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Photochromic properties of thienylpyrrole azo dyes in solution

Paulo J. Coelho,[a,*] Luis M. Carvalho,[a] A. Maurício C. Fonseca[b] and M. Manuela M. Raposo[b]

[a]Centro de Química-Vila Real, Universidade de Trás-os-Montes e Alto Douro, 5001-801 Vila Real, Portugal
[b]Centro de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

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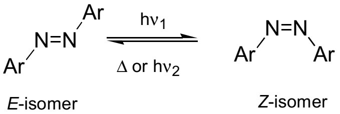
Abstract—The photochromic behaviour of thienylpyrrole azo dyes in THF solutions was studied for the first time. The photochromic properties are strongly dependent on the substitution pattern on the dyes. Nitro-substituted thienylpyrrole azo dyes are particularly interesting since they exhibit very fast colouration/decolouration processes. The activation energies of these compounds are among the lowest values reported for heterocyclic azo dyes. These compounds show aggregation phenomena in freshly prepared solutions of THF, which lead to variable photochromic behaviours. Only after 1–5 h the solutions reach equilibrium and then reproducible photochromic behaviour can be observed.

Azo dyes with heterocyclic diazo components have been extensively investigated to produce bright and strong colour shades ranging from red to greenish blue on synthetic fabrics. These results led to the development of commercial products, which replaced the conventional azobenzene disperse dyes.[1a] A renewed interest in aryl(heteroaryl)-azo dyes has been sparked by efforts to find organic second-order non-linear optical (NLO) materials suitable for applications such as harmonic generation and optical switching.[1a–d]

Usually, azo compounds are chemically stable molecules that display intense absorption bands whose position can be tailored, by appropriate ring substitution, to fall anywhere from UV to near-IR spectrum.[2] One of the most interesting properties of these chromophores is the readily induced and reversible isomerization about the azo bond between the *E*- and *Z*-isomers, which can be photo or thermally interconverted (Scheme 1). The reversible structural change is a space-demanding process and brings important reversible modifications not only on physico-chemical properties of the molecules but also on a variety of compatible matrices, such as solutions, liquid crystals, sol–gel systems, monolayer films or polymers, where they can be incorporated.[3] This opens a wide field of potential applications for systems incorporating azo-chromophores. In fact these systems can be used as photoswitches to control a variety of chemical and physical (e.g., mechanical, electronic and optical) properties. The principal requirements for photonic devices include, thermal stability of both isomers, fatigue resistant character, high sensitivity, rapid response and reactivity when incorporated in solid matrices.



Scheme 1.

The photoisomerization of azoaromatic dyes is an extensively studied phenomenon. Generally, the two isomers exhibit different absorption spectra and are therefore distinguishable. The thermodynamically more stable *E*-isomer is normally highly coloured due to the allowed extension of the π-electronic system while the *Z*-isomer is an uncoloured or weakly coloured species due to an out-of-plane configuration of the aromatic groups attached to the azo group.[4] Upon continuous irradiation with visible light, a coloured solution of an azo dye (normally constituted mainly by the *E*-isomer), exhibits a fast decrease of the absorbance measured at the longer wavelengths due to the conversion to the

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[*] Corresponding author. Tel.: +351 259 350284; fax: +351 259 350480; e-mail: pcoelho@utad.pt

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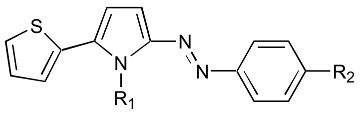
Z-isomer. A photostationary equilibrium between the two isomers is attained and when the irradiation source is removed, the *Z*-isomer thermally (or photochemically) converts back to the highly coloured *E*-isomer following a monoexponential kinetic. This isomerization is completely reversible, free from side reactions and one of the cleanest photoreactions known. Both the spectra of the photoactive molecules and the reaction kinetics are strongly dependent on the nature of the matrix in which the photochromic substances are incorporated.[3a]

The mechanism of the *E*–*Z* interconversion remains unclear and it seems that there may not be one general mechanism, but a competition between rotational (about the –N=N– double bond axis) and inversional (through a transition state where one of the nitrogen atoms is sp-hybridized) mechanisms, depending on the particular molecular structure and the local environment.[5]

Very few reports concerning the photochromic properties of heteroaromatic azo dyes can be found in the literature.[6] In this paper we report the photochromic properties of new thienylpyrrole azo dyes described by some of us recently.[7] As far as we know, this is the first time that the evaluation of the photochromic properties of thienylpyrrole azo dyes is reported.



	R_1	R_2
1a	*n*-propyl	4-NO_2
1b	phenyl	4-NO_2
1c	1-naphthyl	4-NO_2
1d	4-methoxyphenyl	4-NO_2
1e	2,4-dimethoxyphenyl	4-NO_2
1f	3,4,5-trimethoxyphenyl	4-NO_2
1g	4-fluorophenyl	4-NO_2
1h	4-methoxyphenyl	4-CO_2Me
1i	4-methoxyphenyl	4-CN

Thienylpyrrole azo dyes **1a**–**i** were obtained through the coupling reaction of the corresponding aryldiazonium salts, with 1-aryl- and 1-alkyl-2-(2′-thienyl)pyrroles.[8,9]

The photochromic behaviour of these compounds was studied in dry THF solutions by measuring the absorbance of the solution at the maximum wavelength of absorption while irradiating with visible light from a 150 W Ozone free Xenon lamp, equipped with a water filter and a long-pass filter, Schott GG 420, at 20 °C.[10]

The thienylpyrrole azo compounds **1a**–**i** are highly coloured dyes with molar absorptivities in THF ranging from 20,000 to 34,500 $M^{-1}\,cm^{-1}$. The nitrosubstituted dyes **1a**–**g** displayed an intense absorption maxima around 490–508 nm while the ester- and cyano-substituted dyes **1h**–**i** exhibited a maximum wavelength of absorption at lower wavelengths, 464–477 nm. These results are in accordance with recent theoretical studies involving 18 diazo dyes with five-membered rings. Åstrand et al. showed that diazo compounds with one or two five-membered rings should have $\pi \rightarrow \pi^*$ excitation energies considerable lower than azobenzene.[1d]

Irradiation of 2.0×10^{-5} M solutions of these compounds with visible light (>420 nm) led to a very fast decrease in the maximum absorbance at longer wavelengths, indicating the formation of the *Z*-isomer. When the irradiation ceased the system returned to its initial highly coloured state with different rates depending on the substituents present in the molecule. The change in the visible spectra of dye **1c** is depicted in Figure 1. The irradiation of **1c** with visible light led to a decrease of the absorption band at 497 nm, attributed to the *E*-isomer, and the appearance of a band at 380 nm. In less than 30 s a photostationary equilibrium was attained. When the irradiation was stopped the inverse situation was observed, the band at 380 nm decreased and the band at 497 nm increased. The kinetics of the colouration and decolouration process of dye **1c** (2.0×10^{-5} M solution) is shown in Figure 2.

The photochromic properties of readily prepared solutions of these compounds were found to be different from those prepared by dilution. The time between the preparation of the solution and the measurements of the photochromic properties was also found to be important. The heteroaromatic dyes **1a**–**i** were not very soluble in THF and their dissolution was considerable slow. When a small crystal was added to THF, the absorbance of the solution increased with time only reaching equilibrium after some minutes (Fig. 3). Moreover the photochromic properties of the solution varied along the time. Few seconds after the dissolution of the crystals the solution was weakly photochromic with a high rate constant for the *Z*–*E* back isomerization. It was observed that progressively the amplitude of the absorbance variation increased while the colouration rate decreases. This behaviour was always observed for all compounds although the results were very difficult

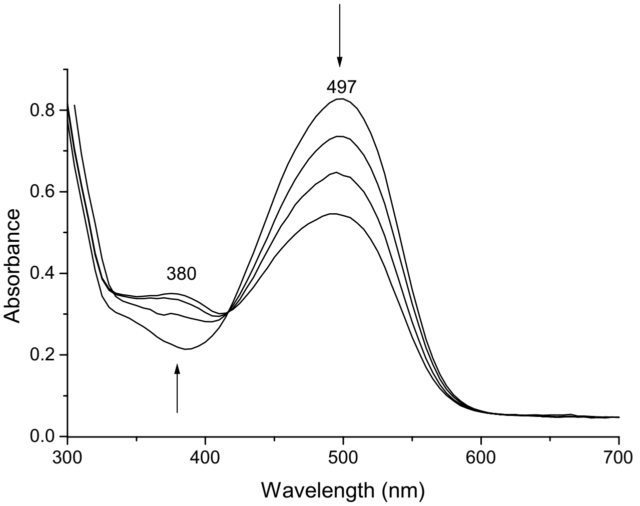


Figure 1. Absorption spectra of dye **1c** under irradiation and in the dark.

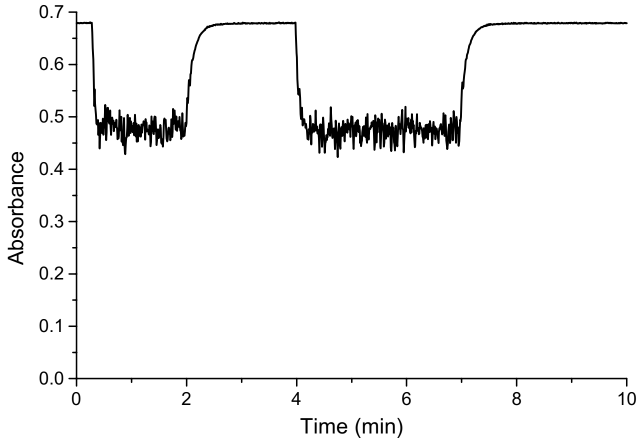


Figure 2. Irradiation/dark cycles for dye **1c**.

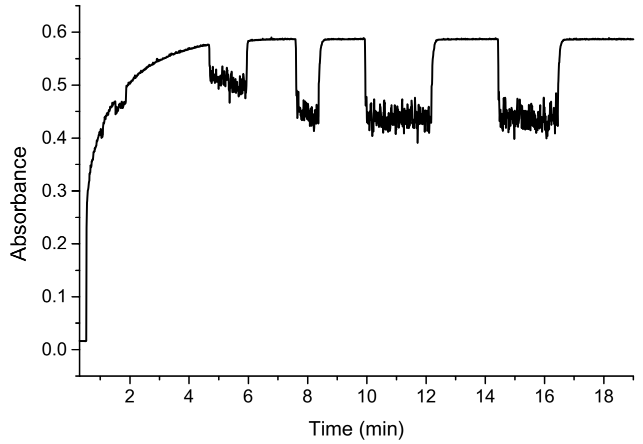


Figure 3. Irradiation/dark cycles for the dissolution of dye **1d**.

to precisely reproduce. Two examples are depicted in Figures 3 and 4. After 1–5 h the solutions reached an equilibrium state and then reproducible photochromic properties were measured.

This behaviour can be explained considering aggregation phenomena that are frequently reported to occur with azo dyes, especially in solvents were they are weakly soluble.[11] For these heteroaromatic dyes the dissolution of the crystals leads to aggregates that progressively liberate the free molecules of azo dyes. These

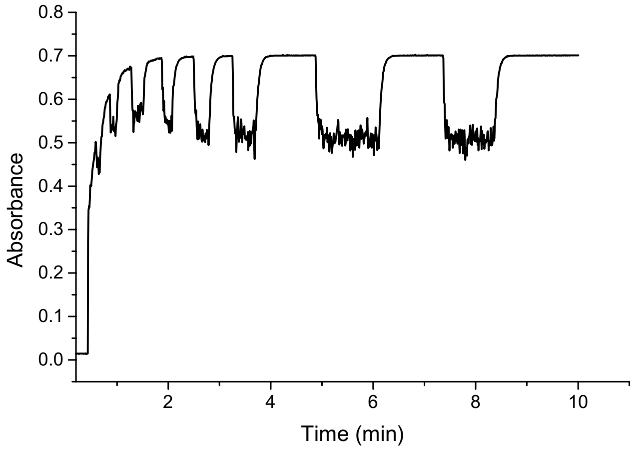


Figure 4. Irradiation/dark cycles for the dissolution of dye **1a**.

aggregates are weakly photochromic, probably due to steric constraints. The dissociation of these aggregates is slow and dependent, among other factors, on the solvent nature, concentration, size of the crystals and presence of water that can explain the irreproducibility of the process. After the equilibration of the solution it was possible to obtain reproducible results. The compounds showed good fatigue resistance as the same initial absorbance was obtained after successive (irradiation/dark) cycles. The results are presented in Table 1.

All compounds exhibit photochromic properties in solution at 20 °C. The absorbance variation obtained upon irradiation varied from 0.10 to 0.37, which corresponds to a loss of 15–56% of the initial absorbance. The kinetic of the colouration step (in the dark) was always monoexponential, which is consistent with a two species system. The rate kinetics of the colouration step (in the dark) was very dependent on the substituents present in the benzene ring: for nitro-substituted dyes **1a**–**g**, very fast kinetics were observed with rate constants from 0.13 to 0.71 s^{-1} that correspond to half-lifes of 1–5 s (Fig. 2). On the other hand azo dyes **1h**–**i** with ester and cyano substituents showed considerably slower colouration rates. For these two dyes rate constants of 0.0011 and 0.011 s^{-1}, respectively, were obtained corresponding to half-life of 11 and 1.0 min (Fig. 5).

As expected the higher absorbance variations were observed with the slower systems, **1h**–**i**, while the lower

Table 1. Spectrokinetic properties under continuous irradiation: maxima wavelength of absorption (λ_{max}), colourability (A_{eq}), absorbance variation (ΔAbs) and thermal bleaching rate (k_Δ) of azo dyes **1a**–**i**

Dye	R_1	R_2	λ_{max} (nm)	A_{eq}	ΔAbs	ΔAbs (%)	k_Δ (s^{-1})
1a	*n*-Propyl	4-NO_2	490	0.58	0.13	22	0.32
1b	Phenyl	4-NO_2	498	0.59	0.16	27	0.21
1c	1-Naphthyl	4-NO_2	497	0.66	0.22	34	0.17
1d	4-Methoxyphenyl	4-NO_2	500	0.42	0.11	26	0.33
1e	2,4-Dimethoxyphenyl	4-NO_2	508	0.68	0.10	15	0.71
1f	3,4,5-Trimethoxyphenyl	4-NO_2	501	0.69	0.14	20	0.41
1g	4-Fluorophenyl	4-NO_2	495	0.49	0.18	37	0.13
1h	4-Methoxyphenyl	4-CO_2Me	464	0.40	0.19	48	0.0011
1i	4-Methoxyphenyl	4-CN	477	0.66	0.37	56	0.011

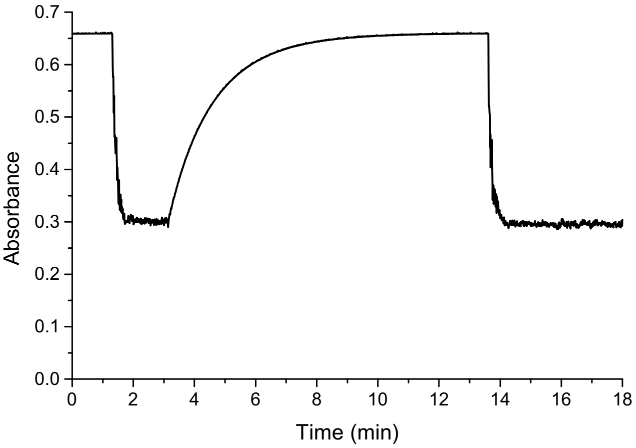


Figure 5. Irradiation/dark cycle for **1i** dye.

absorbance variations were observed for the faster systems, **1e**–**f**, as under continuous visible irradiation conditions the absorbance at the photostationary state is inversely related to the kinetic rate of the colouration process. The kinetics of the colouration step is also dependent on the substituents on the pyrrole ring. The substitution of an alkyl chain (**1a**) by a phenyl or 1-naphthyl ring led to a net decrease on the kinetic of the *Z*–*E* isomerization. On the other hand the introduction of electron-releasing substituents (CH_3O) on the phenyl ring increased the kinetics of this reaction while the introduction of an electron-withdrawing substituent (F) led to a net decrease of the rate constant. The photochromic properties of these heteroaromatic azo dyes, in particular the kinetic of the back isomerization can thus be modulated by the introduction of substituents either on the benzene ring or on the pyrrole ring.

The activation energy calculated for compound **1c** was 56 kJ/mol, which is considerable lower[1d,3a] than the value for azobenzene (94 kJ/mol)[6b] or other heteroaromatic azo dyes like 2-(phenylazo)imidazoles (79 kJ/mol)[6a] or phenylazopyridines (90 kJ/mol).[6b] To our knowledge, these are among the lowest values of the activation energy reported for heterocyclic azo dyes. The photochromic properties described for thienylpyrroles **1a**–**g** make them good candidates for optical data storage devices where it is desirable to use excitation energies of lasers with longer wavelengths and to obtain fast photochromic systems.

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