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Activation volumes for *cis*-to-*trans* isomerisation reactions of azophenols. A clear mechanistic indicator?

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Abstract: The thermal *cis*-to-*trans* isomerisation reaction of a series of hydroxy-substituted azo derivatives were studied kinetico-mechanistically as a function of temperature and pressure in order to investigate the possible role of the solvent in controlling the isomerisation mechanism, viz. inversion *versus* rotation. The variation of the observed first order rate constants for kinetic runs carried out at different temperatures and pressures were used to determine the thermal activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$, and the pressure activation parameter $\Delta V^{\neq}$. In addition, some experiments with deuterated species or solvents were also performed. The reported results could be interpreted as indicative of a changeover from an inversion mechanism for non-polar solvents to a rotation mechanism for polar solvents, capable of hydrogen bonding, for some of the systems studied. However, the operation of a rotation mechanism in all studied cases can account more consistently for the data observed.

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Introduction

Controlling the properties of materials by means of suitable external stimuli, *e.g.* heat, electric and magnetic fields, solvent gradients, and the absence or presence of ligands, is receiving a great deal of attention since it gives rise to novel materials with unique fascinating abilities and properties. Amongst all possible inputs, light, a clean, cheap and ubiquitous energy source, is one of the most used since it can be applied remotely to determined areas of the specimen in a quick and wireless fashion. On this basis, the design and study of light-sensitive organic molecules that could be suitable for such task is essential.

The development of organic synthesis has rendered over the years a wide range of organic photochromes.[1] In this context, the easy and totally reversible inter-conversion between the two isomers of azobenzene of different stability, viz. *trans* and *cis*, in combination with the possibility of the *cis* isomer to revert back to the initial state thermally in the dark,[2] render azobenzenes and their substituted derivatives to be the photochromes of common choice for switching purposes. Indeed, the integration of azo dyes into different host materials has already allowed to access a diversity of applications, covering both materials science and the biomedical field.[3–24]

Since the first observation of the azobenzene isomerisation by Hartley in 1937, the mechanism of the thermal *cis*-to-*trans* isomerisation of azobenzenes and, more specifically azophenols, has attracted much attention, not without some controversy. Actually, the kinetics and mechanism of the thermal back reaction of hydroxy-substituted azo dyes has so far been the subject of many theoretical and experimental investigations. As found for conventional azobenzenes, two different possible mechanisms have been proposed for the process.[25–29] The first one involves the rotation around the N−N bond, while the second one implies inversion, in-plane lateral shift, *via* a linear transition-state. For phenolic azo chromophores, the rate of their thermal back reaction has been found to dramatically depend on the number and position of hydroxyl substituents within the covalent backbone of the azo platform, and surprisingly, also on the solvent and general environment in which the azo photochrome is embedded.[30–32]

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In this respect, we have been involved for some time in the effect that the environment has on the thermal *cis*-to-*trans* isomerisation reaction of an important number of specially and carefully designed azo derivatives. In particular, activation volumes, derived from kinetic measurements at different hydrostatic pressures, have been used as an efficient and useful tool for the mechanistic assignment of the processes.[3,23,24,30,31,33] In this paper we report new insight obtained for the description of some isomerisation processes of azophenols using kinetico-mechanistic studies. The involvement of the solvent in these processes has been studied in a comprehensive manner using a range of solvents going from non-polar aprotic (toluene) to polar aprotic (acetonitrile) and to polar protic (ethanol or methanol). The results obtained by means of high pressure kinetics, have allowed us to gain further insight into the isomerisation mechanism by which the reactions occur, as well as the polar or hydrogen-bonded nature of the interactions taking place in the transition state. Thus, investigation of the structural and environmental factors governing the thermal *cis*-to-*trans* isomerisation kinetics of this particular type of azo chromophores is essential to guide the future design of photoactive analogues with the purpose of creating new light-triggered materials with the desired abilities and functionalities.

Results and Discussion

The structures of the azo derivatives analysed in this study are summarized in Scheme 1. In the first instance, two alkoxy-substituted azo derivatives (**1** and **2**) have been studied for the sake of comparison for systems where hydrogen bonding is less likely. Then, two distinct types of azophenolic dyes were selected for the kinetico-mechanistic studies. Azophenol **3** and its push-pull *para*-substituted cyano- and nitro-substituted counterparts, **4** and **5**, as well as the corresponding *ortho*-substituted analogues, **6** and **7**, were chosen.

All the *para*-alkoxy- and *para*-hydroxy-substituted azo derivatives used in this study exhibit the typical spectral profile of azobenzenes, i.e. a strong band with a maximum between 350 and 380 nm, assigned to the symmetry-allowed π-π* transition of the *trans* isomer, and a weaker broad band peaking at *ca.* 450 nm, associated with a symmetry-forbidden *n*-π* transition (Figure 1a). In the figure it is also clear that the *ortho*-substituted

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azo compounds **6** and **7** show an extra band due to intramolecular hydrogen bonding established between the hydroxyl substituent and one of the azo nitrogens.[30]

The fraction of the *cis* forms of the azo derivatives shown in Scheme 1 was increased via photo-irradiation at λ_{Irrad} (see Experimental Section). Starting from that point, the kinetics of their thermal back *cis*-to-*trans* isomerisation (Figure 1b) was studied in toluene, acetonitrile and ethanol (or methanol) as solvents. Whereas for toluene no polarity or hydrogen bonding interaction with the solvent is feasible, the stabilization of a polar transition state is possible for acetonitrile. Furthermore, for the two protic alcohol solvents, the presence of hydroxyl groups opens up the possibility of hydrogen bonding with the azo chromophore.

While the alkylated azo dye **1** exhibits a slow thermal back isomerisation in all types of organic solvents ($k = 4.5\times10^{-6}$ s^{-1} in toluene and ethanol at 298 K), the corresponding free azophenol **3** presents a much faster and solvent dependent back isomerisation process ($k = 4.9$ and 6.0×10^{-4} s^{-1} in ethanol and toluene, respectively). The same behaviour is observed for the **2** and **4** pair (see Table 1). When comparing the reactions for these same compounds in acetonitrile (non-protic polar solvent), an identical kind of acceleration is observed.[34–36] Thus, two possible scenarios can be considered; either the operating mechanism is rotation for all systems in all the solvents used (with stabilization of charge-transfer in the transition state depending on the nature of the dye), or a switch from inversion to rotation mechanism occurs for polar solvents capable of stabilizing charge transfer situations (Scheme 2). Furthermore, the possible role of the −OH group in **3** and **4** establishing intermolecular interactions, either with the cage of the surrounding solvent molecules or with neighbouring azophenolic units, cannot be ruled out, but is not evident from the kinetic data collected in Table 1.

Table 2 collects the pressure activation parameters $\Delta V^{\neq}$ determined for the systems studied and Figure 2 represents some typical pressure dependent kinetic data for compound **5**. The value of $\Delta V^{\neq}$ has been used in this work as a reliable indicator for the type of thermal isomerisation mechanism operating for these molecules. In fact, this particular activation parameter has been widely employed to evaluate the degree of association and electrostriction in a great number of reactions involving substitution, redox, and different isomerization

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processes.[37–40] Its advantage *versus* activation entropy relies in the fact that the value of $\Delta V^{\neq}$ derives from the slope of a plot within the range of the data used, instead of an intercept outside the experimental temperature range, having thus a smaller mathematical error. The data in Table 2 clearly show that the values of $\Delta V^{\neq}$ are practically zero for all the azo derivatives when the reactions are carried out in toluene, indicating the non-involvement of the solvent in the transition state *via* which the reaction occurs. In addition, the values obtained for the alkoxy-substituted compounds **1** and **2** in polar and protic solvents, zero in both cases, definitely indicate that for these two derivatives an inversion mechanism is operative, with no formation of polar transition states during the process.

Interestingly, as seen in Table 2, for azophenols **3** to **5** the values of $\Delta V^{\neq}$ depend dramatically on the solvent used. Clearly, either a polar transition state, whose stabilization depends on the polarity of the medium, or a changeover from an inversion (in the non-polar medium, toluene) to a rotation mechanism (in the polar media, ethanol or acetonitrile) is occurring. In this respect, the fact that for the alkoxy derivatives **1** and **2** the mechanism is definitely established as inversion, could suggest the same behaviour for compounds **3**, **4** and **5** in non-polar solvents. However, from the data shown in Table 2, a rotational mechanism could be claimed to be preferred in polar media.[37–39] For example in the case of acetonitrile, a polar non-protic solvent, the values determined for the activation volumes are negative in all cases, in good agreement with the electrostriction suffered by the solvent molecules for a charge-separated transition state. Furthermore, for compounds **4** and **5**, both with a strong push-pull electronic configuration, the activation volumes are even more negative than for the parent derivative **3**, in line with the higher polarizing capability of the push-pull species, and thus with the expected higher polar character of the transition state.

Given the fact that the $\Delta V^{\neq}/\Delta S^{\neq}$ correlation trend has been frequently associated with the formation of outer-sphere hydrogen bonded aggregates involved in the transition state,[41–43] systems **1-5** were also studied as a function of temperature to determine the thermal activation parameters associated with the process (Table 3). The enthalpy and entropy of activation for the thermal back isomerisation of alkoxy-substituted azo derivatives **1** and **2** are *ca.* 95 kJ mol^{-1} and −30 J K^{-1} mol^{-1}, respectively, suggesting that the process is enthalpy controlled. In

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the case of the phenolic analogues **3-5**, the values are around 30 kJ mol^{-1} and −150 J K^{-1} mol^{-1} for the same parameters. Indeed, these values suggest a less enthalpy controlled, but strongly entropy controlled transition state for the thermal isomerisation reaction, which can be easily associated with an effective solvation process by the polar solvent molecules, in agreement with a charge-separated nature of the transition state.

In order to find evidence for intermolecular hydrogen bonding that could also be a favourable effect for the rotational mechanism, the effect of azo chromophore concentration on the thermal *cis*-to-*trans* isomerisation rate in toluene was studied for *para*-hydroxy-azobenzene **3** (Figure 3). Whereas in highly diluted solutions (< 1 mM) the isomerisation rate constant shows an average value of 6×10^{-4} s^{-1}, this value increases considerably, reaching a value that is 130-fold higher at 2.5 mM solutions. At higher concentrations the rate constant reaches a plateau, which possibly indicates that the isomerisation step of all the azo dye molecules is effectively assisted by hydrogen bonding promoted by a second azophenol molecule. Nevertheless, it is clear that the solvent-assisted process is still much faster than that of the self-assisted pathway of the azo dye (see Table 1). In this respect, the fact that a deuterated sample of **3** in toluene shows essentially the same kinetic behaviour at low dye concentrations (○ in Figure 3) than the non-deuterated compound **3**, clearly indicates that no intermolecular hydrogen bonding is involved in the process, both in the absence of polar solvents or self-aggregation conditions.

Further evidence that intermolecular hydrogen bonding can effectively assist the thermal back reaction of azophenols in non-protic solvents came from a study of the thermal back isomerisation of *cis*-**3** in methanol and d_1-methanol (Figure 4). As expected, whereas in methanol (pK_a = 15.5)[44] the process is characterized by a rate constant of 8.5 s^{-1}, the value decreases to 4.9 s^{-1} when d_1-methanol is used. Such an isotopic influence due to the lower acidity of the O−D bond was also found for both 4-hydroxy-4'-methoxyazobenzene and 4,4'-dihydroxyazobenzene with similar results. For the former compound the rate constant values changed from 9.4 to 6.0 s^{-1} on going from methanol to d_1-methanol, whereas for the latter compound these values changed from 16.4 to 8.1 s^{-1}.

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The values of $\Delta V^{\neq}$ (Table 2) are a definite indication of the distinct involvement of the solvent in the *cis*-to-*trans* isomerisation process. For the protic polar solvents methanol and ethanol, the activation volumes are significantly positive, which is opposite to the electrostriction contraction expected when polar molecules solvate the charge separated transition state generated in a rotational isomerisation mechanism. The only way to come to terms with this observation is to refer to the involvement of directional outer-sphere hydrogen bonding interactions of the polar transition state with the protic solvent molecules within the solvation cage. This fact has already been observed in a rather large number of cases in coordination chemistry substitution and redox processes in polar and hydrogen-bonding prone solvents, water in particular.[41–43] Furthermore, for compounds **4** and **5** the effect is enhanced due to the higher push-pull character of the process. Summarizing, the experimentally determined values of the activation volumes are more positive for the systems where a larger hydrogen-bonded solvent cage might be expected. That is, azo derivatives showing a push-pull character generate a kind of domino effect that implies an increased number of protic polar solvent molecules in the transition state of the process.

In this context, the analysis of the activation volumes determined for the *ortho*-substituted azophenols **6** and **7** is even more revealing. Table 2 clearly shows that the values of $\Delta V^{\neq}$ for the back *cis*-to-*trans* isomerisation of these derivatives, both in protic and non-protic polar solvents, are consistently negative in line with pure electrostriction contraction in a rotational charge-separated mechanism. Given the fact that for these azo derivatives hydrogen bonding can be established efficiently in an intramolecular way, as a consequence of the placement of the hydroxyl group in the *ortho* position, the thermal isomerisation step occurs *via* a rotation mechanism, independently of the solvent used.

Adding up, $\Delta V^{\neq}$ for the *ortho*-hydroxy azo compounds **6** and **7** in toluene are *ca.* 0 even evolving through a rotational mechanism (as we have shown, see above), and the alkoxy-substituted compounds **1** and **2**, have values of $\Delta V^{\neq} \approx 0$ in toluene, due to the fact that they operate *via* an inversion mechanism. Consequently, the mechanism by which azo derivatives thermally isomerise cannot be unambiguously determined with the sole aid of the activation volumes and, thus, other activation parameters must be considered. In this way, from data

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reported in Table 2 and 3, it can be proposed that the isomerisation mechanism for *para*-hydroxy azo derivatives **3-5** is rotation in polar solvents (ethanol and acetonitrile) and that in non-polar solvents (toluene) it could be essentially the same, since the thermal activation parameters reported, seem to be independent of solvent polarity and within the range for well-established rotation mechanisms.

Conclusion

The thermal *cis*-to-*trans* isomerisation process of a series of hydroxyl substituted azo derivatives has been studied kinetico-mechanistically as a function of temperature, pressure and dye concentration to investigate the type of isomerisation mechanism (inversion *versus* rotation) taking place. Furthermore, some experiments were carried out on deuterated species and solvents with the same purpose. Results clearly indicate that the thermal back *cis*-to-*trans* isomerisation process takes place through an inversion mechanism for the non-hydroxy azo dyes, whatever solvent is used. On the contrary, for azophenols with hydroxy substitution at the *ortho*-position, relative to the azo function, the operational mechanism is determined to be always rotation. Finally, for *para*-substituted azophenols, the transition state is solvent sensitive; while the isomerisation mechanism is clearly rotation in polar solvents, in non-polar solvents the thermal and pressure activation parameters suggest that it can be essentially the same.

Experimental Section

Kinetics. The population of *cis*-azobenzenes was generated by UV photolysis and its back-relaxation to the *trans* form 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 aqueous solution of $Co(NO_3)_2$ ($320 < \lambda_{Irrad} < 390$ nm); irradiation was pursued until no further changes were observed in the UV-Vis spectrum of the sample (*ca.* 10 min). After this time the solutions were thermostated in the dark at the desired temperature and pressure, and the thermal *cis*-to-*trans* isomerisation was monitored by the change in the electronic spectrum of the sample

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(Figure 1b). Atmospheric pressure runs were monitored on a Varian Cary 50 spectrophotometer; for runs at variable pressure, a previously described pressurizing system and pillbox cell were used which was connected to a J&M TIDAS spectrophotometer; the systems have already been described,[45] as well as the software used for the determination of the first order rate constants involved.[46,47]

For short-lived samples at ambient pressure, the thermal *cis*-to-*trans* isomerisation process was studied by nanosecond laser flash-photolysis. The *cis* form of the azo derivative was generated by a Q-switched Nd-YAG laser (λ_{Irrad} = 355 nm, 5 ns pulse width, 1-10 mJ per pulse) and the time evolution of the UV-Vis spectrum of the sample was monitored perpendicularly by a white-light beam produced by a PTI 75 W Xe lamp; a post-sample monochromator and a Hamamatsu R928 photomultiplier were used, and their output fed into a digital oscilloscope through a 50 Ohm resistor. The observation wavelength was set at 370 nm in all the cases, where no isomerisation of the azo compounds took place. For runs at elevated pressure, laser flash photolysis within the nano- to milli-second time scale was carried out at 298 K using a LKS spectrometer (Applied Photophysics, UK) equipped with Nd:YAG laser pump source Surelite I-10 Continuum (λ_{Irrad} = 355 nm, max 100 mJ, 5 ns pulse width). Samples were monitored by a Xe lamp, monochromator and Hamamatsu R11568 photomultiplier. The laser line was connected to a 4-window high-pressure cell in a perpendicular arrangement using a 'pill-box' optical cuvette and pressure gear as described elsewhere.[48] Additional spectral analyses of the solutions were made using a Perkin Elmer Lambda 950 UV-vis-NIR spectrometer.

Unless otherwise stated, the experiments were carried out with *ca.* 1×10^{-5} M solutions of the azo-dye in the corresponding solvent; no photo-degradation of the compounds was observed under the conditions of the study. For the fast reactions, observed rate constants were derived in all cases from the corresponding absorbance *versus* time traces using the standard software indicated above. For long-lived species, the full spectra were collected as a function of time, and no dependence of the values of the observed rate constants on the selected wavelengths was detected, as expected for reactions where a good retention of isosbestic points is observed.[49] All post-run fittings for the determination of the thermal and

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pressure activation parameters were carried out by the standard available commercial programs. Table S1 (ESI†) collects all the observed rate constants measured as a function of all the variables used. In all instances, the experimental error associated to rate constants was of less than 10 %.

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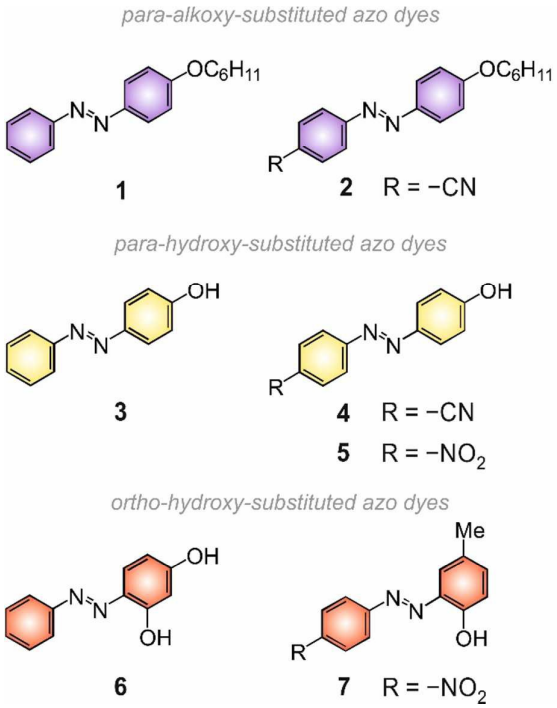
Schemes and Figures



Scheme 1. Chemical structures of *para*-alkoxy- (**1** and **2**), *para*-hydroxy- (**3**-**5**) and *ortho*-hydroxy- (**6** and **7**) substituted azo dyes.

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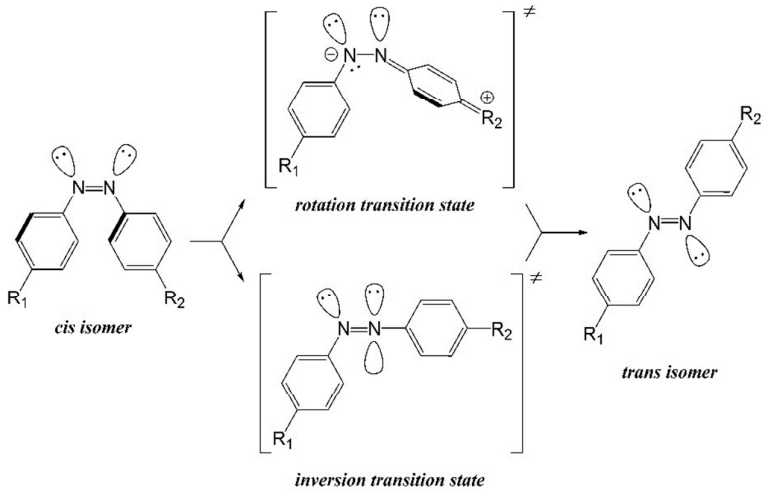

Scheme 2. Rotation and inversion transition states for the thermal back *cis*-to-*trans* isomerisation occurring on azo derivatives.[24]

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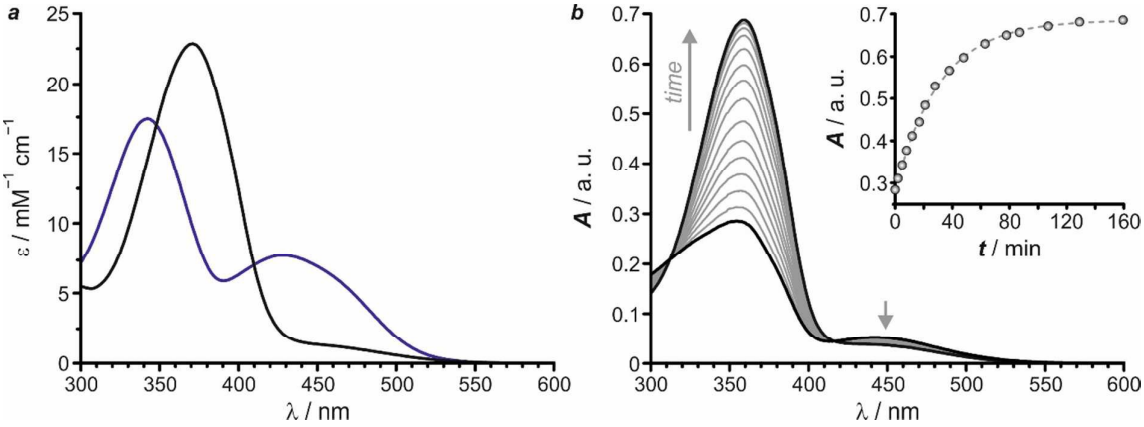

Figure 1. a) Electronic spectra of the *para*- and *ortho*-substituted nitro-azophenols **5** (black) and **7** (blue) in toluene. b) Changes in the electronic spectrum of **4** observed during the thermal *cis*-to-*trans* isomerisation at 25 ºC ([**4**] = 2.7×10^{-5} M).

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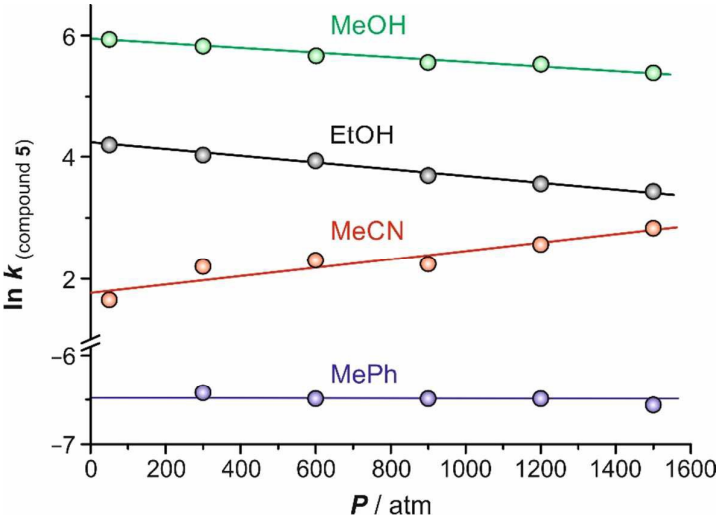

Figure 2. Pressure dependence of the first order rate constants for the *cis*-to-*trans* isomerisation reaction of compound **5** in the different solvents used at 298 K.

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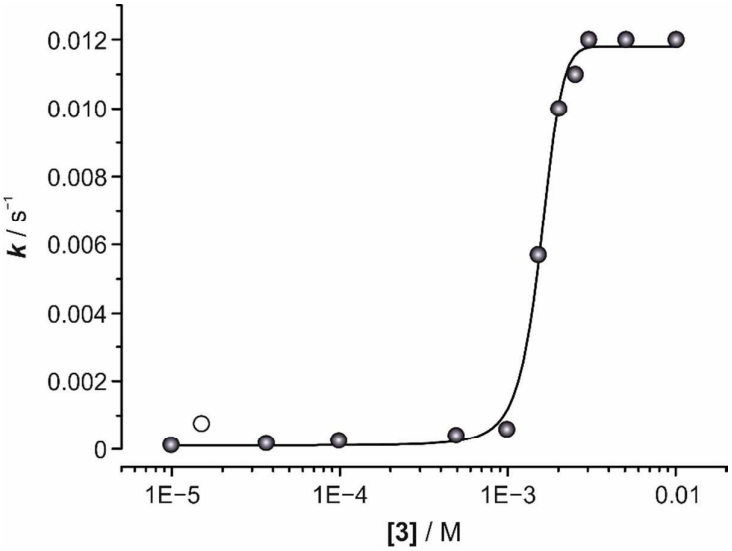

Figure 3. Dependence of the isomerisation rate constant, *k*, on the azo photochrome concentration in toluene for the *para*-hydroxy-substituted azo dye **3** at 298 K (○ corresponds to a deuterated sample).

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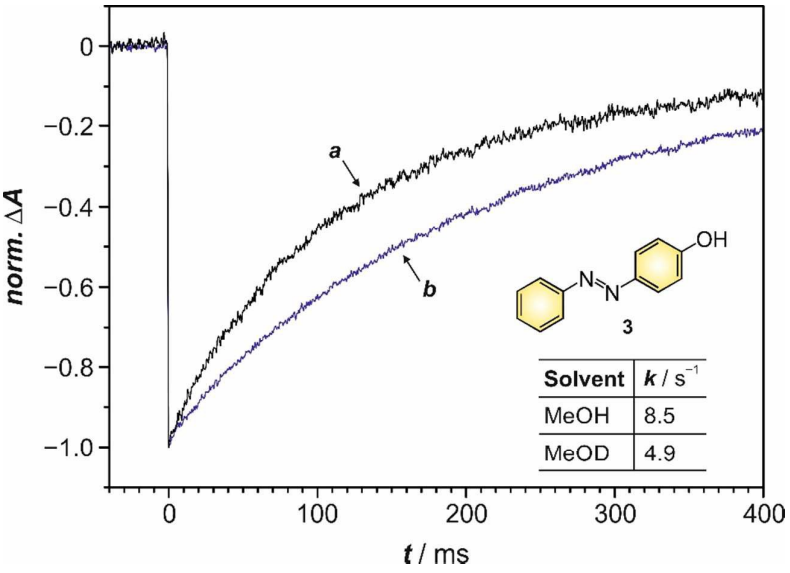

Figure 4. Transient absorption change photo-induced by laser pulsed irradiation with UV light (Nd-YAG laser, 5 ns pulse width, 10 mJ per pulse, λ_{Irrad} = 355 nm, λ_{Obs} = 370 nm) for compound **3** in methanol (***a***) and d_1-methanol (***b***).

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Tables

Table 1. Kinetic data for the thermal isomerisation process of azo dyes **1**-**7** in different solvents at 298 K.

	k /s^{-1}		
Compound	**MePh**	**MeCN**	**EtOH (MeOH)**
1[a]	5.0×10^{-6}	n.d.	4.0×10^{-6}
2[b]	3.2×10^{-5}	2.6×10^{-5}	4.6×10^{-5}
3[a]	6.0×10^{-4}	2.1	4.9 (8.5)
4	1.0×10^{-3}	5.5	3.7×10^{1}
5	1.6×10^{-3}	3.7	2.2×10^{2} (4.2×10^{2})
6[a]	1.9×10^{1}	1.9×10^{1}	8.3×10^{1}
7	3.0	4.5	1.6×10^{1}

n.d.: Not Determined. [a]Data from ref. 30. [b]Data from ref. 3.

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Table 2. Pressure activation parameters for the thermal isomerisation process of the studied azo dyes **1**-**7** in different solvents.

Compound	Solvent	$\Delta V^{\neq}$ /cm^{-3} mol^{-1}
1	EtOH[a]	~0
	MePh[a]	~0
2	EtOH[b]	~0
	MePh[b]	~0
3	EtOH	+3.5 ± 0.5
	MeOH	+3.5 ± 0.7
	MeCN	−2.4 ± 0.6
	MePh	~0
4	EtOH	+14 ± 1
	MeCN	−10 ± 1
	MePh	~0
5	EtOH	+13 ± 1
	MeOH	+9.3 ± 0.9
	MeCN	−13 ± 1
	MePh	~0
6	EtOH	−11 ± 1
	MeCN	−7.3 ± 0.6
	MePh	~0
7	EtOH	−7 ± 1
	MeCN	−6.0 ± 0.4
	MePh	~0

[a]Data from ref. 30. [b]Data from ref. 3.

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Table 3. Thermal activation parameters for the thermal isomerisation process of the azo dyes **1-5** studied in different solvents. Errors rounded to whole integers.

Compound	Solvent	$\Delta H^{\neq}$ /kJ mol^{-1}	$\Delta S^{\neq}$ /J K^{-1} mol^{-1}
1	EtOH[a]	95 ± 1	−33 ± 3
	MePh[a]	94 ± 1	−32 ± 1
2	EtOH[b]	86 ± 1	−42 ± 1
	MeCN[b]	94 ± 1	−19 ± 1
	MePh[b]	94 ± 1	−19 ± 3
3	EtOH[a]	15 ± 1	−186 ± 1
	MePh	61 ± 1	−103 ± 2
4	EtOH	13 ± 1	−171 ± 1
	MeCN	10 ± 1	−200 ± 1
	MePh	47 ± 3	−145 ± 9
5	EtOH	29 ± 1	−117 ± 2
	MePh	44 ± 1	−151 ± 3

[a]Data from ref. 30. [b]Data from ref. 3.

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Graphical Abstract