



Photoswitching in azo dyes bearing thienylpyrrole and benzothiazole heterocyclic systems[☆]

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ABSTRACT

Visible light promotes the conversion of the *E*-isomer of benzothiazol-2-yl and benzothiazol-6-yl diazenes to the thermal unstable *Z*-isomer that reverts in few seconds to the initial form. The kinetics of the thermal *Z*–*E* process is strongly influenced by the linkage position of the N=N function to the benzothiazole heterocycle. Thienylpyrrole azo dyes functionalized with benzothiazol-6-yl groups are particularly interesting since they show an excellent compromise between the switching speed (rate constants: 0.068–0.12 s^{−1}) and the amplitude of the absorbance variation (37–42%).

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1. Introduction

Diaryl azo dyes substituted at the 4 and 4' positions with electron-donating and electron-withdrawing groups (called a 'push/pull' substitution pattern) are characterised by a strong asymmetric electron distribution. These "pseudo-stilbenes" display a strong and broad absorption band in the visible region and the colour exhibited by these chromophores can be controlled by the appropriate choice of substituents. Due to the asymmetric electron distribution they possess important nonlinear optical properties that have been extensively used in designing nonlinear optical materials [1–5]. Among these, heteroaryl azo dyes have recently attracted the attention of many groups due to their diverse optical applications such as second harmonic generation and optical switching [6–9].

However, one of the most important properties of these compounds is their *E*–*Z* isomerisation [10,11]. Typically, under UV or visible light irradiation, the thermally stable *E*-isomer is partially converted to the unstable *Z*-isomer that, in the absence of light, reverts thermally to the *E* form following a mono-exponential

kinetics (Scheme 1). This interconversion is uniquely clean, fast and efficient.

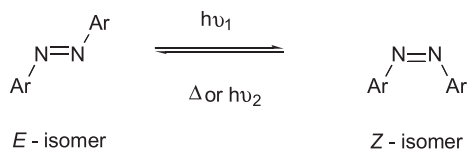
The lifetime of the photogenerated *Z*-isomer is very relevant to practical applications: in dyeing and printing an extended *E*–*Z* photo-conversion is disadvantageous since it results in a pronounced photochromic effect and weakening of the colour constancy as the *Z*-isomer absorbs at lower wavelengths. On the other hand, for more modern applications where the photoisomerisation reaction is used, the control of the kinetics of the thermal back isomerisation process, and therefore the lifetime of the *Z*-isomer, is essential. Ideally the conversion should be extensive and fast. Recent applications try to exploit not only the colour change but mainly the geometrical and electronic modifications that occur due to the *E*–*Z* photo-conversion. For example, when the azo dyes are incorporated in polymers the photoisomerisation induces reversible conformational changes in the polymer chains, which in turn leads to macroscopic variations of the chemical and physical properties of the surroundings [12–17]. The versatility of this class of organic photoswitches has attracted the interest of many research groups and they are now used in diverse optical applications, including memories, molecular switches, photo-modulation materials and molecular machines [18–23].

Although a large variety of diarylazo compounds are used in the design of optical materials, only a few reports concerning the photoisomerisation of heterocyclic azo dyes can be found in the

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Scheme 1. *E–Z* photoisomerisation in diaryl azo dyes.

literature [24–26]. Even more rare are the examples of azo dyes bearing pyrrole or thienylpyrrole systems as donor moieties, functionalized with aryl or heteroaryl diazene acceptors [2,8,27–30]. Recently, we have developed an efficient synthesis of heterocyclic azo dyes, through the coupling of aryl or heteroaryldiazonium salts with thienylpyrrole or bithiophene derivatives [9,27,28,31]. The study of these chromophores showed that their solvatochromic, photochromic and nonlinear optical (NLO) particularly are very dependent on the nature and substitution pattern of the aryl and heteroaryl moieties. In particular the speed of response to an external stimulus (light or absence of light), that induces the *E* → *Z* azo isomerisation reaction, and consequently the amplitude of the absorption variation, are strongly influenced by the electronic nature of the aromatic rings and the position of the azo linkage. While aryldiazene thienylpyrroles [32] exhibit thermal *Z* → *E* back isomerisation rates around 0.30 s^{−1}, aryldiazene bithiophenes [33] showed significant slower rates (0.01–0.04 s^{−1}) indicating more stable *Z*-isomers. On the other hand the substitution of an aryldiazene moiety by a thiazolyldiazene group on thienylpyrrole derivatives led to a very significant increase on the thermal *Z* → *E* isomerisation rate for thiazolyl azo dyes [28]. For the latter compounds the switching between the two stereoisomers can be performed in 2–3 s with a noteworthy change in the visible spectrum. In order to modulate the switching speeds of the latter system we decided to substitute the thiazole ring by a benzothiazole heterocycle which can be linked to the π -conjugated system/donor moiety through different positions. In this respect, two new series of azo benzothiazolyl thienylpyrroles **1–3** were designed and their photochromic properties evaluated. The first series is based on thienylpyrrolyl-benzothiazol-2-yl-diazenes **1a–b** and **2a** and, the second, on thienylpyrrolyl-benzothiazol-6-yl-diazenes **3a–c** (Fig. 1).

2. Experimental

For measurements of λ_{max} , A_{eq} and k_{d} under continuous visible irradiation, 2.0×10^{-5} M acetone 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 thermostated (20 °C) 10 mm quartz cell containing the sample solution (3.5 mL) and equipped

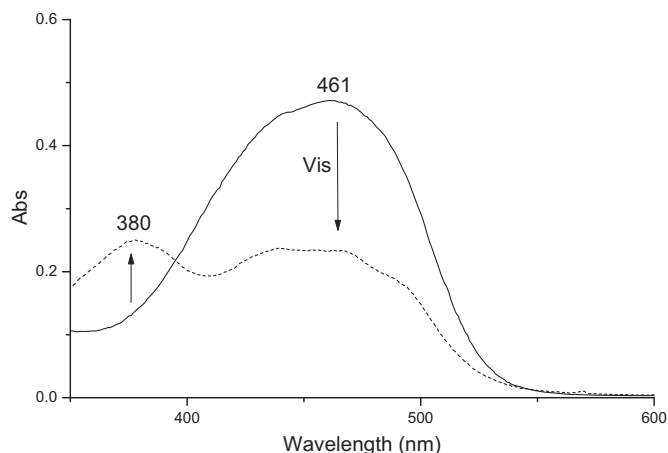


Fig. 2. Absorption spectra of dye **3b** under visible irradiation (—) and in the dark (—).

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 colouration rates (k_{Δ}) and maximum absorbance attained at λ_{\max} (A_{\max}). The colouration kinetics were then studied in the dark. The thermal colouration 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 λ_{\max} at 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.

3. Results and discussion

The synthesis of benzothiazolyl diazenes **1–3** was recently described [34]. The photochromic properties of benzothiazole azo dyes **1a–b**, **2a** and **3a–c** were studied in 2.0×10^{-5} M acetone 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 acetone all compounds afforded deeply coloured solutions (yellow to purple) with molar absorptivities ranging from 1.2×10^4 to $3.2 \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$. The benzothiazol-6-yl azo dyes **3a–c** displayed an intense absorption maxima between 454–461 nm, while the azo dyes **1a–b**, where the azo function is bonded to the thiazole ring of the benzothiazole moiety, exhibit a maximum wavelength of absorption at significantly higher wavelengths 503–515 nm.

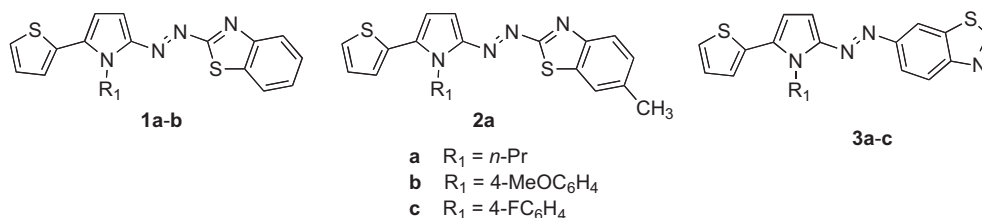
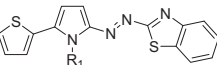
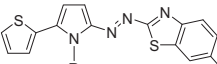
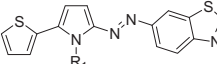
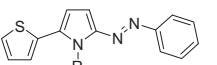
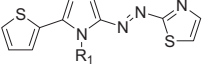


Fig. 1. Structure of benzothiazole azo dyes **1–3**.

Table 1

Spectrokinetic properties under continuous visible irradiation: maximum wavelength of absorption (λ_{\max}), maximum absorbance (A_{\max}), absorbance variation (ΔAbs), thermal colouration rates (k_{Δ}) and half-life ($t_{1/2}$) of azo dyes **1a–b**, **2a**, **3a–c**, **4a** and **5a–b**.

Azo dye	R ₁	λ _{max} /nm	A _{max}	ΔAbs (%)	k _Δ /s ⁻¹	t _{1/2} /s	
1a		<i>n</i> -Pr	503	0.258	0.010 (3.7%)	0.45	1.54
1b	4-MeOC ₆ H ₄	515	0.512	0.017 (3.3%)	1.4	0.50	
2a		<i>n</i> -Pr	507	0.495	0.029 (5.8%)	1.2	0.58
3a		<i>n</i> -Pr	454	0.498	0.185 (37%)	0.098	7.1
3b	4-MeOC ₆ H ₄	461	0.541	0.229 (42%)	0.068	10	
3c	4-FC ₆ H ₄	457	0.656	0.263 (40%)	0.12	5.6	
4a		<i>n</i> -Pr [28]	420	0.523	0.277 (53%)	0.036	20
5a		<i>n</i> -Pr [28]	487	0.592	0.121 (20%)	1.4	0.50
5b	4-MeOC ₆ H ₄ [28]	499	0.542	0.120 (22%)	0.82	0.85	

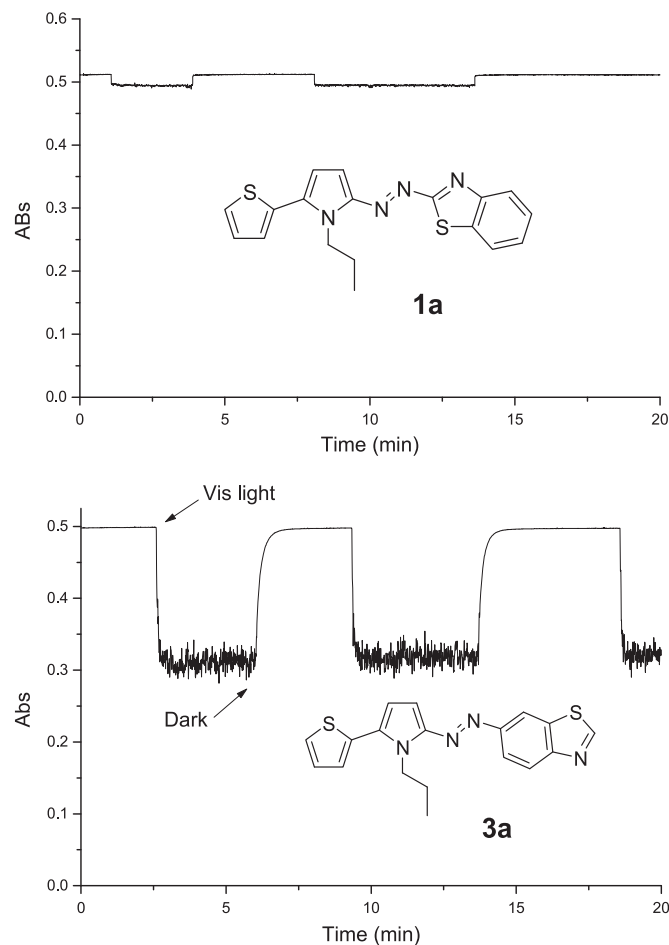
The visible light irradiation of the **1a–b**, **2a**, **3a–c** azo dyes solutions led to a fast decrease of the maximum absorbance at longer wavelengths and, at the same time, an increase in the band located near 380 nm, indicating the transformation of the more stable *E*-isomer to the *Z*-isomer that absorbs at shorter wavelengths. The change in the visible spectrum of dye **3b** is depicted in Fig. 2.

When the irradiation was stopped the inverse situation was observed, the band at 380 nm decreased and the band at 461 nm increased following a monoexponential kinetics. The thermal colouration rate constants (k_{Δ}) of the back *Z* → *E* isomerisation reaction were then measured at λ_{\max} and are shown in Table 1 along with the absorbance variation (ΔAbs) and half-life ($t_{1/2}$) of the *Z*-isomer.

From Table 1 is clear that the position of the linkage between the benzothiazole group and the azo function has a manifest influence on the photochromic properties of these compounds. While the visible irradiation of benzothiazole azo dyes **1a–b** and **2a**, linked through position 2 of the thiazole nucleus, induces the partial conversion of the *E*-isomer to the less stable *Z*-isomer, accompanied by a very small change of the absorbance (3–6% decrease), the irradiation of benzothiazol-6-yl azo dyes **3a–c** led to a more pronounced change of the absorbance (37–42% decrease) (Fig. 3).

This behaviour is related to the kinetics of the colouration reaction in the dark (thermal *Z* → *E* transformation). Under continuous visible irradiation conditions, the decrease in the absorbance at the λ_{\max} of the *E*-isomer is inversely related to the kinetic rate of the colouration process (*Z* → *E*). Consequently, in similar systems, an increase in the thermal back colouration kinetics led to lower absorbance variations and the increase in the stability of the *Z*-isomer led to a more prominent change of the absorbance. Therefore, the *Z*-isomers of azo dyes **3a–c** are more stable than those of azo dyes **1a–b** and **2a**. This can also be seen by comparing the half-life of these species (**3a–b**: $t_{1/2}$ = 7.1–10 s and **1a–b**: $t_{1/2}$ = 0.50–1.54 s).

This particular system allows one to chose between two dependent characteristics. Visible light irradiation of benzothiazol-6-yl azo dyes **3a–c** gives a more perceptible change in the visible

**Fig. 3.** Visible irradiation/dark cycles for azo dyes **1a** and **3a**.

spectrum while benzothiazol-2-yl azo dyes **1a–b** and **2a** exhibits a faster switching speed between the two isomers.

Comparing the photochromic behaviour of these new benzothiazole azo dyes with the similar thienylpyrrole azo dyes functionalized with phenyldiazene **4a**, or thiazoyldiazene **5a–b**, moieties recently reported by us [28] it can be concluded that the fusion of a thiazole ring to the azo phenyl group leads to a 3 fold increase in the colouration kinetics (**4a/3a**) while the annellation of a benzene ring on the thiazole azo dyes (**5a–b/1a–b**) decrease the thermal kinetic rate and induces a much lower absorption variation.

4. Conclusions

For benzothiazole azo dyes, the kinetics of the *E–Z* transformation can be controlled by the appropriate choice of the linkage position of the benzothiazole heterocycle to the N=N function. The linkage of the diazenyl group to the thiazole nucleus (position 2) of the benzothiazole moiety led to azo dyes exhibiting faster switching speeds between the two stereoisomers than the linkage to the benzene nucleus (position 6) of the same molecule. However, for benzothiazol-2-yl azo dyes, only a small percentage of the *E*-isomer is converted to the *Z*-isomer and thus the amplitude of the absorption variation is very small. On the other hand the parent benzothiazoles azo dyes **3a–c** show an excellent compromise between the switching speed and percentage of *E–Z* conversion (37–42%) leading to a strong colour variation perception.

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