Dyes and Pigments 82 (2009) 130–133

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Novel photochromic 2,2′-bithiophene azo dyes

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ARTICLE INFO

Article history:
Received 30 September 2008
Received in revised form
3 December 2008
Accepted 8 December 2008
Available online 16 December 2008

Keywords:
Photochromism
Heterocyclic azo dyes
Bithiophene
Azo dyes
UV/vis spectroscopy

ABSTRACT

The photochromic properties and colour constancy of two series of 2,2′-bithiophene azo dyes in THF solution were strongly dependent on the substitution pattern of the dyes. Under visible irradiation (>420 nm) while some dyes exhibited a significant change in colour intensity others exhibited an almost stable absorption. The photokinetic parameters of the systems are also described.

1. Introduction

Aromatic azo compounds constitute a dominant class of synthetic compounds that have been long and widely employed for colouring and printing. The presence of the stable chromophoric azo group (–N=N–) conjugated with aromatic substituents at the nitrogen atoms allows the acquirement of molecules that displays intense and highly resistant colours that can be tuned over all over the visible spectrum through appropriate ring substitution [1].

The photochemical *E*–*Z* isomerization of aromatic azo dyes, in solution or incorporated in polymeric matrices, is a well-established phenomenon that has been the subject of intense research. Typically, under light irradiation (λ within the broad azo absorption band) the thermally stable *E*-isomer is partially converted to the meta-stable *Z*-isomer and a photostationary equilibrium between the two compounds is attained [1]. Usually when the irradiation is ceased the reaction is thermally reversible, although it can be also photoinduced with light of an appropriated wavelength (Scheme 1).

Despite numerous studies performed the mechanism for the interconversion is still unclear and two major competitive mechanisms for the isomerization are recognized: the in-plane inversion mechanism involving the sp hybridization of one of the azo nitrogens in the transition state and a rotational mechanism involving a rotational activated complex [2]. The predominance of one mechanism over the other is greatly dependent upon the particular substitution pattern of the molecule, the nature of the substituents and the environment [3].

The azoaromatic chromophores enable unique fully reversible and clean photoreactions and constitute a valuable photochemical model system. The spatial arrangement of the *E*-isomer molecules makes possible the extension of the electronic π-conjugation while this is not possible for the *Z*-isomer which presents the two aromatic rings out of the plane. Consequently the thermally stable *E*-isomer can exhibit a much more intense optical absorption than the *Z*-isomer. In other words, azo compounds can exhibit photochromic properties as a reversible change in the absorbance spectrum can be triggered by luminous irradiation. As this can cause an observable loss of colour, this behaviour may be undesirable if the azo compounds are intended to be used with colour constancy (e.g. for dyeing or printing).

The azo isomerization reaction requires a large geometrical change in molecular configuration and is therefore sensitive to steric effects. Moreover, these molecules show a great tendency to aggregate, especially in solvents where they are weakly soluble, leading to self-assemblies in which the photo-isomerization is inhibited [4]. In recent years great attention has been directed to the reversible geometric changes that result from the photochemical isomerization and the possibility to induce macroscopic motions through the interaction of the interconverting forms and the environment where they are incorporated. As the reversible

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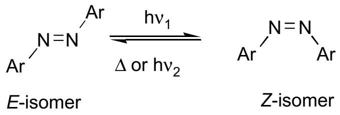
doi:10.1016/j.dyepig.2008.12.005



Scheme 1.

structural changes occur at a single-molecule level the phenomenon is potentially interesting to the modern nanotechnology for fully photon-controlled applications such as photo-switch technologies offering the possibility to control, through photochromic reactions, the physico-chemical properties of materials (e.g. fluorescence, electrical conductivity, magnetism, permeability, reactivity…) [5].

Most of the azo chromophores belong to the azobenzene class which includes compounds with two phenyl rings linked through an azo-bridge. More recently the synthesis and the characterization of heterocyclic azo dyes have been extensively reported [6,7]. Besides their classic applications in synthetic dyes and pigments, heteroaryl diazo chromophores containing five-membered heterocycles (thiophene, pyrrole and thiazole) can also behave as organic second-order nonlinear optical (NLO) materials suitable for applications such as second harmonic generation [6].

Other interesting applications, recently proposed, include memory and recording devices, molecular switches, thermochromic, photovoltaic and fluorescent devices, supramolecular systems, holographic data storage materials, acid–base and metal sensors and active ligands in Pd-catalyzed cross-coupling reactions [6f,7].

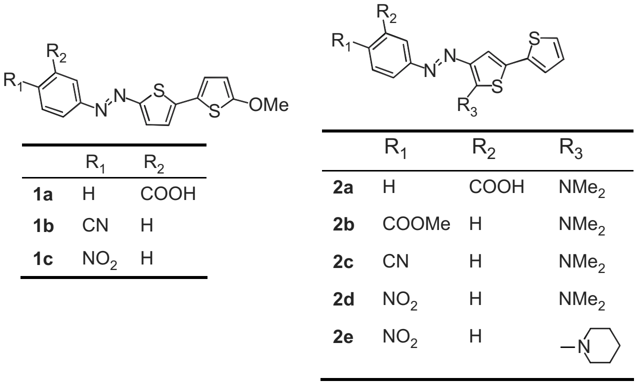
We have recently reported the synthesis and characterization of thienylpyrrole azo dyes as new NLO-chromophores [6e]. These new heterocyclic compounds also exhibit good photochromic properties [7c]. These previous studies motivated us to explore the potential of new 5′-alkoxy-5-phenyldiazenyl-2,2′-bithiophenes [8] and 5-*N*,*N*-dialkylamino-4-phenyldiazenyl-2,2′-bithiophenes [9] as potential photochromic molecules. Therefore, we describe in this paper the photochromic properties of these two series of bithiophene azo dyes.

2. Results and discussion

The new 2,2′-bithiophene azo dyes studied can be divided in two groups according to the linkage between the two aromatic rings: 5′-methoxy-5-phenyldiazenyl-2,2′-bithiophene dyes **1a**–**c** present the bithiophene linked to the azo group through the 5 position while for 5-amino-4-phenyldiazenyl-2,2′-bithiophene **2a**–**e** the azo group is bonded to the bithiophene nucleus at the 4 position adjacent to an amino substituent (Scheme 2).

The photochromic behaviour of these molecules was studied in 2.0×10^{-5} M 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.

In THF 2,2′-bithiophene azo compounds **1**–**2** afforded deeply coloured solutions (yellow to purple) with molar absorptivities ranging from 11,000 to 32,500 $M^{-1}\,cm^{-1}$. The nitro-substituted dyes displayed an intense absorption maxima between 512 and 545 nm while the acid and ester substituted dyes exhibited a maximum wavelength of absorption at lower wavelengths, 472–498 nm (Table 1). The λ_{max} of 2,2′-bithiophene azo compounds **1**–**2** shows a positive solvatochromic effect. For compound **2b** the λ_{max} changed from 477 nm in hexane to 510 nm in DMSO (Fig. 1).



	R_1	R_2
1a	H	COOH
1b	CN	H
1c	NO_2	H

	R_1	R_2	R_3
2a	H	COOH	NMe_2
2b	COOMe	H	NMe_2
2c	CN	H	NMe_2
2d	NO_2	H	NMe_2
2e	NO_2	H	—N

Scheme 2.

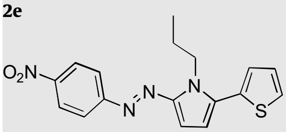
Under visible irradiation (>420 nm) the two sets of compounds showed very different behaviour (Table 1). Irradiation of 2.0×10^{-5} M THF solutions of azo dyes **1a**–**c** led to a very fast and pronounced decrease of the maximum absorbance at longer wavelengths and, at the same time, an increase in the band located at 400 nm, indicating the transformation of the *E*-isomer into the *Z*-isomer [10]. 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 **1b** is depicted in Fig. 2. When the irradiation was stopped the inverse situation was observed, the band at 400 nm decreased and the band at 495 nm increased. The absorbance variation observed under visible irradiation of dyes **1a**–**c** varies from 0.23 to 0.28 absorbance units corresponding to a loss of 35–50% of the initial absorbance. The procedure was consequentially repeated and the behaviour was fully reproducible indicating that under these limited experimental conditions no degradation was observed. The kinetics of the colouration and decolouration process of dye **1c** is shown in Fig. 3.

For compounds **1a**–**c**, the decrease in the absorbance upon visible irradiation was very fast (*E*–*Z* transformation promoted by visible light). The *E*–*Z* isomerization kinetic was mono-exponential with a 0.17 s^{-1} constant rate, which indicates that, under the experimental conditions, in less than 30 s a photostationary equilibrium was attained. The kinetics of the thermal *Z*–*E* back reaction (colouration, in the dark, at room temperature) was slower but also mono-exponential which is consistent with a two species system. The colouration rates were effectively independent on the nature of the substituents present on the benzene ring. For these 3 compounds the half-time life of the *Z*-isomer varied between 18 and 69 s.

As expected the higher absorbance variations were observed with the slower systems. For a system constituted by two *E*–*Z* isomers, where the thermally stable one is highly coloured, under continuous visible irradiation conditions, the decrease in the absorbance at the maximum wavelength of absorption of the *E* isomer is inversely related to the kinetic rate of the colouration process ($Z \rightarrow E$) [11]. When compared to similar azo thienylpyrrole dyes this set of compounds showed slower thermal colouration rate constants (Table 1) [7c]. When the system was irradiated with UV/vis light (without the Schott GG 420 filter) the absorbance decrease was, as expected, lower since the UV light promotes the $Z \rightarrow E$ conversion (Fig. 4).

The activation energy of the thermal colouration step for compounds **1a** and **1b**, determined from the kinetic rates observed at 20, 25, 30, 35, 40 °C, were found to be 81 and 77 kJ/mol respectively, which are similar to the value for azobenzene (94 kJ/mol) or other heteroaromatic azo dyes like 2-(phenylazo)imidazoles (79 kJ/mol) or phenylazopyridines (90 kJ/mol) although higher than azo thienylpyrrole dyes (56 kJ/mol) [7c].

Table 1
Spectrokinetic properties under continuous visible irradiation: maximum wavelength of absorption (λ_{max}), maximum absorbance (A_{max}), absorbance variation (ΔAbs), thermal bleaching rate (k_Δ) and half-time life ($t_{1/2}$) of azo dyes **1a–c**, **2a–e** and a thienylpyrrole azo dye [7c].

Dye	λ_{max} (nm)	A_{max}	ΔAbs	k_Δ (s^{-1})	$t_{1/2}$ (s)
1a	475	0.55	0.28 (50%)	0.010	69
1b	495	0.52	0.23 (44%)	0.021	33
1c	512	0.65	0.23 (35%)	0.039	18
2a	472	0.36	0.072 (20%)	0.032	22
2b	498	0.48	0.014 (3%)	–	–
2c	501	0.22	0.003 (<1%)	–	–
2d	534	0.49	– (<1%)	–	–
2e	545	0.37	– (<1%)	–	–
	490	0.58	0.13 (22%)	0.32	2.2

Bithiophene azo dyes **2a–e** exhibited very weak photochromic properties at room temperature, in THF solutions (Table 1). Under irradiation with visible light, a 2.0×10^{-5} M solution of compound **2a** showed no absorbance decrease, immediately after the solution preparation and a 20% decrease after one day; compound **2b** showed a modest photochromic activity (3%). For the other compounds (**2c–e**) the absorbance decrease was smaller than 1%.

The photochromic behaviour of azo compounds **1–2** was solvent dependent. While in chloroform, ethyl acetate, acetone, DMSO or methanol the photochromic response was essentially similar to that observed in THF, different results were observed in less polar solvents like toluene or *n*-hexane. In this last solvent all compounds showed reversible photochromic properties. However, while the irradiation of azo dyes **1a–c** solutions led to absorbance decreases of 47–54%, for compounds **2a–e** only small changes in the absorbance (from 4 to 20%) were registered.

As compounds **2a–e** exhibit modest fluorescence, precluding the influence of a competing relaxation process, the weak photochromism of these dyes could be due to the formation of aggregates, usual in azobenzene dyes, which might inhibit the photochemical transformation. Since after the visible irradiation ceased a mono-exponential absorbance increase was observed we concluded that only two species were present in the solution. Moreover, the positive solvatochromism exhibited by these compounds was expected and no λ_{max} change was observed when changing the dye concentration. Finally for 2×10^{-5} to 10^{-4} M concentrations no deviation from Lambert–Beer's law was observed. These results indicate that the weak photochromic behaviour of dyes **2a–e** should not be assigned to the formation of aggregates. The difference in the photochromic behaviour between azo dyes **1a–c** and **2a–e** may be related to the steric hindrance of the adjacent substituted amino group, present in compounds **2a–e**, leading to the restrain of the floppiness of the molecule [1b,12].

3. Experimental

The synthesis of azo dyes **1a–c** and **2a–e** was recently reported [8,9]. For measurements of λ_{max}, A_{eq} and k_Δ under continuous vis irradiation, 2.0×10^{-5} M THF solutions were used. Irradiation experiments were made using a CARY 50 Varian spectrophotometer coupled to a 150 W ozone free xenon lamp (6255 Oriel Instruments). The light from the UV–vis lamp was filtered using a water filter (61945 Oriel Instruments) and a long-pass filter (Schott GG 420) at 20 °C and carried to the spectrophotometer holder, perpendicular to the monitoring beam using a fibre-optic system (77654 Oriel Instruments). A 40 Wm^{-2} light flux, measured with a Goldilux photometer with an UV-A probe was used. A thermostated (20 °C) 10 mm quartz cell containing the sample solution (3.5 ml) and equipped with magnetic stirring was used. Three spectrokinetic parameters, normally quoted when describing the properties of photochromic compounds, were evaluated: maximum wavelength of absorption (λ_{max}), thermal bleaching rates (k_Δ) and maximum absorbance attained at λ_{max} (A_{max}). The colouration kinetics was then studied in the dark. The thermal

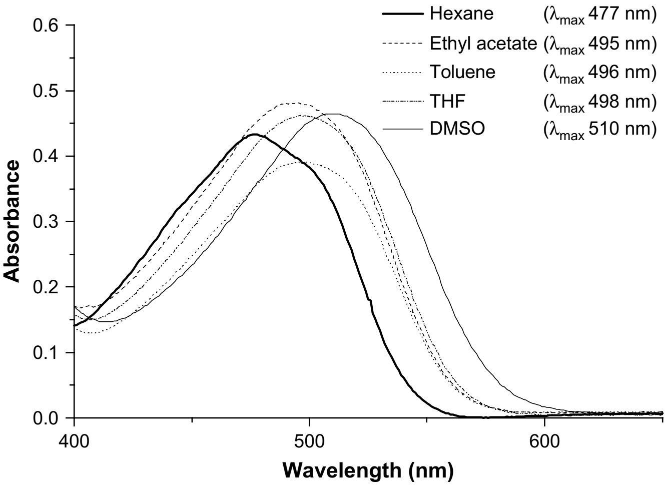


Fig. 1. Absorption spectra of dye **2b** in different solvents.

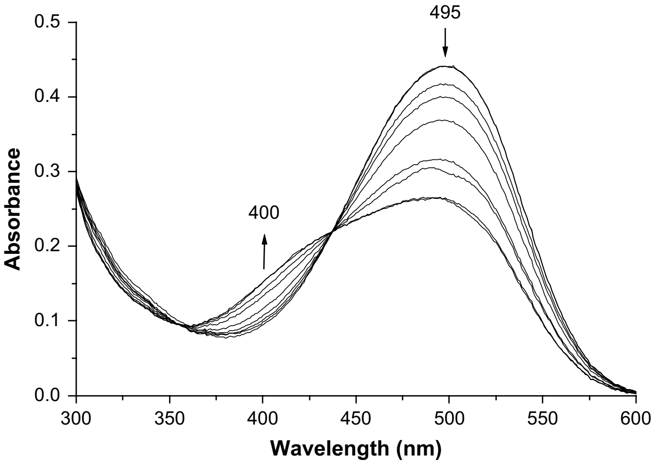


Fig. 2. Absorption spectra of dye **1b** under visible irradiation and in the dark.

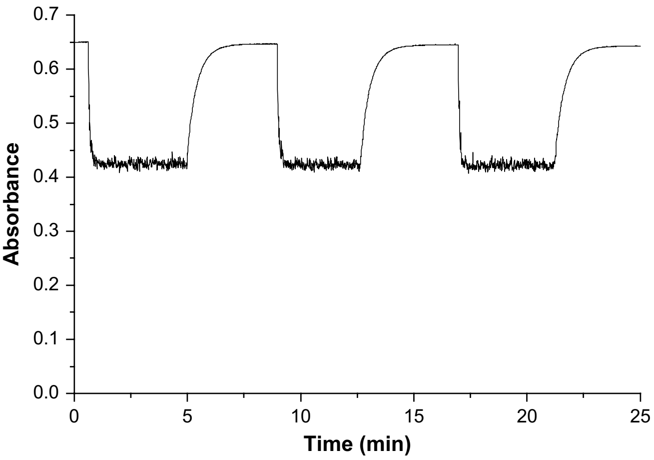


Fig. 3. Visible irradiation/dark cycles for dye **1c**.

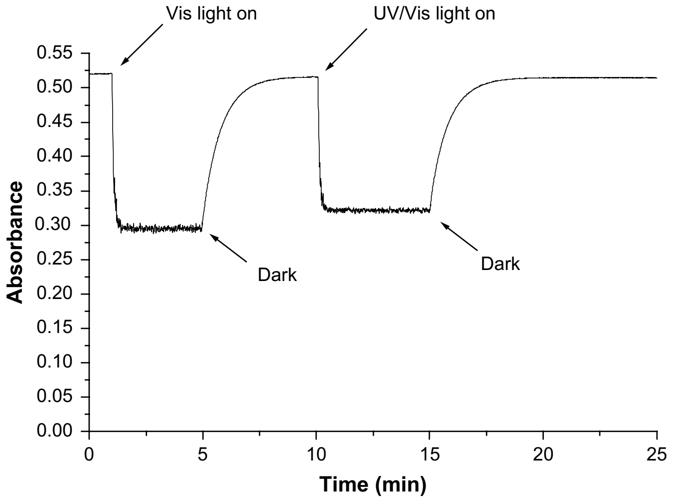


Fig. 4. Irradiation/dark cycles for compound **1b** under visible and UV/vis irradiation.

couloration curves were analysed evaluating the fitting of the experimental data to the mono-exponential equation:

$$A(t) = A_1 e^{-kt} + A_0$$

where $A(t)$ is the absorbance at $\lambda_{\max}$ at any instant t, A_1 a proportional factor, k the thermal colouration rate and A_0 the absorbance in the dark when time approaches infinity. The model was found to accurately fit our data when the quadratic residual errors were 10^{-6} or less.

4. Conclusions

2,2′-Bithiophene azo compounds **1a**–**c** are highly coloured compounds that exhibit significant photochromic properties. Under visible irradiation (>420 nm) a photostationary state is attained in less than 30 s corresponding to a 35–50% conversion of the *E*-isomer to the *Z*-isomer. When the irradiation ceases the system returns readily to the initial state. For these dyes the thermal *Z*–*E* back transformation kinetic was found to be monoexponetial with a half-time between 18 and 69 s, similar to other diaromatic azo compounds. On the contrary differently substituted 2,2′-bithiophene azo compounds **2b**–**e** exhibit weak photochromic properties. In medium to polar solvents, under visible irradiation, almost no absorbance changes were observed. The latter compounds although not interesting for photon-controlled applications can be potentially useful for dying and printing uses where colour constancy is intended.

Acknowledgment

To the Foundation for Science and Technology (Portugal) for financial support through the project PTDC/QUI/66251/2006.

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