J. Phys. Chem. B 2010, 114, 1287–1293 1287

Kinetico-Mechanistic Study of the Thermal Cis-to-Trans Isomerization of 4,4′-Dialkoxyazoderivatives in Nematic Liquid Crystals

Jaume Garcia-Amorós,[†] Manuel Martínez,[‡] Heino Finkelmann,[§] and Dolores Velasco*,[†]

Departament de Química Orgànica, Facultat de Química, Universitat de Barcelona, Martí i Franquès, 1-11, E-08028, Barcelona, Spain., Departament de Química Inorgànica, Facultat de Química, Universitat de Barcelona, Martí i Franquès, 1-11, E-08028, Barcelona, Spain, Institut für Makromolekulare Chemie, Albert-Ludwigs-Universität Freiburg, Hermann-Staudinger-Haus, Stefan-Meier-Strasse 31, D-79104 Freiburg, Germany

Received: October 6, 2009; Revised Manuscript Received: December 11, 2009

4,4′-Dialkoxy-substituted azobenzenes are usually required for technical applications. Here, we study the mechanism through which the azo-dye thermally isomerizes from the unstable cis isomer to the more stable trans isomer when it is incorporated in the nematic liquid-crystalline state. We have determined the kinetic and thermal activation parameters for this process in different nematic environments. Their comparison with those values obtained in isotropic media demonstrates that the mechanism through which the thermal cis-to-trans isomerization takes place is the inversion pathway in all the physical states studied. The nematic order increases the rate of the thermal cis-to-trans isomerization process. This fact is related to a cooperative interaction established between the mesogen molecules and the azo-dye. This effect is not present in the isotropic state.

1. Introduction

Liquid crystals are unique materials that exhibit the molecular order characteristic of the crystalline state and the molecular mobility typical of the liquid phase.[1] The potential application of liquid-crystalline systems arises from the possibility to change the alignment of the mesogens as a response to a diversity of external stimuli, such as light,[2,3] heat,[4−6] mechanical or electromagnetic fields,[7] etc. Light is probably the best alternative to control and modify the properties of liquid-crystalline systems (instead of electricity or heat) because it is a clean and cheap energy source; furthermore, this type of triggering can be controlled quickly and remotely.[8] For this reason, nowadays, there is a growing interest in the study of the properties of photoactive, dye-doped, liquid-crystalline systems, given their possible application as information processing materials.

Azobenzenes are photochromic organic molecules that undergo a clean and reversible isomerization process. The thermodynamically stable trans isomer can be transformed to the metastable cis isomer by irradiation with UV light. The inverse process (cis-to-trans isomerization) can be carried out either by heating or by irradiation with visible light.[9] The conformational changes associated with these isomerization processes make azobenzenes ideal candidates to produce optically controlled materials. The mechanism of its thermal cis-to-trans isomerization has attracted much attention for many years and has given rise to controversy. For the process, two different mechanisms have been proposed (Figure 1): one involving a simple rotation around the N−N bond[10,11] and another implying an inversion, in-plane lateral shift, through a linear state.[12−14]

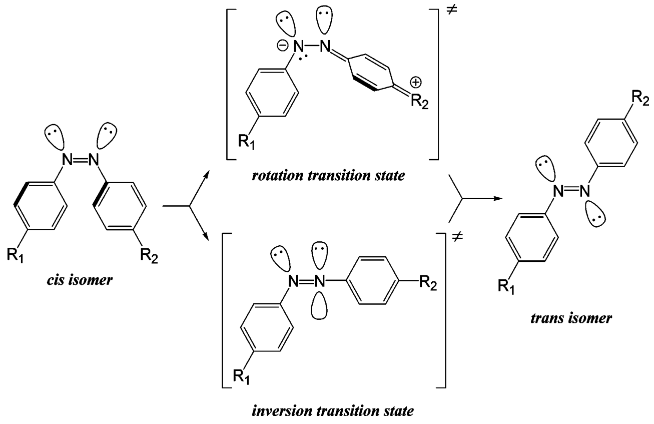


Figure 1. Rotation and inversion mechanisms proposed for the thermal cis-to-trans isomerization processes of azobenzenes.

Since the first observation about azobenzene isomerization from Hartley in 1937,[15] many efforts have been put forth in the investigation of its cis-to-trans isomerization mechanism in isotropic solvents. To the best of our knowledge, only a few studies about this mechanism in liquid-crystalline solvents have been carried out,[16−20] this field being still rather unexplored. Very recently, even the isomerization process has been studied on microcrystals in the absence of any solvent.[21] It is thus clear that, given the great interest generated on azobenzene-doped nematic liquid crystals, a thorough and comprehensive kinetico-mechanistic study about the azobenzene cis-to-trans thermal isomerization process in a mesomorphic environment is needed. The knowledge of the rate and the actuating mechanism of the cis-to-trans isomerization process in azobenzene-doped liquid crystals is of great importance for designing promising new photoactive materials to be used in optical switching, information storage, and artificial muscles, among other applications.[22−25]

This contribution tries to establish the mechanism through which the azobenzene molecules thermally isomerize from the thermodynamically unstable cis isomer to the more stable trans isomer when they are immersed in the nematic liquid-crystalline state. The kinetic and thermal activation parameters for the

---

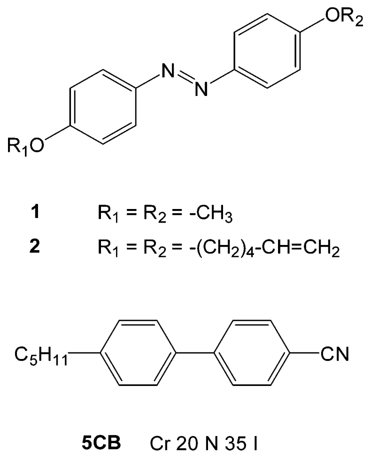
* To whom correspondence should be addressed. Phone: 00 34 93 403 92 60. Fax: 00 34 93 339 78 78. E-mail: dvelasco@ub.edu.

[†] Departament de Química Orgànica, Universitat de Barcelona.

[‡] Departament de Química Inorgànica, Universitat de Barcelona.

[§] Albert-Ludwigs-Universität Freiburg.

10.1021/jp909557h



1 $R_1 = R_2 = -CH_3$

2 $R_1 = R_2 = -(CH_2)_4-CH=CH_2$

5CB Cr 20 N 35 I

Figure 2. Chemical structure of the azoderivatives **1** and **2** and of the nematic mesogen **5CB**.

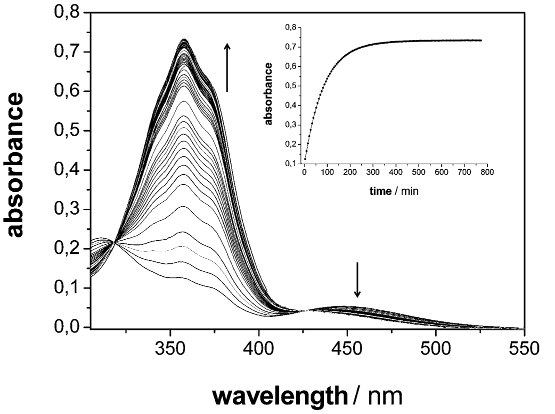


Figure 3. Changes in the electronic spectrum of a **1** cis-to-trans isomerizing toluene solution at 45 °C ($\Delta t = 360$ s, [**2**] $= 3 \times 10^{-5}$ M).

thermal cis-to-trans isomerization process have been determined in nematic monodomain and polydomain phases for two different 4,4′-dialkoxy-substituted azoderivatives and compared with those obtained in isotropic solutions. In isotropic solvents, the pressure activation parameters have been determined as a definite proof of the actuating mechanism for all the processes.[26] The mesogen choice is based on its rodlike structure, similar to that of the dyes and the existence of its nematic phase between 20 and 35 °C, which is convenient for technical applications.

2. Experimental Methods

2.1. Instruments and Materials. Two different azo-dyes have been chosen as photoactive molecules for the kinetic study: 4,4′-dimethoxyazobenzene (**1**) and 4,4′-di-(5-hexenyloxy)-azobenzene (**2**) (Figure 2), which differ in the length of the lateral alkoxy chains; their preparation has been carried out according to the procedures described in the literature.[27,28] All compounds were characterized by ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra collected on a Varian Mercury spectrophotometer. All the solvents used in the kinetic studies—ethanol (Sharlau), toluene (Sharlau), cyclohexane (Aldrich), acetonitrile (Aldrich), and the nematic mesogen 4-cyano-4′-*n*-pentylbiphenyl (**5CB**, Figure 2)[29] (Alpha Aesar)—were used as received.

Polarized optical microscopy (POM) was carried out using a Nikon Eclipse polarizing microscope at room temperature. Polarized electronic spectra of the azobenzene-doped liquid-crystalline mixtures were measured with a Varian Cary 500E instrument using a Glan-Thompson polarizer between the light source and the sample.

2.2. Preparation and Order Analysis of the Nematic Solutions. For the kinetic experiments in the liquid-crystalline state, solid solutions of the different azocompounds in the nematic mesogen **5CB** were used. Samples were prepared by mixing the desired amounts of **5CB** and the corresponding azo-dye, followed by homogenization by magnetic stirring for 10 min in the isotropic state. Standard concentration of the solid solutions was 4×10^{-3} M, to avoid possible effects derived from self-aggregation of the dye.

Monodomain samples were prepared in 10 and 4 μm optical path quarz cells. The cell surface was rubbed with a piece of cloth in a single direction, causing the alignment of the mesogens due to their electrostatic interaction with the cell surface. Homogeneity of the samples was checked by local probe microscopy. POM experiments were run by rotation of the analyzer of the microscope with respect to the rubbing direction. On reaching 45°, the expected change from darkness to brightness associated with the monodomain was observed. The absence of characteristic textures was also detected by POM. Polydomain samples were prepared using the above solid solutions in 1 mm optical path cells. The order parameter of the monodomain and polydomain solutions was analyzed by means of polarized UV−vis spectroscopy. POM microphotographs of a monodomain and polydomain of a solid solution of **2** in **5CB** before irradiation at room temperature are shown in Figures S1 and S2 in the Supporting Information section.

2.3. Kinetic Experiments. For the experiments in isotropic solvents, $\sim 3 \times 10^{-5}$ M solutions of the azo-dye in the corresponding solvent were used. In this case, 1 cm optical path quarz cells were used. For the solid solutions, the concentration was $\sim 4 \times 10^{-3}$ M (see above). Irradiation of the samples was carried out with a Philips high-pressure mercury lamp (500 W nominal power) and using a 0.5 M solution of $Co(NO_3)_2$ as an optical filter; irradiation was pursued until no changes were observed in the electronic spectrum of the sample on further irradiation; the usual irradiation times were 10 min for isotropic solutions and 45 min for solid solutions in **5CB**. Afterward, solutions were thermostatted in the dark at the desired temperature, and the thermal cis-to-trans isomerization was monitored by the change in the electronic spectrum of the sample. Atmospheric pressure runs were monitored on a Varian Cary 500E spectrophotometer. For runs at variable pressure, a previously described pressurizing system and pillbox cell was used, which was connected to a J&M TIDAS spectrophotometer.[30]

Observed rate constants were derived in all cases from absorbance versus time traces at the wavelengths of maximum absorption for the corresponding trans isomers using standard software packages.[31] No dependence of the values of the observed rate constants on the selected wavelengths was detected, as expected for reactions in which a good retention of isosbestic points is observed, and in all cases, the absorbance versus time traces fit perfectly to a first-order rate profile (Figure 3). No dependence of the rate constants on the concentration of the azo-dye was observed, as expected for first-order processes. All postrun fittings for the determination of the thermal and pressure activation parameters[32] were carried out by the standard available commercial programs. Table S1 (Supporting Information) collects all the observed rate constants measured as a function of the solvent, temperature, and pressure.

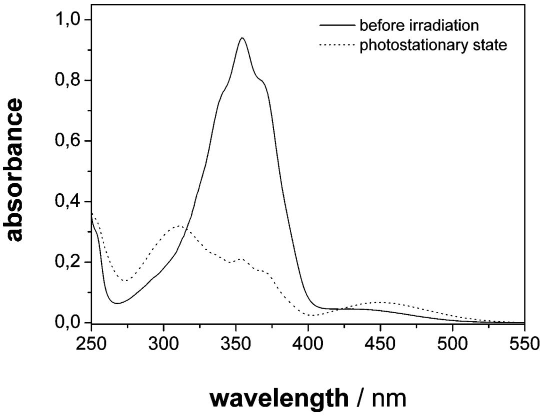


Figure 4. Electronic spectrum of a **2** (3×10^{-5} M) solution in cyclohexane before irradiation (solid line) and once the photostationary state has been reached (dotted line).

3. Results

The thermodynamically stable trans form of azobenzenes **1** and **2** can be converted to the metastable cis isomers by irradiation with UV light. To quantify the relative stability of the metastable cis form, the fractional amount of cis isomer present in the system after the photostationary state is reached has been determined. Different methodologies, such as nuclear magnetic resonance (NMR),[33,34] high-pressure liquid chromatography (HPLC),[35] or UV−vis spectroscopy, can be used for this purpose.[33,36,37] In our case, the extent of the trans-to-cis photoisomerization of azocompounds **1** and **2** in the isotropic solvents used (cyclohexane, toluene, ethanol, and acetonitrile) as well as in a monodomain solution of the nematic mesogen **5CB** was determined via UV−vis spectroscopy at 298 K. The cis isomer fraction in the photostationary state, *Y*, can be determined by eq 1.[38]

$$Y = \frac{1 - A_{\mathrm{ph}}/A_0}{1 - \varepsilon_{\mathrm{cis}}/\varepsilon_{\mathrm{trans}}} \qquad (1)$$

A_0 and A_{ph} correspond to the initial and the photostationary state absorbance values measured at $\lambda_{\max}$ (trans form), and $\varepsilon_{\mathrm{cis}}$ and $\varepsilon_{\mathrm{trans}}$ are the molar absorption coefficients of the cis and trans isomers at this wavelength ($\lambda_{\max}$). We have used the $\varepsilon_{\mathrm{cis}}/\varepsilon_{\mathrm{trans}} = 0.056$ literature value[38] determined for 4,4′-dimethoxyazobenzene in DMSO, which has been considered to be independent of the length of the alkoxy lateral chains and the solvent used.

Figure 4 shows the changes observed in the absorption spectra of azocompound **2** in cyclohexane at 298 K. The spectra of the stable trans isomer exhibit the expected peak at ~355 nm, corresponding to the $\pi-\pi^*$ transition, plus a weak broad band signal at ~450 nm, associated to the $n-\pi^*$ transition. Similar absorption spectra have been registered for both azocompounds in all the solvents studied. A minor red-shift of the absorption maximum and a broadening of the $\pi-\pi^*$ band was detected for the nematic samples. It is associated with the influence of the host on the dye-host aggregation equilibria.[39] On UV light irradiation, the trans-to-cis photoisomerization occurs accompanied by a decrease in the intensity of the 355 nm band and an increase in the 450 nm signal until the photostationary state is reached; that is, the inverse process of that shown in Figure 3. Table 1 collects the wavelength of the maximum absorption for the trans isomer and the extent of the photoisomerization (*Y*, eq 1) for azocompounds **1** and **2** in all the solvents studied. For the four isotropic solvents studied, the extent of the trans-to-cis photoisomerization for azocompounds **1** and **2** at 298 K is in the 80−85% range, whereas for the monodomain nematic phase (10 μm) of mesogen **5CB**, lower values of *Y* around 40% have been found. The measurement of *Y* in a thinner cell of 4 μm of optical path afforded the same value, indicating that the incident light power is enough to perform the photoisomerization throughout the nematic phase cells without gradient concentration. It has been reported for thin polystyrene films that there is no difference in the experimental *Y* value for the azo-photoisomerization in film thicknesses among the range from 40 nm to 1.5 μm.[37] Important differences in the rate of the trans-to-cis photoisomerization were also observed and qualitatively analyzed. Although the photostationary state was reached after 5 min in isotropic solvents, 30 min was needed to reach the corresponding equilibrium in the nematic phase of the liquid crystal **5CB** for our setup (see Experimental section).

TABLE 1: Electronic Spectral Data for the Trans Isomer of Azocompounds 1 and 2 in Different Solvents in the Thermodynamically Stable State and Extent of the Photoisomerization of 1 and 2 at 298 K[a]

solvent	azocompound	$\lambda_{\max}$/nm	*Y*/%
cyclohexane	**1**	352	83
	2	354	83
acetonitrile	**1**	355	84
	2	358	84
ethanol	**1**	354	79
	2	356	84
toluene	**1**	357	84
	2	356	84
5CB monodomain	**1**	364	37
	2	365	40[b]
			45

[a] [azocompound] = 3×10^{-5} M in isotropic solvents and [azocompound] = 4×10^{-3} M in nematic solvents. [b] Obtained in a measurement using a cell with an optical path of 4 μm.

The global order parameter of the nematic solutions, *S*, has been determined to account for possible differences in the kinetics of the cis-to-trans isomerization and in the actuating mechanism for this process. Figure 5 (left) shows the polarized electronic spectra of azocompound **2** in the nematic mesogen **5CB** at 298 K; the dichroic ratio, $\mathrm{DR} = A_{\parallel}/A_{\perp}$, was calculated for all the samples using the corrected absorbance of the host−guest mixture at $\lambda_{\max}$ for the trans isomer of the corresponding dye with respect to the polarized absorption of the pure nematic mesogen **5CB** in the corresponding direction. The nematic global order parameter of the nematic solutions can be then calculated as $S = (\mathrm{DR} - 1)/(\mathrm{DR} + 2)$.[40−43] For the monodomain solutions, values of *S* of 0.46 and 0.55 were determined for azocompounds **1** and **2**, respectively, whereas for the polydomain solutions, the value of *S* was effectively zero. Although for the polydomain solutions, the value of the global nematic order parameter is null, it is evident that the local order parameter should be larger and approaching the *S* value of the corresponding monodomain nematic solutions. Figure 5 (right) shows the dependence of *S* for a **2-5CB** mixture with the reduced temperature, $T_{\mathrm{red}} = T/T_{\mathrm{LC}}$. The global order parameter diminishes with an increase in the reduced temperature, as expected, until the nematic-to-isotropic phase transition ($T_{\mathrm{red}} = 1$) is reached. At this point, the global order parameter has a value around $S = 0.4$ (as predicted by Maier−Saupe theory[44]), and it becomes $S = 0$ when the isotropic phase is obtained.

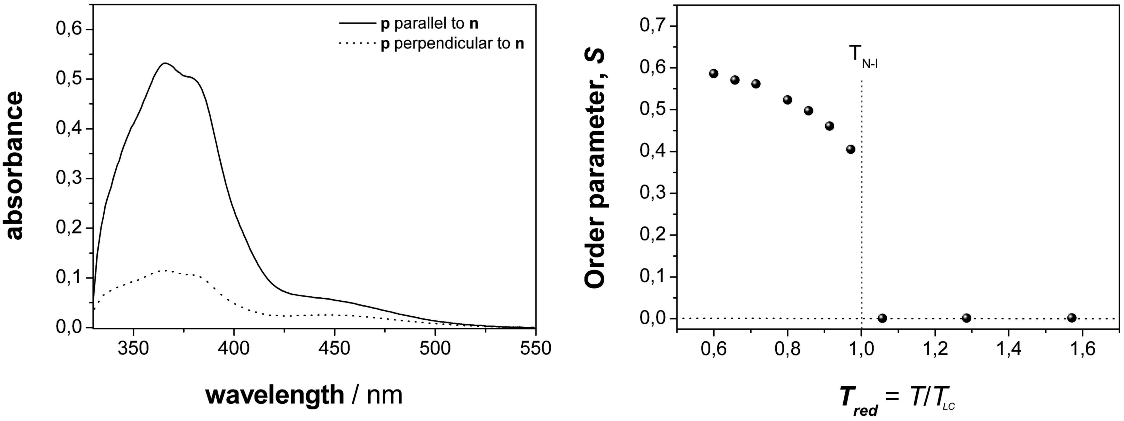


Figure 5. Electronic spectra of a solid solution of azocompound **2** (4×10^{-3} M) in **5CB** at 298 K with the incident light polarized parallel (solid line) and perpendicular (dotted line) to the nematic director (left). Evolution of the global order parameter, S, with the reduced temperature $T_{red} = T/T_{LC}$ (right).

TABLE 2: Kinetic and Thermal and Pressure Activation Parameters for the Thermal Cis-to-Trans Isomerization of Azocompounds 1 and 2 in Different Isotropic and Nematic Solvents

solvent		$10^5 \times {}^{298}k^{th}$/s^{-1}	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J K^{-1} mol^{-1}	$\Delta V^{\neq}$/cm^3 mol^{-1}
acetonitrile ($\varepsilon = 37.5$)	**2**	1.47	92 ± 1	−30 ± 3	
ethanol ($\varepsilon = 24.6$)	**1**	1.90	92 ± 1	−29 ± 3	~0
	2	2.30	91 ± 1	−30 ± 4	~0
toluene ($\varepsilon = 2.4$)	**1**	1.81	91 ± 1	−33 ± 3	~0
	2	1.95	91 ± 1	−32 ± 1	~0
cyclohexane ($\varepsilon = 2.0$)	**2**	2.38	89 ± 1	−39 ± 3	
5CB (isotropic)	**1**	2.81[a]	88 ± 1	−37 ± 2	
	2	2.72[a]	88 ± 1	−38 ± 1	
5CB (nematic) polydomain	**2**	3.42	82 ± 2	−59 ± 7	
5CB (nematic) monodomain	**1**	3.55	77 ± 1	−73 ± 3	
	2	4.28	68 ± 1	−102 ± 2	

[a] Extrapolated from the thermal activation parameters.

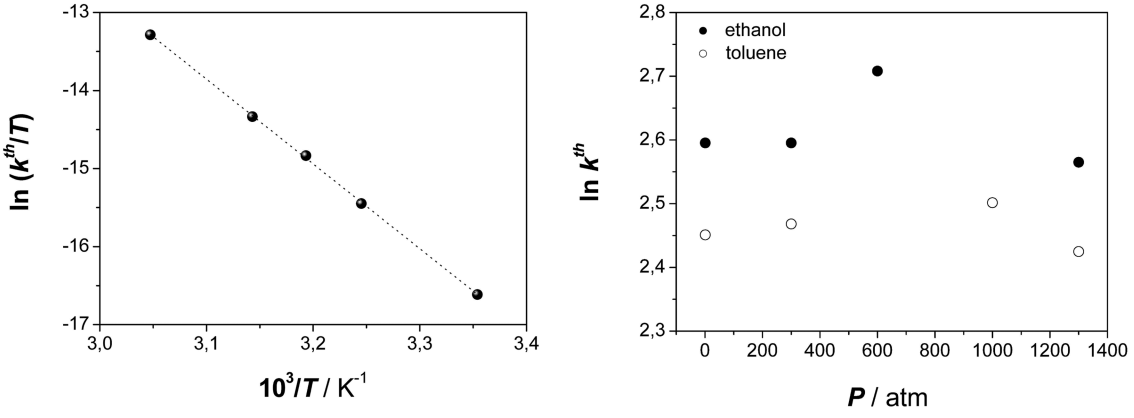


Figure 6. Eyring plot for the thermal cis-to-trans isomerization of azocompound **1** in toluene solution (left) and ln k^{th} vs P plots for azocompound **2** in the different solvents studied at 313 K (right).

Finally, the kinetico-mechanistic study of the thermal cis-to-trans isomerization process for the 4,4′-dialkoxyazoderivatives **1** and **2** in different media at different temperatures and pressures was conducted. No dependence of the rate of the thermal process on the use of scanning or diode-array instruments has been observed, which is indicative of the fact that, under the conditions used for the thermal kinetic study, all the photochemical processes can be neglected, and first-order rate constants for the thermal cis-to-trans isomerization, k^{th}, can be derived from first-order absorbance versus time traces indicated in Figure 3. The variation of these rate constants with temperature and pressure for each solvent allows for the determination of the enthalpies, entropies, and volumes of activation, $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta V^{\neq}$, using Eyring and ln k versus P plots.[45−47] Table 2 collects all the relevant kinetic and activation parameters determined in all the solvents used; Figure 6 collects the Eyring plot of azocompound **1** in toluene (left) and the ln k versus P plots of azocompound **2** in ethanol and toluene (right).

4. Discussion

Our main objective was the study of the kinetic and the actuating mechanism of the thermal cis-to-trans isomerization process of 4,4-dialkoxy-substituted azobenzenes in nematic mesophases and the analysis of the differences with respect to the conventional isotropic solvents. Given the fact that a nematic mesophase is an anisotropic environment in which the mesogens are aligned along the director direction, any deviation of this

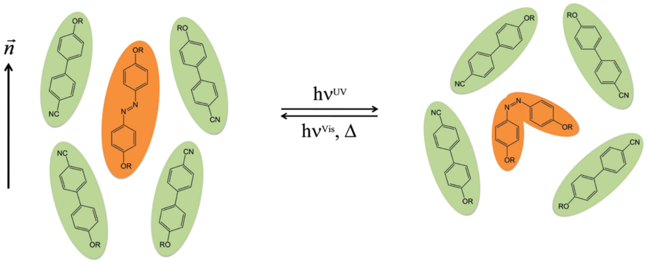


Figure 7. Schematic representation of the disorganization produced in the nematic mesophase as a consequence of the azocompound isomerization.

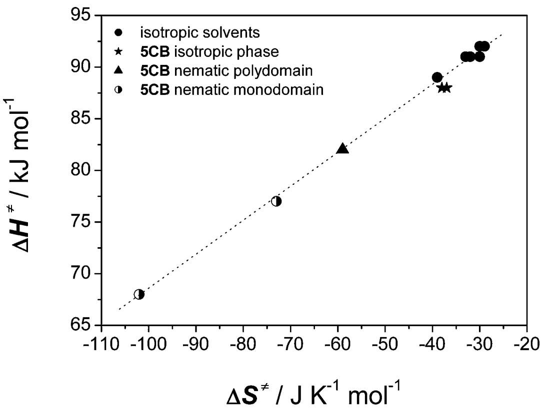


Figure 8. Plot of $\Delta H^{\neq}$ versus $\Delta S^{\neq}$, for the cis-to-trans thermal isomerization process of azocompounds **1** and **2** in all the solvents studied.

mean orientation will reduce the state of order of this phase. In this respect, trans-4,4′-dialkoxy-substituted azobenzenes, with a rodlike geometry, can be easily incorporated in the liquid-crystalline phase, thereby contributing to the nematic potential. In contrast, the cis form of the same chromophores presents a bent shape that contributes less to the nematic potential and reduces the local order parameter. When the trans-to-cis photoisomerization takes place (Figure 7), a decrease in the local order parameter occurs, and it is extended to all the nematic mesophase (domino effect).[48] This effect is evident, for example, in the decrease in the nematic-to-isotropic phase transition temperature, $T_{\mathrm{N-I}}$, of a **2**−**5CB** mixture with an azobenzene molar fraction of $x = 0.1$ after irradiation with UV light. When the trans isomer of azocompound **2** is present in the mixture, it shows a $T_{\mathrm{N-I}}$ value of 38.5 °C, but when the sample is irradiated with UV light, the $T_{\mathrm{N-I}}$ of the mixture decreases to 34.3 °C due to the presence of the bent cis isomer in the nematic solution.[28] Similar results were obtained with mixtures of azocompound **1** with **5CB** at the same molar fraction of the dye. This mixture decreased its $T_{\mathrm{N-I}}$ value from 43.0 to 37.1 °C under irradiation with UV light. Otherwise, no changes were detected by POM in the nematic samples used in the kinetic study due to the small content of the dye. In this way, these nematic samples exhibited the same $T_{\mathrm{N-I}}$ value as the pure **5CB** (35 °C), and they did not experience any change in their $T_{\mathrm{N-I}}$ under irradiation with UV light. The trans-to-cis photoisomerization produces a decrease in the local order parameter of the nematic mesophase. Therefore, in isotropic solvents, the trans-to-cis isomerization of the chromophore can be attained more easily than in nematic liquid crystals. Consequently, the trans-to-cis photoisomerization will be more favorable and faster in an isotropic environment. The data indicated in Table 1, as well as the time needed for achieving the photostationary state (see above), fully agree with this fact.

As for the thermal cis-to-trans kinetico-mechanistic study, the solvents have been chosen to cover different structural features: polar protic solvents, aprotic solvents with strong polar functions, nonpolar solvents, nonpolar solvents able to establish $\pi-\pi$ interactions with the azo-dye, and the monodomain and polydomain nematic phase and isotropic phase of **5CB**. As a whole, the processes clearly occur via the same intimate mechanism for all the solvents and phases used in the study, as can be seen in the compensation plot of $\Delta H^{\neq}$ versus $\Delta S^{\neq}$ shown in Figure 8. A common isokinetic relationship has been found to be indicative of the existence of a single reaction mechanism.[49−51] According to this, the mechanism actuating in the isotropic solvents is the same as in the liquid crystalline matrix, independent of whether it is in the isotropic or in the nematic state or if it is a monodomain or a polydomain mesophase. The isokinetic temperature of the plot, that is, the temperature at which the rate of the process is coincident for all the environments studied, corresponds to ∼40 °C. This value is close to the nematic-to-isotropic phase transition temperature of the **5CB**-azo mixtures (35 °C).

The measurement of the volumes of activation produces for these processes unequivocal evidence about the operation of the inversion or rotation isomerization mechanism (Figure 1).[49,52] The sensitiveness to medium polarity changes of the azocompound during the activation process should produce an acceleration of the thermal cis-to-trans isomerization 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 nonpolar solvents if the reaction takes place via the inversional mechanism depicted in Figure 1.[53] The thermal cis-to-trans isomerization 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.[54] The determination of the volumes of activation for the thermal cis-to-trans isomerization process of this azo-crown ether in several solvents has been carried out, and the values found in the literature were all close to zero, as expected.[53] In contrast, for push−pull azobenzenes, which undergo isomerization via the rotation mechanism, the values of the volumes of activation have been reported in the -20 cm^3 mol^{-1} range in several solvents.[26,55] It is thus clear from the experimental data collected in Table 2 that the isomerization of azocompounds **1** and **2** occurs via the inversional mechanism ($\Delta V^{\neq} \sim 0$, Figure 6 right).

Further evidence that azocompounds **1** and **2** undergo their thermal isomerization through the inversion mechanism comes from the analysis of the dependence of the first-order rate constant values with the dielectric constant of the solvent used. The values of the kinetic and activation parameters in Table 2 show no dependence of the rate constant on the dielectric constant of the solvent. For the push−pull 4-*N*,*N*-(dimethylamino)-4′-nitroazobenzene, which has been proposed to isomerize through the rotational mechanism, rate constants have been reported that show a dramatic dependence on the dielectric constant of the solvent (2.71×10^{-3} s^{-1} in pentane; 298 s^{-1} in dimethylsulfoxide).[55,56]

Once the isomerization mechanism actuating for azocompounds **1** and **2** has been unequivocally established as the inversional one (Figure 1) and found to be invariable for all the solvents studied, a detailed examination of the differences in Table 2 on the solvent nature is needed. Whereas the cis form has a $t_{1/2}$ between 8 and 13 h at 298 K in all the isotropic

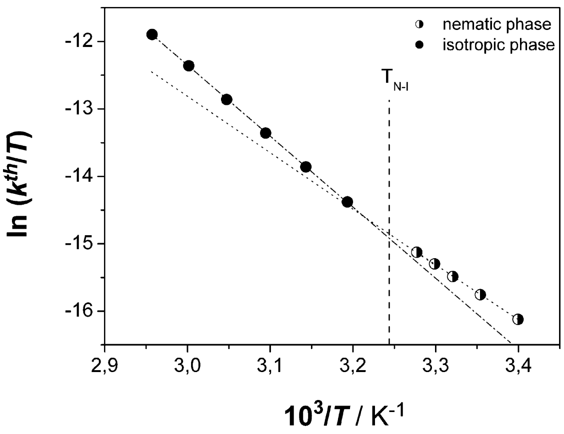


Figure 9. Eyring plot for the thermal cis-to-trans isomerization process of azocompound **2** in the nematic and isotropic phases of mesogen **5CB**.

solvents, this value decreases to around 4−5 h in the oriented nematic phase of the mesogen **5CB** at the same temperature. In a polydomain nematic solution, the value for $t_{1/2}$ is slightly larger than that registered in the monodomain sample. This difference is accompanied by changes in both enthalpies and entropies; that is, a more organized transition state, including solvent environment, implies lesser enthalpic demands.

Figure 9 shows the Eyring plot for the thermal isomerization process carried out in a **2−5CB** mixture in a temperature range that covers both nematic and isotropic phases. Two well-defined regions that correspond to the nematic and isotropic phases can be identified. The crossing between the two lines is about at 37 °C which is, within error, the measured T_{N-I} value of the **2−5CB** mixture (35 °C). Below this temperature, the sample is in the nematic phase with thermal activations parameters (Table 2) distinct from those observed at higher temperatures in the isotropic state and enthalpy and entropy of activation in line with the other isotropic solvents used in this study. Similar results were obtained for **1−5CB** mixtures.

It is evident that when dyes **1** and **2** are under the influence of the orientational field of a nematic phase, they undergo an increase in the rate of the thermal cis-to-trans isomerization. Given the fact that the trans-to-cis photoisomerization produces a modification of the nematic order decreasing the local order parameter, the thermal cis-to-trans isomerization process should effectively suffer acceleration in the nematic phase. The cooperative interaction established between the nematogen and the chromophore molecules can be held responsible for this fact.[28] For the polydomain sample **2−5CB**, with a global nematic order parameter of $S = 0$, the kinetic and activation parameters for the thermal isomerization are intermediate between the values registered in isotropic and nematic solvents. Clearly, the kinetics of the thermal cis-to-trans isomerization depends mainly on the local order parameter, which should be higher in the monodomain nematic solution than under polydomain conditions, even though the local order parameter in the latter conditions has not been obtained.

5. Conclusions

The existence of a neat isokinetic plot for all the solvents, isotropic and nematic, used in the study evidence that the mechanism for **1** and **2** cis-to-trans thermal isomerization is the same in all cases. The study of the dependence of the rate constant with the dielectric constant of the solvent and hydrostatic pressures up to 1200 atm demonstrates that the transition state of the isomerization process has a non-polar character, indicating the operation of an inversion mechanism. The analysis of the kinetic and activation parameters obtained for the thermal cis-to-trans isomerization process of azo-dyes **1** and **2** in isotropic and in a liquid-crystalline environment indicates that, even though the actuating mechanism is the same, there is a great influence of the system order in the rate of the process. An acceleration of the thermal cis-to-trans isomerization process in the liquid crystalline media is observed, and it is related to a cooperative interaction established between the mesogenic molecules and the azo-dye; the effect is lost when the isotropic state is reached.

Acknowledgment. Financial support from the European project: Functional Liquid-Crystalline Elastomers (FULCE-HPRN-CT-2002-00169) and from the Ministerio de Educación y Ciencia (Projects CTQ-2009-13797-C02-02 and CTQ-2009-14443-C02-02) is gratefully acknowledged. J. Garcia-Amorós is grateful for the award of a doctoral grant from the Universitat de Barcelona. The authors thank Carlos Rodríguez del Río for his help in the measurement of volumes of activation.

Supporting Information Available: Microphotographs of a monodomain and a polydomain sample obtained with a solid solution of azocompound **2** in the nematic mesogen **5CB** at 298 K. Values of the observed rate constants for all the reactions studied as a function of solvent, temperature and pressure for azoderivatives **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Gray, G. W. *Handbook of Liquid Crystals*; Wiley-VCH: New York, Weinheim, 1998.
(2) Ikeda, T. *J. Mater. Chem.* **2003**, *13*, 2037.
(3) Yu, Y.; Ikeda, T. *J. Photochem. Photobiol. C: Photochem. Rev.* **2004**, *5*, 247.
(4) Thomsen, D. L.; Keller, P.; Naciri, J.; Pink, R.; Jeon, H.; Shenoy, D.; Ratna, B. R. *Macromolecules* **2001**, *34*, 5868.
(5) Wermter, H.; Finkelmann, H. e-polymers; 2001, 13; www.e-polymers.org.
(6) Naciri, J.; Srinvasan, A.; Jeon, H.; Nikolov, N.; Keller, P.; Ratna, B. R. *Macromolecules* **2003**, *36*, 8499.
(7) Smela, E. *Adv. Mater.* **2003**, *15*, 481.
(8) Kondo, M.; Yu, Y.; Ikeda, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 1378.
(9) Rau, H. *Photochemistry and Photophysics*; CRC Press: Boca Raton, Fl, 1990.
(10) Talaty, E. R.; Fargo, J. C. *Chem. Commun.* **1967**, 65.
(11) See, for example, Binenboym, J.; Burcat, A.; Lifshitz, A.; Shamir, J. *J. Am. Chem. Soc.* **1966**, *88*, 5039, and references therein.
(12) Schulte-Frohlinde, D. *Justus Liebigs Ann. Chem.* **1958**, *612*, 138.
(13) Le Fevre, R. J. W.; Northcott, J. O. *J. Chem. Soc.* **1953**, 867.
(14) Jaffe, H. H. *Chem. Rev.* **1953**, *53*, 191.
(15) Hartely, G. S. *Nature* **1937**, *140*, 281.
(16) Matczyszyn, K.; Sworakowski, J. *J. Phys. Chem. B* **2003**, *107*, 6039.
(17) Matczyszyn, K.; Chwialkowska, A.; Sworakowski, J. *Thin Solid Films* **2008**, *516*, 8899.
(18) Bossi, M. L.; Murgida, D. H.; Aramedia, P. F. *J. Phys. Chem. B* **2006**, *110*, 13804.
(19) Leigh, W. J.; Frendo, D. T.; Klawunn, P.-J. *Can. J. Chem.* **1985**, *63*, 2131.
(20) Otruba, J. P.; Weiss, R. G. *J. Org. Chem.* **1983**, *48*, 3448.
(21) Koshima, H.; Ojima, N.; Uchimoto, H. *J. Am. Chem. Soc.* **2009**, *131*, 6890.
(22) Camacho-Lopez, M.; Finkelmann, H.; Palffy-Muhoray, P.; Shelley, M. *Nat. Mater.* **2004**, *3*, 307.
(23) Cviklinski, J.; Tajbakhsh, A. R.; Terentjev, E. M. *Eur. Phys. J. E* **2002**, *9*, 427.
(24) Ikeda, T.; Mamiya, J.; Yu, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 506.
(25) Balzani, V.; Credi, A.; Venturi, M. *Chem. Soc. Rev.* **2009**, *38*, 1542.
(26) Asano, T.; Okada, T. *J. Org. Chem.* **1984**, *49*, 4387.
(27) Sanchez-Ferrer, A.; Hinkelmann, H. *Macromolecules* **2008**, *41*, 970.

(28) Garcia-Amorós, J.; Szymczyk, A.; Velasco, D. *Phys. Chem. Chem. Phys.* **2009**, *11*, 4244.

(29) Landolt-Börnstein, H. *Transition Temperatures and Related Properties of One-Ring Systems and Two-Ring Systems without Bridging Groups*; Springer Verlag: Berlin, New York, 1992.

(30) Gallego, C.; Martínez, M.; Safont, V. S. *Organometallics* **2007**, *26*, 527.

(31) Binstead, R. A.; Zuberbuhler, A. D.; Jung, B.; Spectrum Software Associates; *SPECFIT32. (3.0.34)*, 2005.

(32) Levine, I. N. *Fisicoquímica*; McGraw Hill: New York, 1988.

(33) Moniruzzman, M.; Talbot, J. D. R.; Saboy, C. J.; Fernando, G. F. *J. Appl. Polym. Sci.* **2006**, *100*, 1103.

(34) Tait, K. M.; Parkinson, J. A.; Bates, S. P.; Ebenezer, W. J.; Jones, A. C. *J. Photobiol. Photochem. A: Chem.* **2003**, *154*, 179.

(35) Ruslim, C.; Ichimura, K. *Macromolecules* **1999**, *32*, 4254.

(36) Eisenbach, C. D. *Makromol. Chem.* **1978**, *179*, 2489.

(37) Tateishi, Y.; Tanaka, K.; Nagamura, T. *J. Phys. Chem. B* **2007**, *111*, 7761.

(38) Sasaki, T.; Ikeda, T.; Ichimura, K. *Macromolecules* **1993**, *26*, 151.

(39) Maruszewski, K. *J. Mol. Struct.* **1999**, *479*, 53.

(40) West, J. L.; Magyar, G. R.; Kelly, J. R.; Kobayashi, S.; Iimura, Y.; Yoshida, N. *Appl. Phys. Lett.* **1995**, *67*, 155.

(41) Nishikawa, M.; West, J. L. *Jpn. J. Appl. Phys.* **1999**, *38*, L331.

(42) Park, W. S. *J. Korean Phys. Soc.* **2000**, *37*, 331.

(43) Millaruelo, M.; Oriol, L.; Serrano, J. L.; Piñol, M.; Saez, P. L. *Mol. Cryst. Liq. Cryst.* **2004**, *411*, 451.

(44) Maier, W.; Saupe, A. *Z. Naturforsch.* **1960**, *15*, 287.

(45) Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1935**, *31*, 875.

(46) Eyring, H. *J. Chem. Phys.* **1935**, *3*, 107.

(47) Tobe, M. L. *Inorganic Reaction Mechanisms*; Nelson: London, 1977.

(48) Sung, J. H.; Hirano, S.; Tsutsumi, O.; Kazanawa, A.; Shiono, T.; Ikeda, T. *Chem. Mater.* **2002**, *14*, 385.

(49) Asano, T. *High Pressure Chemistry*; Wiley-VCH, Weinheim, 2002.

(50) Crespo, M.; Martínez, M.; Sales, J. *Organometallics* **1993**, *12*, 4297.

(51) Favier, I.; Gómez, M.; Granell, J.; Martínez, M.; Font-Bardía, M.; Solans, X. *Dalton Trans.* **2005**, 123.

(52) Leffler, E.; Grundwald, E. *Rates and Equilibria of Organic Reactions*, Wiley-VCH: New York, 1963.

(53) Asano, T.; Okada, T.; Shinkai, S.; Shigematsu, K.; Kusano, Y.; Manabe, O. *J. Am. Chem. Soc.* **1981**, *103*, 5161.

(54) Shinkai, S.; Kusano, Y.; Shigematsu, K.; Manabe, O. *Chem. Lett.* **1980**, 1303.

(55) Asano, T.; Yano, T.; Okada, T. *J. Am. Chem. Soc.* **1982**, *104*, 4900.

(56) Nishimura, N.; Kosako, S.; Sueishi, Y. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1617.

JP909557H