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Fast Isomerizing Methyl Iodide Azopyridinium Salts for Molecular Switches

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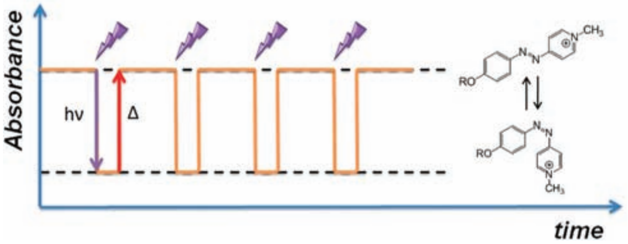
ABSTRACT



The usefulness of azopyridinium methyl iodide salts for designing new promising light-controlled molecular switches is presented. Large absorbance changes have been produced in the samples by irradiation with light at $\lambda = 355$ nm. The thermal recovery of the initial state took place completely within 130−450 ms, which is much faster than that reported previously for other push−pull azobenzene-doped nematic mixtures.

Liquid crystals (LCs) are very attractive materials because they combine the fluidity from the liquid phase and the molecular order typical of the solid state. The doping of nematic liquid crystalline matrixes with photochromic molecules, such as azobenzenes, offers a cheap and clean wireless control of the host mesophase properties, which depend mainly on the molecular alignment of the mesogens.[1,2] Irradiation of azobenzene-doped LC mixtures with UV light at a constant temperature slightly below that of the nematic-to-isotropic phase transition produces a huge decrease of the nematic order parameter due to the presence of the bent *cis* isomer in the mixture.[3,4] As a consequence, the optical properties of the whole sample suffer a dramatic change due to a cooperative motion between the mesogen molecules and those of the azo-dye (domino effect). Optical switches benefit from this phenomenon and emerge as a new type of promising light-controlled material.[5]

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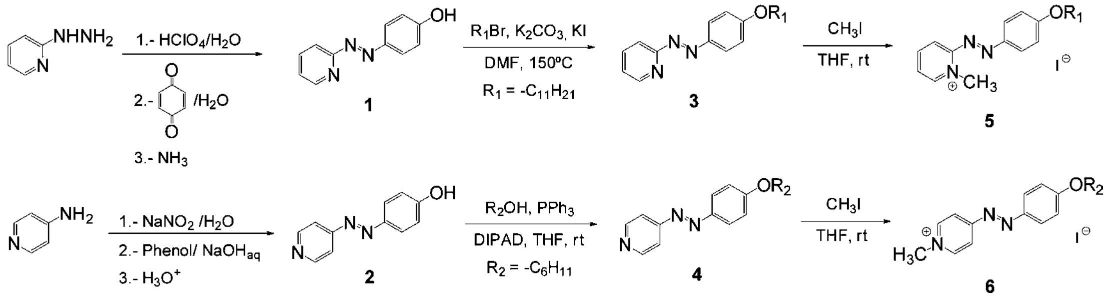
Scheme 1. Synthetic Route for Azocompounds **1**−**6**



The response time of the photoswitch is a key feature in their overall performance. Fast systems, working on the time scale of milliseconds, have been reported previously by Ikeda et al. using push−pull azoderivatives.[6] Unfortunately, they require temperatures substantially above 298 K, which limits the usefulness of the final device.

The response time of the switch depends mainly on the isomerization rate of the azo-dye. We report herein two new azopyridinium methyl iodide salts with a very fast thermal *cis*-to-*trans* relaxation process, on the time scale of a few milliseconds at room temperature. Azopyridinium salts are excellent photoactive guests able to induce great optical changes in host nematic mesophases with a short response time.

Azocompound **1** was obtained by the reaction between 2-hydrazinopyridine and 1,4-benzoquinone in acidic media.[7] The synthesis of azocompound **2** was carried out *via* the coupling of the 4-aminopyridine diazonium salt with phenol in basic media at 0−5 °C.[8] The subsequent alkylation of the free hydroxyl group of azocompounds **1** and **2** via the Williamson and Mitsunobu methodologies with 1-bromo-10-undecene and 5-hexen-1-ol yielded **3** and **4**, respectively. Further methylation of the pyridinic nitrogen atom of **3** and **4** with methyl iodide in anhydrous THF provided the methyl iodide azopyridinium salts **5** and **6**, respectively (Scheme 1).

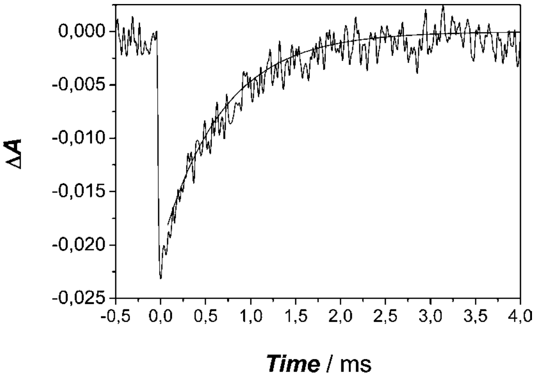


Figure 1. Transient absorption generated by UV irradiation (λ = 355 nm) of **5** in ethanol at 298 K ([**5**] = 0.02 mM, λ_{obs} = 405 nm). The continuous curve was determined by fitting of a monoexponential growth function to the data.

The electronic spectra of the stable *trans* isomers of azocompounds **5** and **6** exhibit an intense peak at 405 and 410 nm, respectively, which corresponds to the allowed $\pi-\pi^*$ transition. It should be highlighted that this band is red-shifted by 50−60 nm relatively to that of non-push−pull azobenzenes at *ca.* 350 nm (Figure S1 in Supporting Information). This notable red-shift is related to a strong charge transfer from the alkoxy group to the positively charged nitrogen atom.

The thermal *cis*-to-*trans* isomerization of azobenzenes **5** and **6** was studied by laser flash photolysis in two solvents: ethanol and acetonitrile. Figure 1 shows the transient bleaching of the 405-nm band of azocompound **5** upon pulsed laser irradiation in ethanol (Continuum Surelite I-10 Q-switched Nd:YAG laser, 355 nm, 5 ns pulse width, 1−10 mJ per pulse). The relaxation time for *cis*-**5** and *cis*-**6** was 4.6 and 4.2 ms in acetonitrile and 570 μs and 2.8 ms in ethanol, respectively (Table 1). It can be stated that the *para*-substituted azo dye **5** is always fastser than the corresponding *ortho* counterpart **6**. However, no relation has been found between the relaxation time and the solvent polarity.

Table 1. Wavelength of Maximum Absorption for the *trans* Isomer, λ_{max}, Relaxation Time at 298 K, τ, and Enthalpies and Entropies of Activation for the Thermal *cis*-to-*trans* Isomerization Process, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, of Azo-dyes **5** and **6** in Ethanol and Acetonitrile ([AZO] = 0.02 mM)

	solvent	λ_{max} (nm)	τ (ms)	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})
5	ethanol	407	0.57	48 ± 2	−22 ± 5
	acetonitrile	399	4.6	54 ± 1	−20 ± 1
6	ethanol	415	2.8	53 ± 1	−19 ± 4
	acetonitrile	409	4.2	53 ± 2	−22 ± 6

The activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) for the back reaction of azo-dyes **5** and **6** were determined in both solvents (Table 1). The enthalpy of activation for **5** and **6** was *ca.* 50 kJ mol^{-1} lower than that registered for non-push−pull azo-dyes,[9] although the entropies of activation for both types of azoderivatives were comparable (around −20 J K^{-1} mol^{-1}).

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The activation parameters reveal that the transition state is easily reached and the system does not experiment a strong molecular reorganization on achieving it from the initial *cis* state, thereby pointing to a rotational isomerization mechanism.

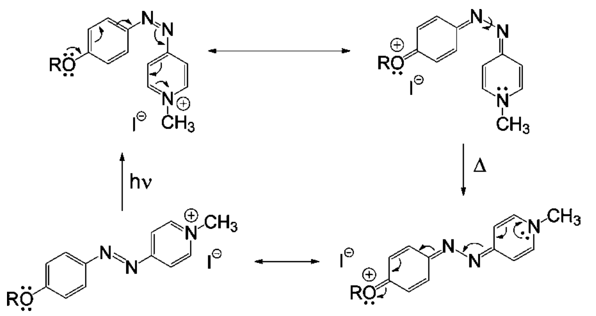

Figure 2. Mechanism proposed for the thermal *cis*-to-*trans* isomerization process for the azopyridinium methyl iodide salt **5**.

Figure 2 shows the proposed mechanism for the thermal back isomerization of *cis*-**5** and *cis*-**6**. Electron transfer from the alkoxy group to the pyridinium salt produces a partial breaking of the double N−N bond of the azo moiety, thereby facilitating the rotation around this bond to recover the more stable initial *trans* configuration. The rotational mechanism has been demonstrated previously for other push−pull azobenzenes such as *N*,*N*-dialkylaminoazobenzenes.[10]

The very fast thermal relaxation process exhibited by azocompounds **5** and **6** is exploited herein for the design of new molecular switches. Two host nematic liquid crystals, **5CB** and **6CB** (4-cyano-4-*n*-alkylbiphenyls), were doped with the corresponding azo-dyes at two different molar fractions, 0.003 and 0.01. Both mesogens were chosen for their clarification temperatures, T_{N-I} (308 and 300 K respectively), conveniently close to room temperature, which is appropriate for their application as photoswitches.

Trans isomers, with a rod-like shape, tend to align themselves along the director direction. Therefore, they can be introduced into nematic mesophases at low concentrations without destroying the LC order because of their positive contribution to the nematic potential of the mesophase. However, when *trans*-to-*cis* photoisomerization occurs, the nematic potential decreases.

Figure 3 shows that the absorbance of all of the AZO-LC mixtures increased considerably within the time scale of nanoseconds upon irradiation with a laser light pulse (λ = 355 nm) at the corresponding observation wavelength, λ_{obs}. When the sample is irradiated with UV light, two simultaneous processes occur: the *trans*-to-*cis* isomerization of the azo-dye and the photoinduced nematic-to-isotropic phase transition. The absorbance of the AZO-LC mixtures in the isotropic phase is higher than in the nematic one. Thus, an increase in the probe absorbance is observed when the photoinduced phase transition takes place. When the irradiation is ceased, the initial absorbance value of the probe is recovered isothermally in the dark as a result of the thermal back-isomerization of the azo-dye and also the restoring of the nematic order of the host mesophase.

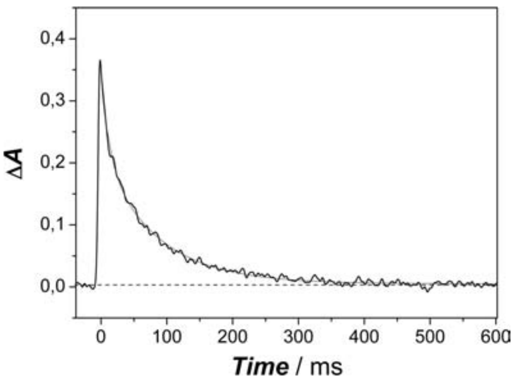

Figure 3. Transient absorption generated by UV laser pulse irradiation (λ = 355 nm) of the nematic mixture **5**−**5CB** at 306 K (x_{azo} = 0.003, λ_{obs} = 405 nm).

The kinetics of the thermal *cis*-to-*trans* isomerization deviated from a first-order profile and were fitted to a biexponential decay function (eq 1).

$$\Delta A = A{\bullet}e^{-t/\tau_1} + B{\bullet}e^{-t/\tau_2} \qquad (1)$$

The first term of the function corresponds to the back-isomerization of the chromophore. The second one can be related to the reorientation of the surrounding mesogen molecules toward the director direction.[11] Four different parameters have been used to quantify properly the actuation of the optical switch: the absorbance change produced upon UV light irradiation, ΔA, the relaxation times of the fast and slow terms, τ_1 and τ_2, and the response time of the switch, t_R, defined as the time required to restore the absorbance to 90% of its preirradiation value (Table 2).

The *cis*-to-*trans* isomerization of both chromophores took place in around 15−35 ms. The reorientation of the mesogen molecules that are close to that of the azo-dye occurred in around 78 and 205 ms, depending on the host mesogen and on the azo-dye concentration. Finally, the response times of the different optical switches ranged between 135 and 454 ms at room temperature, which are much shorter than those previously reported. The increase of the azo-dye concentration produced higher absorbance changes upon UV irradiation of the nematic mixture as well as an increase in the rate of the thermal isomerization process. At higher molar fraction

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Table 2. Absorbance Change, Δ*A*, Produced upon UV Irradiation of Nematic Samples, Characteristic Relaxation Times, τ_1 and τ_2, and Response Time for the Thermal Relaxation Process, t_R, for the Different AZO-LC Mixtures[a]

mixture	x_{azo}	ΔA	τ_1, ms	τ_2, ms	t_R, ms
5-5CB	0.003	0.287	17	111	239
5-6CB	0.003	0.550	35	205	454
	0.01	0.760	21	160	251
6-5CB	0.003	0.326	28	170	352
	0.01	0.361	15	78	145
6-6CB	0.003	0.430	19	109	135

[a] The measurement temperatures were 298 and 306 K for the **6CB** and **5CB** samples, respectively.

of the chromophore, the larger *cis* isomer population created upon photoisomerization produces a more pronounced decrease of the nematic potential. Accordingly, the more stable initial state, where all rod-like molecules point into the director direction, will be more quickly recovered after turning off the irradiation.

The temperature range in which the switches work depends on the T_{N-I} of the host mesogen used. This range was 294−300 K for the **6CB** mixtures and 305−308 K for the **5CB** ones, which are suitable ranges for further applications in optical devices. Particularly noteworthy is the combination of the azo-dye **6** and the mesogen **6CB**, whose response time of 135 ms outperforms by a factor better than 2 the earlier systems,[6] with the added benefit of the lower operation temperature.

The switching repeatability of our prototypes was checked by submitting them to several UV light−dark cycles. Neither the change of the optical properties nor the relaxation time of the molecular switch was altered by the continuous work of the system (Figure 4).

In summary, finding new azoderivatives with fast *cis*-to-*trans* isomerization kinetics at room temperature is a huge challenge in obtaining quicker molecular switches. Our results provide evidence that azopyridinium methyl iodide salts are excellent guests in this respect, enabling the modification of the optical properties of host nematic mesophases at temperatures close to 300 K. These fast responding AZO-LC systems are attractive systems from the point of view of applications of dye-doped LCs to photonic devices.

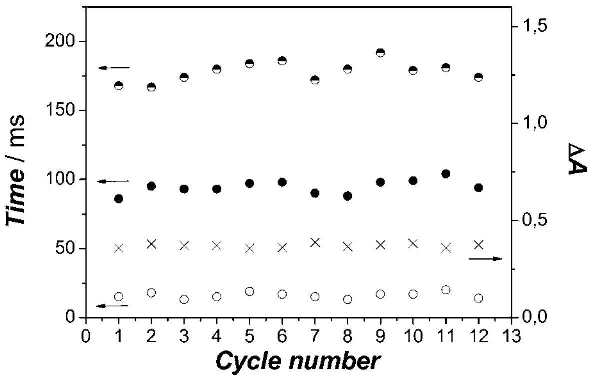

Figure 4. Repeatability of the absorbance change, Δ*A* (crosses), characteristic relaxation times, τ_1 and τ_2 (empty and filled circles, respectively), and response time for the thermal isomerization process, t_R (half-filled circles), for a **6-5CB** mixture at 306 K (x_{azo} = 0.01, λ_{obs} = 420 nm).

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Supporting Information Available: Experimental procedures and full spectroscopic data for all new compounds (**3**−**6**). First-order rate constants for the thermal *cis*-to-*trans* isomerization process of azocompounds **5** and **6** in ethanol and acetonitrile at different temperatures. This material is available free of charge via the Internet at http://pubs.acs.org.

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