it was about 7% in acetonitrile (Fig. 2) and at all insignificant in 3MP. In such circumstances, the determined quantum yields of TDO and BTDO are only indicative. Typical examples of spectral evolution upon UV irradiation are shown in Figs. 5 and 6 for TDO and BTDO, respectively. For both molecules, isosbestic points were not maintained under irradiation. Differently from BTDT, the ring-closure quantum yields were higher than the ring-opening quantum yields (Table 1).

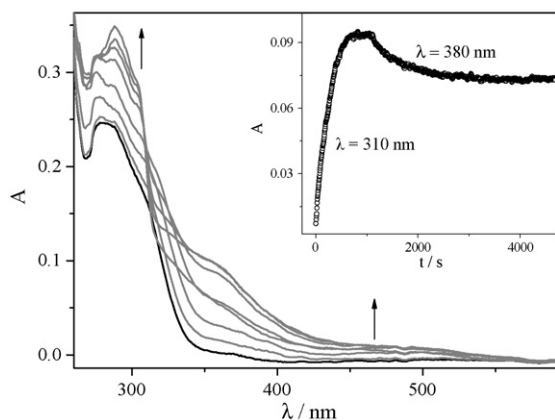


Fig. 5. Spectral evolution upon UV-photocolouration of $2.9 \times 10^{-5} \text{ mol dm}^{-3}$ TDO in 3MP at 280 K. *Inset*: Colour-forming ($\lambda_{\text{exc}} = 310 \text{ nm}$) and photobleaching ($\lambda_{\text{exc}} = 380 \text{ nm}$) kinetics monitored at 360 nm.

3.2. Time-resolved photochemistry

Nanosecond laser flash photolysis measurements showed formation of transients for all four compounds. Very short-lived transients were observed for TDT and BTDT, therefore the oxygen effect was undetectable for these species.

The TDT, upon 355 nm laser excitation, yielded a clean and intense transient absorption with a principal maximum at 470 nm and secondary maxima at 550 and 660 nm. The decay kinetics were unchanged ($\tau = 35 \text{ ns}$) over the entire wavelength range explored (300–700 nm) showing the presence of a unique transient species (Fig. 7). No residual absorption was observed, that is, the recovery of the open form ground state was complete within few hundred nanoseconds. This confirmed what was found upon continuous irradiation, namely, the closure reaction does not occur for this compound.

The BTDT exhibited a more complicated behaviour upon laser excitation. In the spectral evolution the triplet of the open form, the coloured closed form and the fluorescence emission of the latter could be detected. The first spectra recorded after the laser shot showed a transient absorption with maxima at 490 and 590 nm ($\tau = 60 \text{ ns}$) and an emission signal around 650 nm which decayed in few nanoseconds, $\tau < 10 \text{ ns}$, Fig. 8. The emis-

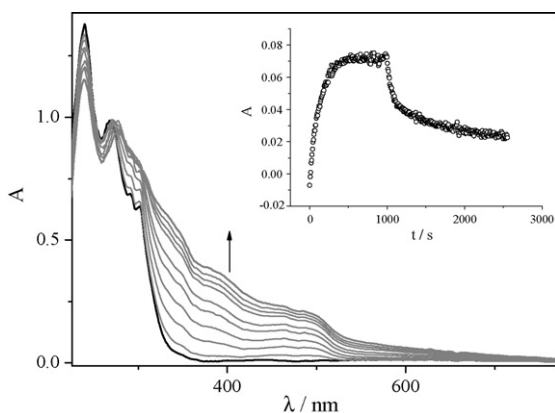


Fig. 6. Spectral evolution upon UV irradiation of $8 \times 10^{-5} \text{ mol dm}^{-3}$ BTDO in 3MP at 200 K. *Inset*: Colour-forming and photobleaching kinetics at 465 nm.

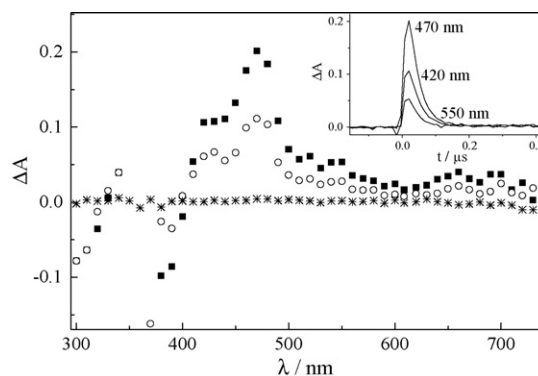


Fig. 7. Time-resolved spectra of TDT in toluene ($A_{355} = 0.3$): (■) 0.02 μs ; (○) 0.044 μs ; (*) 1.6 μs after the laser pulse ($\lambda_{\text{exc}} = 355 \text{ nm}$). *Inset*: Kinetics at different wavelengths.

sion signal well corresponded to the fluorescence of the coloured form revealed by stationary techniques. It came from excitation of the closed form, which accumulated in the flashed solution. At longer delay, absorption signals ($\lambda_{\text{max}} = 410, 520 \text{ nm}$) were observed, that fairly corresponded to the spectrum of the coloured form obtained from the stationary experiments. The rise kinetics of the coloured form at 540 nm matched the decay kinetics of the transient at 490 nm, as shown in the inset of Fig. 8, thus indicating that the short-lived transient is the precursor of the closed form. It can be supposed to be a triplet state, even though no oxygen effect could be detected because of the very short lifetime. This assignment was also supported by sensitized reaction measurements carried out using benzophenone as a triplet energy donor ($E_T = 288 \text{ kJ mol}^{-1}$ [13]) and quenching measurements of benzophenone phosphorescence by BTDT. The phosphorescence quenching occurred at a diffusion controlled rate ($k_q = 2.8 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), as expected for exothermic triplet–triplet energy transfer. The sensitized reaction yield ($\Phi_{\text{sens}} = 0.07$) was very close to that of the directly excited reaction ($\Phi_{\text{O} \rightarrow \text{C}} = 0.09$), therefore the process can be considered to proceed via the triplet state only. This can also be inferred from the absence of photoproduct formation within the laser pulse.

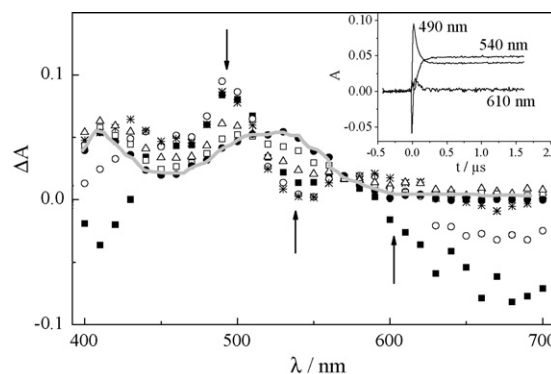


Fig. 8. Time-resolved spectra of BTDT in toluene ($A_{355} = 0.3$): (■) 0.008 μs ; (○) 0.02 μs ; (*) 0.032 μs ; (△) 0.08 μs ; (□) 0.13 μs ; (●) 1.62 μs after the laser pulse ($\lambda_{\text{exc}} = 355 \text{ nm}$, spectrum of the closed form). *Inset*: Kinetics at different wavelengths.

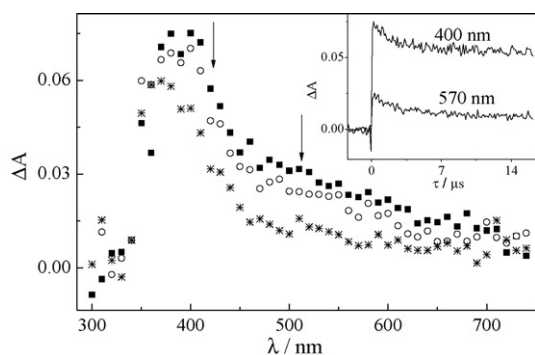


Fig. 9. Time-resolved spectra of TDO in toluene ($A_{355} = 0.3$): (■) 0.2 μ s; (○) 1.2 μ s; (*) 16.2 μ s after the laser pulse ($\lambda_{\text{exc}} = 355$ nm). *Inset*: Kinetics at 400 and 570 nm.

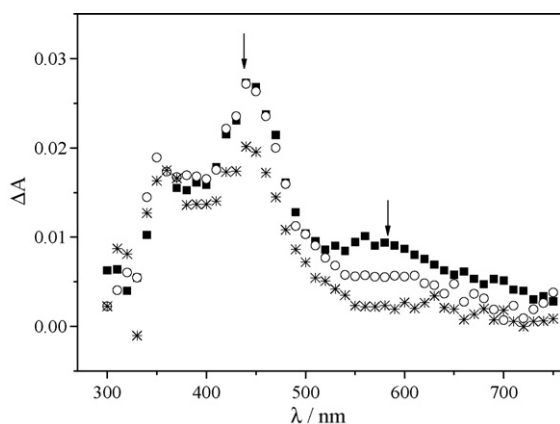


Fig. 10. Time-resolved spectra of BTDO in toluene ($A_{355} = 0.38$): (■) 2.8 μ s; (○) 7.6 μ s; (*) 80.8 μ s after the laser pulse ($\lambda_{\text{exc}} = 355$ nm). *Inset*: Kinetics at 440 and 560 nm.

The spectrum obtained from TDO upon laser flash photolysis showed a transient ($\tau = 2.5$ μ s) with a maximum at 400 nm which extended over all the visible region up to about 650 nm. Diffusion controlled quenching by oxygen could be detected ($k_{\text{O}_2} = 2.3 \times 10^9$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$), suggesting that the transient has a triplet nature. Spectra and kinetics of TDO, observed upon flashing, are shown in Fig. 9. The residual spectrum roughly corresponds to that of the coloured form observed under stationary irradiation, which was here generated within the laser pulse. There were no kinetic evidences that the transient was a precursor of the closed form.

The results obtained upon laser flash photolysis of BTDO are shown in Fig. 10. Two transients were observed, a short-lived one ($\tau = 7.3$ μ s), which absorbs in the 550–600 nm region, with triplet characteristics (quenching by oxygen, $k_{\text{O}_2} = 1.9 \times$

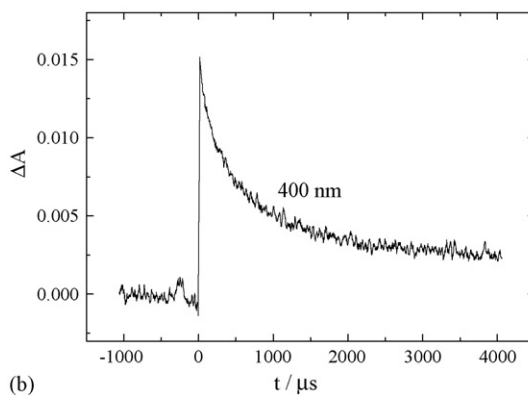
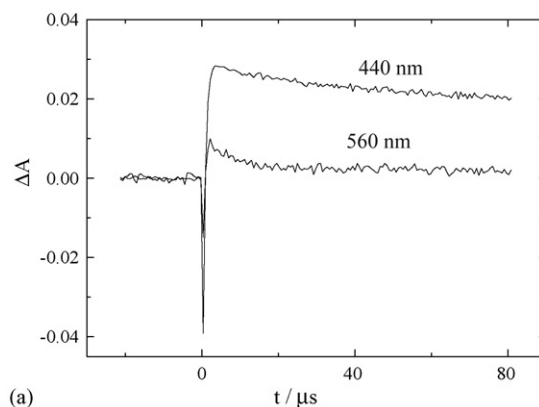


Fig. 11. Decay kinetics of BTDO transients produced by laser flash photolysis in toluene on short (a) and longer (b) time scale.

10^9 $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) and a longer lived one ($\tau = 660$ μ s) at shorter wavelengths ($\lambda_{\text{max}} = 440$ nm), which was not quenched by oxygen. The decay kinetics of the two transients are shown in Fig. 11 on appropriate time scales. There are no proofs that either of these transients be the precursor of the coloured form which is probably generated from the singlet state within the laser pulse.

The results obtained from the time-resolved spectrophotometric study of the four molecules are resumed in Table 2.

4. Discussion

From the absorption spectra, it can be seen that the C=S group in the ring bearing the ethenic double bond generates a localized transition approximately with the same spectral characteristics for the two thione derivatives ($\lambda_{\text{max}} \sim 370$ –380 nm). In turn, the absorption spectra of the two molecules with the C=O group are very similar one to each other, with a broad absorption band in the UV region extending towards lower energies up to 330 nm.

Table 2

Spectral and dynamic characteristics (λ_{max} , τ and k_{O_2}) of the transients obtained by laser flash photolysis of the compounds investigated in toluene

Compound	λ_{max} (nm)	τ (ns)	k_{O_2} ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	Photoproduct
TDT	420, 470, 550, 660	35	Undetectable	Not observed
BTDT	490, 580	60	Undetectable	Closed form
TDO	400, 510 (sh)	2500	2.3×10^9	Closed form
BTDO	400	6.6×10^5	Not affected	Closed form
	550	7300	1.9×10^9	

Table 3

Enthalpy differences between the closed and open forms (ΔH_f) and the parallel and anti-parallel forms ($\Delta H_{a-p/p}$) obtained by semiempirical calculations, and their percentage obtained by the Boltzmann equation and ^1H NMR measurements (experimental value in parenthesis)

Compound	ΔH_f (kJ mol $^{-1}$)	$\Delta H_{a-p/p}$ (kJ mol $^{-1}$)	a-p/p ratio
TDT	100	1.30	37/63
BTDT	58.5	−3.41	80/20 (62/38)
TDO	96	1.21	38/62
BTDO	46	−3.89	83/17 (64/36)

Inspection of data in Table 2 points to triplet states of different character originated from thiones and ones. The latter have markedly longer lifetimes, therefore they can be assigned to π , π^* triplet excitation, whereas the very short-lived thione triplets are of n , π^* character. Even if absolute triplet yields were not determined, it is noteworthy that high $T_1 \rightarrow T_n$ absorbances, found for thiones, indicate high triplet population. In agreement with El-Sayed rules [14], the n , π^* thione triplets are efficiently populated through the lowest π , π^* singlet states.

The condensed benzo-ring in thiones has the role of increasing the colourability, since steric hindrance enhances the relative amount of anti-parallel conformation with respect to parallel.

To obtain an approximate evaluation of the anti-parallel (ρ_{a-p}) and parallel (ρ_p) populations, they were determined by semiempirical calculations from the enthalpy difference between the parallel and anti-parallel conformations, $\Delta H_{a-p/p}$, and the Boltzmann distribution law, $\rho_{ap}/\rho_p = e^{-\Delta H_{a-p/p}/RT}$. The results are reported in Table 3, along with the calculated enthalpy differences between the closed and open form (ΔH_f). Their values indicate a marked stabilization of the closed forms in the benzoannellated compounds.

As regard the calculated ρ_{a-p}/ρ_p ratios, they can be compared with those obtained in solution by ^1H NMR experiments. Since at the equilibrium (in CDCl_3 at 298 K) the interconversion process between the two conformations is slow with respect to the chemical shift time scale, two separate sets of signals for the parallel and anti-parallel conformers are observed and can be quantified by standard integration (see Fig. 12A). According to literature [15], the most abundant isomer is assigned to the anti-parallel conformer on the basis of the chemical shift corresponding to the methyl resonance. In fact the shielding effect exerted by the phenyl ring belonging to the opposite benzothio-phenone moiety should shift the resonance of the methyl to a lower frequency in the a-p conformer. ^1H NOESY experiments (see Fig. 12B) unambiguously confirm this assignment. The strong NOE peak observed between the methyl group in position 2 of the thiophene ring and a single aromatic resonance is expected in the a-p conformer. The experimentally determined a-p/p ratios for BTDT and BTDO were in line with the ratios predicted using the Boltzmann distribution law. For both compounds, especially for BTDT, the a-p percentage largely exceeded the forward reaction yield. Since the rate of interconversion was estimated to be slower than the excited state lifetime [16], this means that some competitive relaxation processes should occur at the reactive excited level.

The low colourability and incomplete reversibility of BTDO (and possibly also of TDO) could be due to the formation of byproducts during UV irradiation. Previous reports [17,18] on the photoreactivity of compounds of this class, showed that the loss of carbon monoxide is highly probable. In the reaction mechanism, an intermediate biradical has been hypothesized, which undergoes cyclization, ring fragmentation, and a further cyclization to give thieno[3,4-c]dithiine. Similar side reactions could be involved in our compounds.

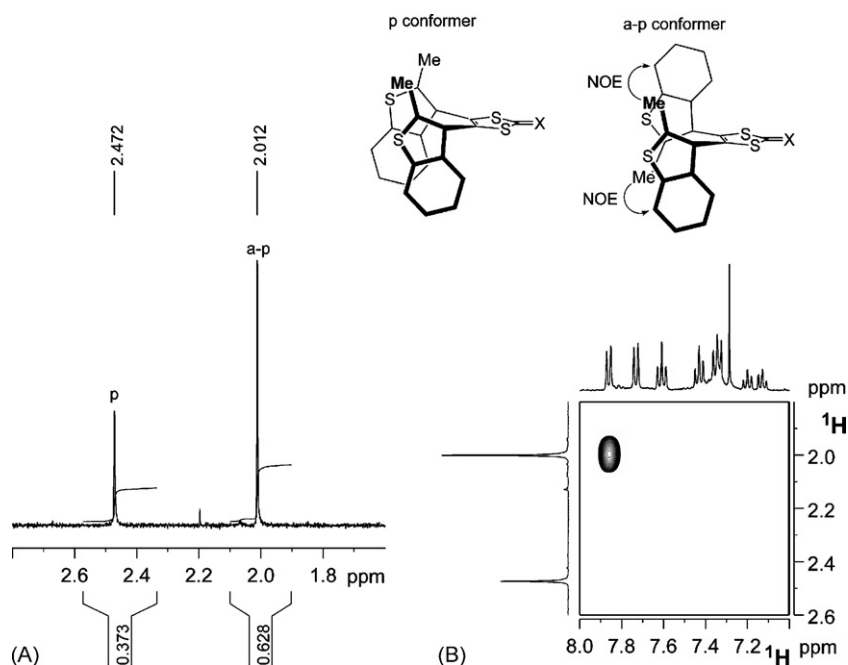


Fig. 12. (A) Section of the ^1H NMR spectrum of BTDT showing the methyl region (CDCl_3 , 298 K, 400 MHz). (B) Section of the ^1H NOESY spectrum of BTDO (CDCl_3 , 298 K, 400 MHz).

5. Summary

The thermally irreversible diarylethenes investigated, which, in principle, could have been interesting from the point of view of potential applications, showed poor photochromic properties, with the exception of BTDT, for which a good photochromic response was observed. Due to its bistability, the photocolouration reaction could be followed by HPLC and the two isomers present at the photostationary state be isolated. The TDT was unreactive, whereas for the other two compounds the occurrence of side processes affected photocolourability and reversibility. Very unusual for photochromic systems, intersystem crossing to the triplet state contributed efficiently, or most likely exclusively, to the photocolouration of BTDT, whereas no evidence for triplet contribution to the photocolouration of TDO and BTDO was found. NMR measurements allowed the percentage of inactive parallel and reactive anti-parallel isomers to be determined and compared with calculated values for the benzoannellated compounds. The high percentage of a-p compounds, in front of the low reaction yield, indicates that there are other excited state relaxation paths competing with photocolouration.

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