Kinetic study of the fast thermal *cis*-to-*trans* isomerisation of *para*-, *ortho*- and polyhydroxyazobenzenes†

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The thermal *cis*-to-*trans* isomerisation process has been studied for a series of *para*-, *ortho*- and polyhydroxy-substituted azobenzenes in different solvents. The kinetics of the thermal back reaction for the *p*-hydroxy-substituted azobenzenes depend strongly on the nature of the solvent used, with relaxation times ranging from 200–300 milliseconds in ethanol to half an hour in toluene. Otherwise, the process rate is mainly independent of the solvent nature for the *ortho* substituted analogues. Polyhydroxy-substituted azobenzenes show very much faster kinetics than the *para*- and *ortho*- monohydroxyazoderivatives. With relaxation times of 6–12 milliseconds in ethanol, they are optimal molecules for designing fast optical switching devices. All the hydroxyazoderivatives thermally isomerise from the metastable *cis* form to the thermodynamically stable *trans* isomer through a rotational mechanism.

Introduction

Photochromic molecules are attracting growing interest as guests in the field of materials science due to their ability to change the properties of the host system, such as its electronic or ionic conductivity, fluorescence, magnetism, and shape, upon irradiation with light of the appropriate wavelength. Several photochromic systems are well known in photochemistry, *e.g.* stilbenes, imines, spiropyranes, fulgides and diarylethenes, among others. The most studied are azobenzenes.[1] These compounds exhibit a reversible isomerisation process between two geometric isomers of different stability, *trans* and *cis*. *trans*-to-*cis* isomerisation takes place by irradiation with UV light and the photo-generated *cis* isomer can be converted back to *trans* by irradiation with visible light or by thermal relaxation. This easy interconversion between the two isomers makes azobenzene the most used organic chromophore for technical applications, including optical waveguides and shutters,[2] switching display devices,[3] optical memories,[4] electro-optical modulators,[5] photo-active artificial muscles,[6–9] micro-electro-mechanical systems (MEMS),[10] *etc*.

Azobenzenes with a very slow thermal *cis*-to-*trans* isomerisation process are required for optically-controlled information storage devices. However, for optical switching and real-time optical information processing it is essential that the return to the initial state elapses much faster, within tens of milliseconds.[11] Polyhydroxy-substituted azobenzenes are a very interesting type of azoderivatives for this purpose because they are endowed with a very fast thermal *cis*-to-*trans* isomerisation. A few years ago, Kojima *et al*.[12] determined that the relaxation time for 4-hydroxyazobenzene at room temperature is less than a minute in polar protic solvents, such as ethanol, although its exact value has not been reported yet. Given the great interest and challenging applications of hydroxy-substituted azobenzenes, a thorough and comprehensive kinetic study of the thermal *cis*-to-*trans* isomerisation process of these azo-dyes is warranted.

The mechanism of the thermal *cis*-to-*trans* isomerisation of azobenzenes has been the subject of many theoretical and experimental studies since its first report by Hartley in 1937.[13] Two different pathways have been proposed: the inversional one, where the inversion of one of the nitrogen atoms of the azo group takes place through a linear transition state,[14,15] and the rotational one, which involves the rotation around the N–N bond.[16–18] *o*-Hydroxyazobenzenes have attracted less attention than the corresponding *para* isomers and only some mechanistic evidences have been reported for such azoderivatives.[19–22] Herein we present a kinetic study of the thermal *cis*-to-*trans* isomerisation process of several *para* and *ortho* substituted hydroxyazobenzenes. The position of the hydroxyl groups in the azobenzenic core as well as the nature of the solvent used are the main factors that control the rate and the mechanism of the thermal isomerisation of these azoderivatives.

Experimental section

Materials and general instrumentation

All reagents for synthesis were used as received without further purification. THF (Sharlau) was distilled from sodium/benzophenone. DMF (Fluka) was dried by storing it over

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activated 4 Å molecular sieves under nitrogen atmosphere. Ethanol and toluene (Sharlau) used in the kinetic studies were of spectroscopic grade and used as supplied. Flash column chromatography was carried out over silica gel (SDS, 230–240 mesh). Compounds were characterized by ^{1}H (400 MHz) and ^{13}C NMR (100 MHz), MS and FT-IR. NMR spectra were collected in a Varian Mercury spectrometer. HRMS was performed in a LC/MSD-TOF Agilent Technologies apparatus by means of the electrospray (ESI-MS) technique. FT-IR spectroscopy was carried out in a FT-IR Nicolet 6700 spectrometer.

Preparation of the azoderivatives

4-Hydroxyazobenzene (**4-OH**),[23] 4-hydroxy-4′-methoxy-azobenzene (**4-OH-4′-OMe**),[24] 2-hydroxy-5-methylazobenzene (**2-OH**),[25] 2-hydroxy-4′-methoxy-5-methylazobenzene (**2-OH-4′-OMe**),[24] 2,4-dihydroxyazobenzene (**2,4-OH**)[26] and 4-hydroxy-2′,4′-dimethoxyazobenzene (**4-OH-2′,4′-OMe**)[26] were prepared from aniline, 4-methoxyaniline or 2,4-dimethoxyaniline by coupling the respective diazonium salt with phenol, 4-methylphenol or resorcinol in basic media at 0–5 °C, as reported previously. 4,4′-Dihydroxyazobenzene (**4,4′-OH**),[27] 2,4′-dihydroxy-5-methylazobenzene (**2,4′-OH**) and 2,4,4′-trihydroxyazobenzene (**2,4,4′-OH**)[28] were obtained by cleaving the methyl ether of **4-OH-4′-OMe**, **2-OH-4′-OMe** and **4-OH-2′,4′-OMe**, respectively, with BBr_3 in dry CH_2Cl_2 at room temperature.[29] Williamson's dialkylation of azocompounds **4,4′-OH** and **2,4′-OH** with 6-bromo-1-hexene using NaH as a base in dry DMF under reflux provided azoderivatives **4,4′-OC$_6$**[30] and the novel azo-dye **2,4′-OC$_6$**. Azocompounds **4-OC$_6$** and **4-OC$_6$-4′-OMe**[31] were attained *via* Mitsunobu's reaction between **4-OH** or **4-OH-4′-OMe** and 5-hexen-1-ol using PPh_3 and diisopropylazodicarboxylate (DIPAD) in dry THF at room temperature.[32] 2,4,4′-Trimethoxyazobenzene (**2,4,4′-OMe**)[33] was afforded by reaction of **2,4,4′-OH** with CH_3I in THF at room temperature. All reactions were realized with yields higher than 85%. The detailed syntheses of the novel azoderivatives **2,4′-OH**, **2,4′-OC$_6$** and **4-OC$_6$** are described in the Supplementary Material section.†

Kinetic experiments

A population of *cis*-azobenzenes was generated by UV photolysis and its relaxation was followed by time-resolved UV-Vis spectroscopy. For long-lived *cis*-azobenzenes, the samples were irradiated with a Philips high-pressure mercury lamp (total nominal power 500 W) filtered with a 0.5 M solution of $Co(NO_3)_2$ in water. Irradiation was pursued until no further changes could be observed in the electronic spectrum of the sample; the usual irradiation time was 10 min. Afterwards, the solutions were thermostated in the dark at the desired temperature (±0.1 K) and the thermal *cis*-to-*trans* isomerisation was monitored by absorption spectroscopy using a Varian Cary 500E UV-Vis-NIR spectrophotometer. For short-lived samples, the thermal *cis*-to-*trans* isomerisation process was studied by means of laser flash-photolysis. Thus, the *cis* isomer of the corresponding azoderivative was generated by a Q-switched Nd-YAG laser (355 nm, 5 ns pulse width, 1–10 mJ per pulse) and the time evolution of the sample absorbance was monitored at 90 degrees by a white-light beam produced by a PTI 75 W Xe lamp. The light transmitted by the sample was spectrally resolved using a monochromator and detected with a Hamamatsu R928 photomultiplier, whose output was fed into a digital oscilloscope through a 50 Ohm resistor. The observation wavelength was set at 370 nm in all cases. No isomerisation of the azocompounds was promoted by observation wavelength of the spectrophotometer. Kinetic analysis of the transients was done with software developed in our laboratory. Unless otherwise stated, the experiments were realized in 1 cm optical path quartz cells at 298 K with *ca.* 2×10^{-5} M solutions of the azo-dye in the corresponding solvent. No photo-degradation of the compounds was observed.

Results and discussion

The unimolecular thermal *cis*-to-*trans* isomerisation process in the dark obeys eqn (1).

$$\Delta A_t = \Delta A_\infty + \Delta A_0 e^{-t/\tau} \quad (1)$$

where ΔA_t, ΔA_0 and ΔA_∞ correspond to the absorbance change at time t, zero and infinity, respectively, and τ is the relaxation time of the corresponding *cis* isomer. The relaxation times were derived from plots of the absorbance, ΔA, *versus* time by fitting eqn (1) to the data. The recovered relaxation times were independent of the observation wavelength and, with the exception of the *p*-hydroxyazocompounds in toluene, also of the concentration of the azo dye. The different relaxation times were determined with an associated error lower than 10% in all cases.

The chemical structures of all the azoderivatives studied are displayed in Fig. 1. All hydroxy-substituted azoderivatives exhibit a strong band peaking in between 350 and 380 nm, corresponding to an allowed π–π* transition of the *trans* isomer, and also a weaker broad band peaking at *ca.* 450 nm, which belongs to a forbidden *n*–π* transition. In addition, a broad absorption band was detected for all the *ortho* substituted hydroxyazocompounds in both ethanol and toluene, peaking at *ca.* 405–425 nm, which is associated with the azo-hydrazone tautomerism.[34]

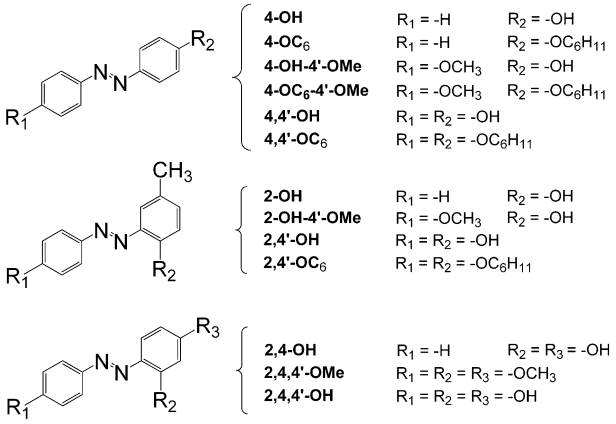

Fig. 1 Chemical structure of the different azoderivatives.

Table 1 Relaxation times at 298 K, τ, enthalpies and entropies of activation, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, for the alkoxy-substituted azocompounds **4-OC$_6$**, **4-OC$_6$-4′-OMe**, **4,4′-OC$_6$**, **2,4′-OC$_6$** and **2,4,4′-OMe**

Azocompound	Solvent	τ/h	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J K^{-1} mol^{-1}
4-OC$_6$	Ethanol	70	95 ± 1	−33 ± 3
	Toluene	56	94 ± 1	−32 ± 1
4-OC$_6$-4′-OMe	Ethanol	13	93 ± 1	−25 ± 2
	Toluene	15	91 ± 1	−33 ± 2
4,4′-OC$_6$	Ethanol	12	91 ± 1	−30 ± 4
	Toluene	14	91 ± 1	−32 ± 1
2,4′-OC$_6$	Ethanol	58	92 ± 1	−41 ± 3
	Toluene	64	93 ± 1	−37 ± 2
2,4,4′-OMe	Ethanol	10	87 ± 1	−42 ± 1
	Toluene	19	89 ± 1	−43 ± 2

The kinetics of the thermal *cis*-to-*trans* isomerisation process for the *para* and *ortho* alkoxy-substituted azoderivatives **4-OC$_6$**, **4-OC$_6$-4′-OMe**, **4,4′-OC$_6$**, **2,4′-OC$_6$** and **2,4,4′-OMe** were studied in ethanol, a polar protic solvent, and toluene, a non-polar aprotic one. Compared to their hydroxy-substituted counterparts, these azoderivatives presented a very slow thermal *cis*-to-*trans* isomerisation in all the solvents studied (Table 1). All the *para-para* and *ortho-para* alkoxy-substituted azoderivatives showed relaxation times from several hours to a few days, and their kinetics were almost independent of the solvent used. This latter feature suggests that the transition state for their thermal *cis*-to-*trans* isomerisation has a non-polar character, pointing to an inversion mechanism.[35] The measurement of the volumes of activation produces for these processes unequivocal evidence about the operation of the inversion or rotation isomerisation mechanism.[36,37] The sensitiveness to medium polarity changes of the azocompound during the activation process should produce an acceleration of the thermal *cis*-to-*trans* isomerisation on increasing the pressure for the rotational mechanism on polar solvents; that is, electrostriction. In contrast, this effect should not be observed in either polar or non-polar solvents if the reaction takes place *via* the inversional mechanism. The thermal *cis*-to-*trans* isomerisation process of the azobenzene-bridged crown ether 3,3′-[1,10-diaza-4,7,13,16-tetraoxa-18-crown-6]-biscarbonylazobenzene cannot occur *via* the rotational mechanism due to structural restrictions, and it is normally taken as a defined standard for the inversion mechanism.[38,39] The determination of the volumes of activation for the thermal *cis*-to-*trans* isomerisation process of the representative azobenzenes **4,4′-OC6** and **2,4′-OC$_6$** were all close to zero as expected, being very similar to the values found in the literature for the standard azobenzene bridged crown-ether. It can be stated from the experimental data that the thermal isomerisation process for the alkoxy-substituted azocompounds occurs *via* the inversional mechanism independently of the solvent used.

In contrast, a dramatic acceleration was detected for the *p*-hydroxyazocompound **4-OH** in ethanol. In fact, the relaxation time for *cis*-**4-OH** could not be determined by "slow" methods, and laser flash-photolysis experiments had to be used instead. A value of τ = 205 ms was observed in ethanol at 298 K (Fig. 2). Remarkably, the relaxation time for this compound increased in toluene by four orders of magnitude up to 31 min (Table 2). The analogous *p*-hydroxy-substituted azocompounds **4-OH-4′-OMe** and **4,4′-OH** showed a similar behaviour: relaxation times of 28 and 33 min in toluene (Fig. 3), and 306 and 265 ms in ethanol, respectively (Table 2). The large decrease of the relaxation time evidences clearly that intermolecular interactions between the chromophore and the solvent molecules control the rate of the isomerisation process for these *p*-hydroxyazoderivatives. Formation of intermolecular hydrogen bonds between the nitrogen atom of the azo group and the solvent proton, as well as between the OH group of the azo-dye and the solvent oxygen atom, favours

Table 2 Relaxation times at 298 K, τ, for azocompounds **4-OH**, **4-OH-4′-OMe**, **4,4′-OH**, **2-OH**, **2-OH-4′-OMe**, **2,4′-OH**, **2,4-OH** and **2,4,4′-OH**

Azocompound	Solvent	τ/ms
4-OH	Ethanol	205
	Toluene	1.9×10^6
4-OH-4′-OMe	Ethanol	306
	Toluene	1.7×10^6
4,4′-OH	Ethanol	265
	Toluene	2.0×10^6
2-OH	Ethanol	399
	Toluene	650
2-OH-4′-OMe	Ethanol	302
	Toluene	418
2,4′-OH	Ethanol	175
	Toluene	416
2,4-OH	Ethanol	12
	Toluene	53
2,4,4′-OH	Ethanol	6
	Toluene	33

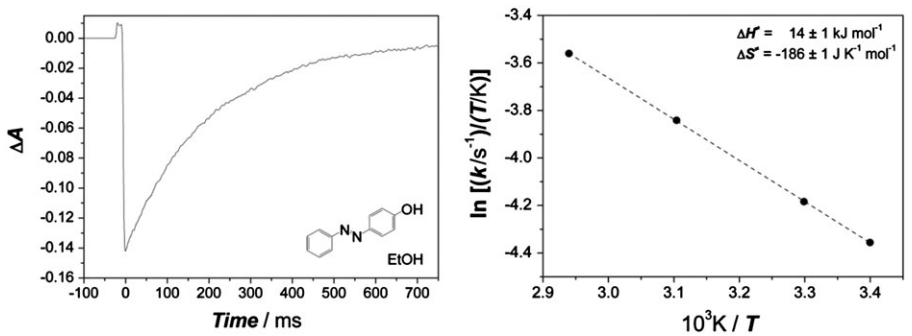

Fig. 2 Transient generated by irradiation with UV light (λ = 355 nm) for azobenzene **4-OH** in ethanol ([**4-OH**] = 2×10^{-5} M) at 298 K (left) and Eyring plot for its thermal *cis*-to-*trans* isomerisation (right).

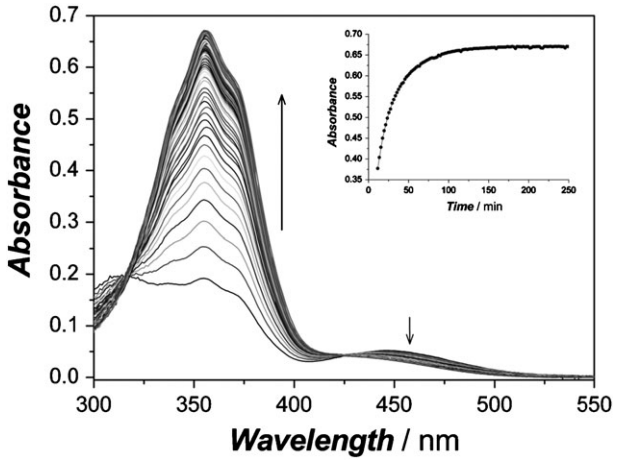

Fig. 3 Changes in the electronic spectrum of a **4-OH-4′-OMe** *cis*-to-*trans* isomerising toluene solution at 298 K (Δt = 120 s, [**4-OH-4′-OMe**] = 2×10^{-5} M).

a hydrazone-like electronic distribution with a simple N–N bond, which seems to be the key of the fast isomerisation kinetics observed.[12,40–42] In this way, the rotation around the N–N bond facilitates the recovery of the more stable *trans* isomer.

The rate of the thermal back reaction for all the *p*-hydroxy-azoderivatives in a non-polar aprotic solvent, toluene, is slower than in ethanol, although it is still faster than that of the alkoxysubstituted compounds (Table 1). In hydrocarbon solvents, *p*-hydroxyazobenzenes may undergo dimerization by intermolecular hydrogen bonding between azo molecules. In this case, the corresponding *cis* isomer can evolve to the hydrazone-like situation *via* an intermolecularly-promoted process by means of two azobenzene molecules.[12,42] Obviously, the solvent-assisted process is faster than that produced by the self-aggregation of the azo-dye, especially when working with solutions of low chromophore concentration. A comprehensive study of the dimerisation of *p*-hydroxysubstituted azocompounds in non-polar aprotic solvents and its influence on their thermal *cis*-to-*trans* isomerisation kinetics will be reported in a forth-coming paper. Interestingly, *ortho*-substituted azobenzenes showed much shorter *cis*-relaxation times than the *para*-substituted azo-dyes, *e.g.* 31 min for *cis*-**4-OH** *vs.* 650 ms for *cis*-**2-OH**. This can be understood bearing in mind that azocompound **4-OH** should undergo dimerisation prior to isomerisation in toluene. However, formation of an intramolecular hydrogen bond in the *ortho* substituted compound **2-OH** can take place independently of the solvent and therefore a fast isomerisation process occurs in both ethanol and toluene. A detailed analysis of the kinetic parameters presented by azocompounds **2-OH**, **2-OH-4′-OMe** and **2,4′-OH** in ethanol shows that the kinetics of the thermal back reaction increases as **2,4′-OH** > **2-OH-4′-OMe** > **2-OH**. All three azoderivatives gave slightly slower kinetics in toluene than in ethanol, because there is no possibility of hydrogen bonding with the solvent molecules in the former.

Fig. 4 shows the transients for the *ortho* hydroxy-substituted azobenzenes **2,4-OH** and **2,4,4′-OH** in ethanol. The relaxation times fell between 6–12 ms in ethanol and 33–53 ms in toluene. The presence of two hydroxyl groups in the *ortho* and *para* positions of the same ring of the azobenzene core produced a significant acceleration of the process by a cooperative effect. This was not observed when the two hydroxyl groups were placed in different rings of the azobenzene molecule (see Table 2: **4,4′-OH** and **2,4′-OH**). The *cis* isomers of both azoderivatives **2,4-OH** and **2,4,4′-OH** showed the lowest relaxation times of all the azo-dyes studied. The poly-hydroxy-substitution of the azobenzene core, such as in **2,4,4′-OH**, decreases further the relaxation time down to 6 milliseconds. The completely different kinetic behaviour observed between the alkoxy- and hydroxy-substituted azo-dyes reflects that some alteration in the intimate isomerisation mechanism occurs between these two types of azoderivatives. The much faster thermal *cis*-to-*trans* isomerisation of the hydroxy-substituted azo-dyes indicated that their back reaction takes place *via* the rotational pathway, through a polar transition state with a partial breaking of the N=N double bond, as has been also proposed for other push-pull azobenzenes, like the 4-*N*,*N*-(dimethylamino)-4′-nitroazobenzene, which presents a short relaxation time of *ca.* 4 ms in DMSO at 298 K.[43,44]

The activation parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) for all the alkoxy-substituted azoderivatives and for some representative hydroxyazocompounds were determined in toluene and ethanol (Tables 1 and 3, S1 and S2†). Fig. 2 and 4 show Eyring plots[45,46] for azoderivatives **4-OH** and **2,4,4′-OH** in ethanol. The enthalpies of activation for the thermal *cis*-to-*trans* isomerisation process for *ortho* and *para* alkoxy-substituted azocompounds fell between 87 and 95 kJ mol^{-1}. Likewise, low negative values were found for their entropies of activation, namely −25 to −42 J K^{-1} mol^{-1}. On the other hand, the

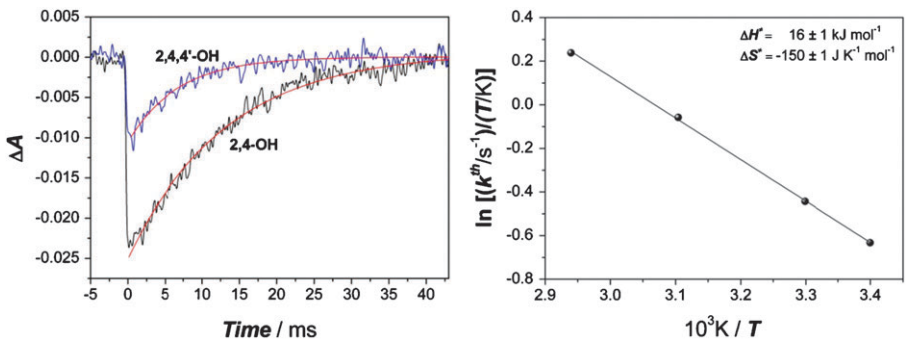

Fig. 4 Transients generated by irradiation with UV light (λ = 355 nm) for azobenzenes **2,4-OH** and **2,4,4′-OH** in ethanol at 298 K ([**AZO**] = 2×10^{-5} M, left) and Eyring plot for the thermal *cis*-to-*trans* isomerisation of azocompound **2,4,4′-OH** in ethanol (right).

Table 3 Enthalpies and entropies of activation, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, for azocompounds **4-OH**, **2-OH** and **2,4,4′-OH**

Azocompound	Solvent	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J K^{-1} mol^{-1}
4-OH	Ethanol	15 ± 1	−186 ± 1
	Toluene	—	—
2-OH	Ethanol	28 ± 1	−142 ± 2
	Toluene	22 ± 1	−168 ± 1
2,4,4′-OH	Ethanol	16 ± 1	−150 ± 1
	Toluene	11 ± 1	−181 ± 4

enthalpy of activation for all hydroxyazocompounds was remarkably lower (11 to 28 kJ mol^{-1}). The entropies of activation were also more negative for both the *para* and *ortho* hydroxy-substituted azocompounds (−142 to −186 J K^{-1} mol^{-1}, Table 3) than for the alkoxyderivatives, revealing a more organized transition state in the former because of the presence of intermolecular hydrogen bonding. Thus, the activation parameters found for the mono- and polyhydroxy-substituted azobenzenes point to a rotational polar pathway for their thermal *cis*-to-*trans* isomerisation process.

Conclusions

The thermal *cis*-to-*trans* isomerisation process has been studied for several mono- and polyhydroxy-substituted azobenzenes with *para*- and *ortho*- substitution. In the case of *p*-hydroxyazobenzenes, relaxation times of about 200–300 ms are found in polar protic solvents, whereas an increase to 30 min is observed in non-polar aprotic solvents such as toluene. The interactions between chromophore and solvent molecules play a crucial role in determining the rate of this process. Accordingly, polar protic solvents accelerate the thermal *cis*-to-*trans* isomerisation process.

In the *ortho* hydroxyazoderivatives, which can form intramolecular hydrogen bonds, a fast thermal *cis*-to-*trans* isomerisation is observed independently of the solvent nature. Among all the systems studied, the polyhydroxyazobenzene **2,4,4′-OH** is the fastest one with a relaxation time of only 6 ms in ethanol.

The kinetic parameters determined for the thermal *cis*-to-*trans* relaxation process for both *para* and *ortho* hydroxy-azobenzenes match with a rotational mechanism for this process. The fast back isomerisation exhibited by polyhydroxy-substituted azo-dyes makes them excellent candidates for optical switching and real-time information processing technology.

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