

Photochemical and thermal isomerization of anionic azobenzene amphiphiles in homogeneous and aggregated systems

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Abstract

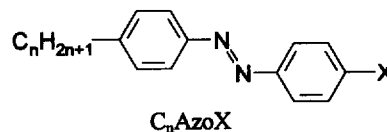
Kinetic and thermodynamic parameters of the *trans*–*cis* photoisomerization of *trans*-4-(4'-alkylphenylazo)phenyl derivatives ($C_n\text{AzoX}$; $n = 4, 8$; $X = \text{SO}_3, \text{COONa}$) by 366 nm UV irradiation as well as the *cis*–*trans* thermal reversion of the azobenzene moiety have been determined by means of the ^1H NMR technique in homogeneous and micellar systems of $C_n\text{AzoX}$. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Photochemical isomerization; Thermal isomerization; Anionic azobenzene; UV irradiation

1. Introduction

Para-substituted azobenzene derivatives have received considerable attention because of practical use of these compounds for the study of their undesirable photochromism [1] and photodegradation [2,3]. Much attention has been devoted to photoisomerization of azobenzene-containing amphiphiles in solutions [4], monolayers and multilayers [4], thin films [4], membranes [4], host–guest complexes [4], and polymers [5], because they are one of the representative photochromic compounds [6]. Azobenzene and many of its derivatives performed reversible transformation from the generally more stable *trans* form to the less stable *cis* form upon irradiation with UV or temperature dependent [7]. Many theoretical and experimental papers deal with the roto-resistant property of the $\text{N}=\text{N}$ double bond [1,5–8]. Photo-induced isomerism of azobenzene proceeds with large structural change in geometry [5] and is relatively insensitive to fluid reaction media [7,8]. The thermal *cis*–*trans* isomerization is enhanced in polar aprotic solvents [7,8]. It has also been found that the donor–acceptor substituted azobenzenes exhibit strong solvatochromic behavior both with respect to absorption spectra of the thermally stable *trans*-isomers and to rates of thermal isomerization of the photochemically generated *cis*-isomers [8]. The *cis*–*trans* azobenzene isomeri-

zation of the azobenzene moiety represents virtually a model photochemical process for the photochromism. The investigation of chemical and physical behavior of the amphiphilic photochromic azobenzene moieties in micellar systems is relatively recent [4]. Contrast between the behavior in homogeneous and microheterogeneous solutions provide important details of the distribution and dynamics of the guest with respect to the hydrophobic–hydrophilic interface. We have chosen *trans*-4-(4'-alkylphenylazo)phenyl derivatives, abbreviated as $C_n\text{AzoX}$ ($n = 4, 8$; $X = \text{SO}_3, \text{COONa}$) which offer the possibility to study in detail the photochemical and thermal processes in homogeneous water solution and aggregated systems of $C_n\text{AzoX}$ amphiphiles.



Kinetic and thermodynamic parameters of the *trans*–*cis* photoisomerization by the 366-nm UV irradiation as well as the *cis*–*trans* thermal reversion of the photochromic group have been determined in the temperature range of 15–35°C in order to develop ways to control the photochemical reactivity of a new group of photochromic amphiphiles.

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2. Experimental section

2.1. General

Photochromic surfactants $C_n\text{AzoSO}_3\text{Na}$ and $C_n\text{AzoCOONa}$ were obtained and purified according to the published procedure [9]. ^1H NMR (300 MHz) NMR spectra were run on a Bruker DRX-300 spectrometer, with residual $\text{CHD}_2\text{COCD}_3$ protons as an internal reference (δ 2.05). UV-VIS spectra were recorded with a Cary 3E spectrophotometer (Varian), using quartz cuvettes of a 1- or 10-mm path length. Pure *cis*- $C_n\text{AzoX}$ compounds were obtained via the photoisomerization using 313 nm light, followed by the radial chromatography (Chromatotron, Harrison Research) in the absence of visible light.

2.2. Preparation of samples

Water used for all experiments was obtained from Millipore Milli-Q system and deoxygenated with argon. The homogeneous aqueous solutions of $C_n\text{AzoX}$ were obtained by heating at 50°C for 6 h.

2.2.1. Electrochemical measurements

All measurements were performed using EMU Universal Electrochemical Meter [10] with an undivided three-electrode cell and CdCl_2 at the concentration 1.7×10^{-5} M as an electroactive probe. A saturated calomel reference (SCE) electrode was employed in this study, the working electrode was platinum with a platinum counter electrode. The area of the working electrode was 0.51 cm². The potential sweep rate was ranging between 0.49–1.69 V s⁻¹. The voltammograms reported were recorded with *iR* compensation. No additional electrolyte was added to the studied system. The detailed procedure has recently been described in Ref. [11]. Micellar diffusion coefficient was calculated from the following equation [12]:

$$i_p = 2.99 \times 10^5 n(\alpha n_\alpha)^{1/2} A D_M^{1/2} C_p \nu^{1/2} \quad (1)$$

where i_p is the peak current, n is the number of electrons involved in oxidation or reduction ($n = 2$), D_M is the micellar diffusion coefficient, F is the Faraday constant, R is the gas constant and T is the absolute temperature. The value of αn_α was evaluated from the peak semi-half-width $|E_p - E_{p/2}|$:

$$|E_p - E_{p/2}| = \frac{47.7}{\alpha n_\alpha} \quad (\text{mV}) \quad (2)$$

2.3. Irradiation and analysis of photoproducts

Irradiations were performed at 15, 25, 35 ± 0.1°C in a 300-ml immersion-type reactor (Photochemical Reactors) equipped with a 16-W low-pressure mercury lamp (365/366 nm). The irradiation intensity was calibrated against the azobenzene actinometer [13,14]. During the irradiation experi-

ment aliquots were taken and water was removed by lyophilization at -10°C/0.1 Torr. Dry samples were dissolved in 25% $\text{CD}_3\text{COCD}_3/\text{D}_2\text{O}$. The composition of these samples was determined by ^1H NMR. The number of FID accumulations were 512, resolution 0.2 Hz/point.

2.4. Thermal reversion

Irradiation was stopped after reaching the photostationary state and the sample was moved to a temperature-controlled sample-holder. Solutions of $C_n\text{AzoX}$ were stirred in the dark at 15, 25, 35 ± 0.1°C and aliquots were taken every 4 h for 72 h, worked up, and analyzed as described above.

3. Results and discussion

Amphiphilic *trans*-4-(4'-alkylphenylazo)benzenesulfonates and carboxylates, possessing distinct regions of hydrophilic-hydrophobic character, aggregate in water [11,15]. Cyclic voltammetry (CV) studies revealed that the transparent solutions of $C_n\text{AzoX}$ at concentrations below critical micelle concentration [11,15] contain molecular aggregates with a hydrodynamic radius, $R_{H,M}$, ranging between 2.49–3.47 nm (Table 1). According to the literature, simple micelles are characteristically spherical in shape with a diameter of 2–10 nm [16], hence it is reasonably assumed that the aggregates of $C_n\text{AzoX}$ may be of a spherical nature. For dilute solutions, a concentration of 0.02 mM, the absence of pre-micellar aggregates was also verified by CV [11,15].

Spectra of aqueous solutions of all molecules under study contain, within the spectral range covered by our experiments (280–500 nm), two distinct bands at ca. 440 nm and ca. 340 nm, characteristic of the azobenzene moiety [17]. The small absorption coefficient of azobenzene in the visible region is due to the symmetry-forbidden $n-\pi^*$ transition. Reduction of coplanarity of the azobenzene moiety brings about mixing of n -orbitals with π -orbitals to result in the increase in the $n-\pi^*$ absorption coefficient. This explains why a *cis*-azobenzene with distorted structure has a larger $n-\pi^*$ absorption coefficient.

The solutions of $C_n\text{AzoX}$ exhibited a clear photochromic behavior; upon 366-nm irradiation, spectrum changes markedly (Fig. 1). The absorbance around 340 nm decreased and absorbance around 290 nm increased, indicating that *trans*-*cis* photoisomerization occurred. The appearance of isosbestic points indicates that the *trans*-*cis* isomerization process proceeds without side-reaction. Similar changes in the absorption spectra were also observed in micellar solutions (Fig. 1b). The reverse reaction was found to be thermally driven, although rate constant of this process is distinctly different (Table 2). Upon irradiation by the 366-nm light, the absorption of *trans*-azobenzene chromophore disappeared together with the appearance of the absorption of the *cis*-isomer. At the photostationary state for the aggregated entities the equilibrium amount of the *cis* isomer, x_{pss} , was

Table 1
Experimental conditions and micellar parameters for C_n AzoX amphiphiles

n	X	Homogeneous media			Micellar aggregates			
		c (mM)	cmc^a (mM)	Temperature (°C)	c (mM)	$10^6 \times D_M^b$ ($cm^2 s^{-1}$)	$R_{H,M}^c$ (nM)	N^d
4	COONa	0.02	9.71	15	14.5	1.24	2.53	58
				25		0.98	2.49	54
				35		0.79	2.41	50
8	COONa	0.02	0.72	15	5.5	1.05	3.51	100
				25		0.70	3.47	96
				35		0.62	3.44	92
4	SO ₃ Na	0.02	25.8	15	16.0	1.30	2.36	55
				25		1.05	2.32	52
				35		0.84	2.29	49
8	SO ₃ Na	0.02	0.36	15	1.2	1.08	3.45	95
				25		0.72	3.40	91
				35		0.60	3.34	87

^aCritical micelle concentration at 25°C (surface tension method) from Ref. [11].

^bMicellar diffusion coefficient from the CV measurements.

^cHydrodynamic radius, calculated from the Stokes–Einstein equation: $R_{H,M} = kT/6\pi\eta D_M$, where k is the Boltzmann constant, and η is the solvent viscosity.

^dMicellar aggregation number, calculated as the micelle volume/surfactant volume ratio, according to Ref. [11].

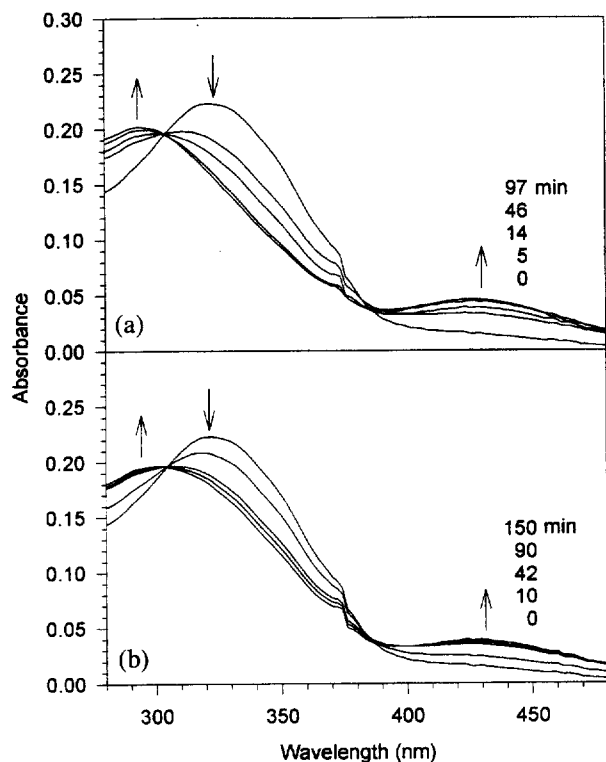
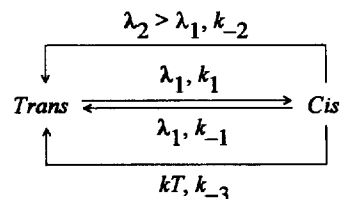


Fig. 1. Temporal evolution of the spectra of the aqueous C_8 azoSO₃Na solution under 365-nm irradiation at 25°C: (a) $[C_8AzoSO_3Na] = 0.02$ mM and (b) $[C_8AzoSO_3Na] = 16.0$ mM.

ranging between 0.42–0.44, and in homogeneous solution was ranging between 0.52–0.57. The configurational change was reversible. The *cis*-isomers quantitatively regenerated the *trans*-isomers upon irradiation with > 420 nm light and in dark. In the next four irradiation–thermal reversion cycles, the changes in the spectra were completely reversible. Table 3 lists the values of activation parameters for the photochem-

ical *trans*–*cis* isomerization and the thermal *cis*–*trans* reversion of C_n AzoX in homogeneous and micellar media, calculated by means of the standard approach, using Arrhenius equation (Fig. 2), and the intermediate state theory. The activation parameters have been evaluated at the temperature range of 15–35°C.

Pure *cis*- C_n AzoX compounds were prepared from the *trans* isomers by photoisomerization using 313 nm light and were purified while protected from light by radial chromatography. The purity was confirmed by a combination of techniques including UV absorption spectra, nuclear magnetic resonance spectra, and thin layer chromatography. As might be expected the stable form, both in homogeneous and micellar media, is the *trans*-isomer. The forward process (i.e., the *trans*–*cis* isomerization) occurs only upon the photophysical excitation whereas the reverse reaction may be driven both by photo-process and thermally. Photostationary state concentrations of *cis* and *trans*- C_n AzoX were found by monitoring the concentration of both *cis* and *trans*- C_n AzoX as a function of time and the photolysis was continued until the ratio of *cis* to *trans* remained constant. Upon irradiation at 366 nm C_n AzoX compounds gave the same photostationary state ratio regardless of the identity of the starting azobenzene (*trans* or *cis*). Hence one may write a scheme:



where *Trans* stands for *trans*- C_n AzoX, *Cis*-for *cis*- C_n AzoX, and $k_1, k_{-1}, k_{-2}, k_{-3}$ are the rates of the elementary processes.

Table 2

Rate constants and photostationary state equilibrium for the photochemical *trans*–*cis* isomerization and *cis*–*trans* thermal reversion of C_nAzoX in homogeneous and micellar media

n	X	Temperature (°C)	Homogeneous media			Micellar aggregates		
			x _{pss}	k ₁ ± 2σ ^a (10 ⁻⁴) (s ⁻¹)	k ₋₃ ± 2σ (10 ⁻⁷) (s ⁻¹)	x _{pss}	k ₁ ± 2σ (10 ⁻⁴) (s ⁻¹)	k ₋₃ ± 2σ (10 ⁻⁷) (s ⁻¹)
4	COONa	15	0.52	3.4 ± 0.4	1.9 ± 0.2	0.43	0.69 ± 0.05	0.22 ± 0.01
		25		13.5 ± 0.6	7.8 ± 0.3		3.4 ± 0.4	0.95 ± 0.06
		35		49.6 ± 1.2	29.8 ± 1.5		14.2 ± 1.0	3.85 ± 0.2
8	COONa	15	0.54	3.3 ± 0.1	2.1 ± 0.1	0.42	0.82 ± 0.07	0.24 ± 0.02
		25		13.6 ± 0.4	8.5 ± 0.5		4.0 ± 0.3	1.06 ± 0.08
		35		50.9 ± 0.8	31.8 ± 2.0		16.8 ± 1.2	4.26 ± 0.3
4	SO ₃ Na	15	0.55	3.4 ± 0.2	1.9 ± 0.2	0.43	0.60 ± 0.04	0.18 ± 0.02
		25		15.2 ± 0.5	8.1 ± 0.4		3.0 ± 0.2	0.88 ± 0.07
		35		60.1 ± 1.2	31.8 ± 2.0		12.8 ± 0.9	3.80 ± 0.2
8	SO ₃ Na	15	0.57	3.2 ± 0.3	2.0 ± 0.1	0.44	0.7 ± 0.05	0.28 ± 0.03
		25		13.9 ± 0.5	8.3 ± 0.3		3.3 ± 0.2	1.23 ± 0.1
		35		54.3 ± 0.9	31.4 ± 1.7		14.0 ± 0.8	4.98 ± 0.3

^aConfidence interval at significance level 95%.

The differential equation describing the photochromic process is given below:

$$\frac{d[Trans]}{dt} = -\Phi_1 I_{Trans,1} + \Phi_{-1} I_{Cis,1} + \Phi_{-2} I_{Cis,2} + k_3 [Cis] \quad (3)$$

where I_{Trans} and I_{Cis} are the intensities of light absorbed by *trans*- and *cis*-isomers, respectively, at λ_1 , and λ_2 . Because we performed all experiments in the absence of the visible light, thus $I_2 = 0$, and we can abandon term $\Phi_{-2} I_{Cis,2}$, and simplify Eq. (1) to the following form:

$$\frac{d[Trans]}{dt} = -\Phi_1 I_{Trans,1} + \Phi_{-1} I_{Cis,1} + k_3 [Cis]. \quad (4)$$

In the case of thermal reversion we have performed measurements in the absence of UV light, then $I_1 = 0$, and we obtain the first-order kinetic equation as below:

$$\frac{d[Trans]}{dt} = k_3 [Cis]. \quad (5)$$

The rate constants achieved for the thermal process, calculated by means of the non-linear regression (Marquardt method, Statgraphics 6.0 software), are given in Table 2, and the activation parameters: energy, $E_{a,1}$, enthalpy, ΔH^\ddagger , entropy, ΔS^\ddagger , and pre-exponential factor, A are given in Table 3.

From the preliminary studies we know that at $\lambda_1 = 366$ nm the thermal process can be neglected, as it is slower by the factor of 10^3 – 10^4 than the photochemical one. We have also monitored the reaction at its initial stage, i.e., when there is only 2% of the product, and we extrapolated the photochemical reaction rate constant, k_1 , to $t = 0$. Thus, we can abandon the *cis*–*trans* photochemical reversion, $\Phi_{-1} I_{Cis,1}$, due to small initial concentration of the *cis*-isomer. Then the kinetic equation can be written as:

$$\frac{d[Trans]}{dt} = -\Phi_1 I_{Trans,1}. \quad (6)$$

According to the Lambert–Beer law the intensity of the light absorbed by the isomer *trans*, $I_{Trans,1}$ is given as:

Table 3

Activation parameters for the photochemical *trans*–*cis* photoisomerization and the *cis*–*trans* thermal reversion of C_nAzoX in homogeneous and micellar media

n	X	E _{a,1} ± 2σ (kcal mol ⁻¹)	ΔH ₁ [‡] (kcal mol ⁻¹)	ΔS ₁ [‡] (cal mol ⁻¹ K ⁻¹)	log A ₁	E _{a,-3} ± 2σ (kcal mol ⁻¹)	ΔH ₋₃ [‡] (kcal mol ⁻¹)	ΔS ₋₃ [‡] (cal mol ⁻¹ K ⁻¹)	log A ₋₃
<i>Homogeneous media</i>									
4	COONa	23.8 ± 1.0	23.2	-1.1	14.57	26.1 ± 1.2	25.5	1.2	15.65
8	COONa	24.1 ± 1.1	23.5	-0.2	14.79	26.2 ± 1.5	25.6	1.0	15.80
4	SO ₃ Na	25.1 ± 0.9	24.5	-0.9	15.57	26.6 ± 1.3	26.0	0.8	15.97
8	SO ₃ Na	24.9 ± 0.9	24.3	0.1	15.39	26.5 ± 1.7	25.9	1.4	15.93
<i>Micellar aggregates</i>									
4	COONa	24.5 ± 1.9	23.9	-15.8	11.84	25.6 ± 1.3	25.0	-22.0	11.73
8	COONa	24.1 ± 2.1	23.5	-16.2	11.59	25.5 ± 2.5	24.9	-22.2	11.63
4	SO ₃ Na	25.0 ± 2.0	24.4	-17.3	12.23	26.7 ± 1.4	26.1	-19.9	12.51
8	SO ₃ Na	24.3 ± 2.8	23.7	-15.0	11.73	25.5 ± 1.8	24.9	-21.8	11.77

^aConfidence interval at significance level 95%.

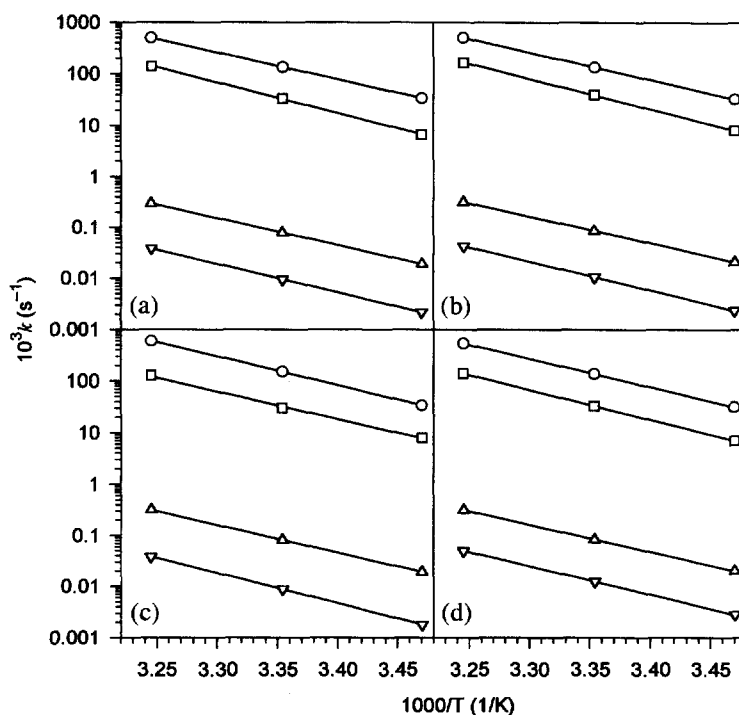


Fig. 2. Arrhenius plots for the *trans*–*cis* photoisomerization (O, □) and *cis*–*trans* thermal reversion (Δ, ▽) in homogeneous (□, Δ), and micellar (□, ▽) media for: (a) C₄AzoCOONa; (b) C₈AzoCOONa; (c) C₄AzoSO₃Na; (d) C₈AzoSO₃Na.

$$I_{Trans,1} = I_1 (1 - e^{\varepsilon[Trans]l}) \quad (7)$$

where I_1 is the incident intensity of the light beam, ε is the molar extinction coefficient at the wavelength λ_1 , and l is the optical path length.

Eq. (5) could be solved for the extreme cases. When $\varepsilon[Trans]l > 2$, i.e., in the micellar environment the reaction carried out is zero-order:

$$\frac{d[Trans]}{dt} = -\Phi_1 I_0 = k_1^{obs} \quad (8)$$

where k_1^{obs} is observed rate constant (Table 2). When $\varepsilon[Trans]l < 0.1$, i.e., in homogeneous media the reaction becomes the first-order type:

$$\frac{d[Trans]}{dt} = -2.303\Phi_1 I_0 \varepsilon[Trans]l = k_1^{obs}[Trans]. \quad (9)$$

The first-order *trans*–*cis* and *cis*–*trans* isomerization rate constants for C_{*n*}AzoX in homogeneous solution are remarkably faster than that obtained for the micellar assemblies (Table 2). Generally, the *trans*–*cis* photoisomerization decreases in the micellar media. This trend is expected since the range of media investigated represent an increase of viscosity ‘seen’ by the azobenzene group. The observation that entropy of isomerization ΔS_1^\ddagger is higher in the homogeneous than micellar media is an evidence for some organization of the micellar system. The lack of an unusual A factor in the Arrhenius plot suggest that relatively little order is present in the micelle [18], eventually, may be related to the energy transfer between the azobenzene moieties, due to the λ -electron interactions. There is no clear evidence for this effect,

but Fukuda and Nakahara [19,20], have studied various groups of the azobenzene surfactants, and found some evidences for the intermolecular interactions. However, the lack of fluorescence allows relatively little to be determined about the excited states occurred.

For the *cis*–*trans* thermal reversion entropy decrease remarkably with increasing environment rigidity. It is apparent that the micelles act in more complicated fashion than a simple liquids; microenvironment certainly have an effect upon the relative energies of the reactant molecule and the transition state. In micellar state, as the *cis*-C_{*n*}AzoX molecule reacts, the *cis*–*trans* isomerization tends to organize the microenvironment. Thus, the entropy of the system will be decreased overall and $\Delta S \ll 0$. Alternatively, in the polar homogeneous medium the solvent molecules in the cybotactic region are already relatively structured (water tends to form a structured dynamic lattice of solvent–solvent hydrogen bonds). As the dissolved C_{*n*}AzoX reacts, it will not inflict as great an increase upon the structure of the environment as in the case of aggregates; hence ΔS (micelle) < ΔS (homogeneous).

A study on the temperature dependence of the isomerization for the azobenzenes in homogeneous solution indicates that the enthalpy of activation ΔH^\ddagger is 1.5–2.1 kcal mol⁻¹ smaller than the values obtained for the same compounds in the aggregated systems (Tables 2 and 3). This is a strong suggestion that the mechanism of the *trans*–*cis* and *cis*–*trans* isomerization in both media must be the same. The ΔS_{-3}^\ddagger values are very large and negative for the *cis*–*trans* thermal reversion in both homogeneous and aggregated systems in

contrast to the *trans*–*cis* photoisomerization, especially in homogeneous solution.

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