Trans-cis isomerization of an azoxybenzene liquid crystal

Dina Aronzon[a]; Eric P. Levy[a]; Peter J. Collings[a]; Andro Chanishvili[b]; Guram Chilaya[b]; Gia Petriashvili[b]

[a] Department of Physics & Astronomy, Swarthmore College, Swarthmore, PA 19081 [b] Institute of Cybernetics of the Georgian Academy of Sciences, 0186 Tbilisi, Georgia

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DINA ARONZON†, ERIC P. LEVY†, PETER J. COLLINGS*†, ANDRO CHANISHVILI‡, GURAM CHILAYA‡ and GIA PETRIASHVILI‡

†Department of Physics & Astronomy, Swarthmore College, Swarthmore, PA 19081
‡Institute of Cybernetics of the Georgian Academy of Sciences, Euli Str. 5, 0186 Tbilisi, Georgia

Trans–cis isomerization was investigated in a room temperature liquid crystal mixture of two azoxybenzene compounds. Experiments were performed on isolated molecules in dilute solutions and on the liquid crystal phase composed of the pure compounds. The absorption spectra of the *trans* and *cis* isomers were found to be similar to those of azobenzene compounds, as were the birefringence and order parameter of the nematic liquid crystal phase. The photo-optic properties were also similar in that irradiation by ultraviolet light caused the conversion from *trans* to *cis* isomers, while short wavelength visible light incident on these compounds resulted in the conversion from *cis* to *trans* isomers. The activation energy for thermal relaxation from the *cis* to *trans* isomer in the liquid crystal phase was determined to be (66 ± 7) kJ/mole, which is less than for azobenzene in solution. While a photostationary state in a dilute solution with approximately equal numbers of *trans* and *cis* isomers was achieved, the nematic–isotropic transition of the mixture of the pure compounds decreased from 70°C to room temperature with a *cis* concentration of only about 12%. One unusual finding was that the photostationary concentration of *trans* and *cis* isomers due to irradiation with light of a specific visible wavelength depended on the starting concentrations of the two isomers, indicating that there may be a molecular conformation that is not photo-responsive and relaxes only thermally.

1. Introduction

One of the most exciting developments in liquid crystal science and technology is the possibility of using light instead of electricity to control the behaviour of a material. Since the liquid crystal phase owes its stability to the anisotropic shape of the molecules, changing the molecular conformation by irradiation with light is perhaps the most direct way to control the properties of the liquid crystal. To this end, there has been considerable research into utilizing *trans–cis* isomerization as the photo-active mechanism, with azobenzene compounds attracting by far the most attention [1]. These materials have their peak absorption between 325 and 375 nm; irradiation with light in this region produces a higher concentration of *cis* isomers. There is also a weak absorption peak around 450 nm, and light of this wavelength increases the concentration of *trans* isomers. While the *trans* isomers are linear in shape and tend to form liquid crystals, the *cis* isomers are not linear, and tend not to form liquid crystals. Changing the relative concentration of *trans* and *cis* isomers therefore changes the temperature range of the liquid crystal phase, resulting in a large change in liquid crystal properties (order parameter, birefringence, etc.) at a given temperature. A smaller effect is that liquid crystal properties also depend directly on the molecular properties, which are different for the two isomers [2].

There are many ways to produce a liquid crystal sample that is photo-active because of the presence of azobenzene compounds. Such molecules can be used exclusively as the liquid crystal forming material [3]. More often, small amounts of azobenzene compounds, perhaps liquid crystalline when pure, are added to a liquid crystal material that is not photo-active [4, 5]. The presence of chiral compounds causes a nematic liquid crystal to adopt a helical structure. Whether the chiral dopant is an azobenzene compound or whether the azobenzene compound is one of the achiral components of the sample, an additional effect is that the pitch of the helical structure (the distance over which the helix makes one full revolution) depends on the relative concentration of *trans* and *cis* isomers. If the pitch of the helix corresponds to a visible wavelength, dramatic changes in the optical properties of the liquid crystal are possible with only a small amount of ultraviolet or visible light irradiation [6, 7].

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*Corresponding author. Email: pcollin1@swarthmore.edu

While most of the work has involved the nematic or chiral nematic phase of low molecular weight liquid crystals, a good deal of research has been done on photo-active polymeric materials [8, 9]. For example, copolymerization of photo-inactive mesogenic units and photo-active units (mesogenic or non-mesogenic) allows for precise control of both phase stability and optical properties. Photo-active polymers with nematic, chiral nematic, and smectic phases have been produced in this way. This procedure is useful for side chain and main chain polymers, but photo-active dendritic polymers have also been synthesized [10]. Thin films can be fabricated from photo-active polymers, and a subfield investigating the photo-alignment of such films is quite active at present [11, 12]. Other applications utilizing *trans–cis* isomerization include polarization gratings [13], optical data storage systems [14], liquid crystal elastomers [15], and dynamic holography [16].

Even though it is known that azoxybenzene compounds form liquid crystals with properties similar to azobenzene materials, such systems have not been investigated to any extent at all, even though they have been employed as the photo-active compound in a few experiments [17, 18]. Azoxybenzene compounds are stable and can be formulated into mixtures with wide liquid crystal ranges. It is therefore of interest to know whether the optical properties of azoxybenzene compounds differ from similar azobenzene materials, or whether their liquid crystal properties are affected differently due to *trans–cis* isomerization. With this in mind, irradiation experiments were performed on a mixture of azoxybenzene compounds with a wide range of liquid crystal stability. In order to learn about the basic optical properties of these compounds, some irradiation experiments were carried out in dilute solutions. Since this mixture has been used as the host liquid crystal material in photo-active experiments, the order parameter and birefringence of the liquid crystal phase formed by these compounds were also investigated.

These experiments reveal several important findings. The absorption spectra of azobenzene compounds and azoxybenzene compounds differ slightly, and both undergo *trans–cis* isomerization due to incident light in much the same ways. For azoxybenzene compounds, ultraviolet light is quite effective in promoting the conversion of *trans* isomers to *cis* isomers, and short wavelength visible radiation is effective in changing *cis* isomers to *trans* isomers. A moderate intensity of ultraviolet light can achieve roughly equal amounts of *trans* and *cis* isomers in less than a minute, while it takes slightly longer for a moderate intensity of short wavelength visible light to convert most of the *cis*

isomers back to *trans* isomers. It was found that the thermal relaxation of *trans* isomers to *cis* isomers is governed by an activation energy of (66 ± 7) kJ/mole for this azoxybenzene material, which is smaller than azobenzene compounds. This means that the rate constant at room temperature for this relaxation process in azoxybenzene compounds is quite low, about $0.25\,\mathrm{hr}^{-1}$. Also, it was observed that irradiation of these azoxybenzene compounds, both in solution and in the liquid crystal phase, with light of a wavelength between the ultraviolet and visible range produced a *cis* isomer concentration that was dependent on the *cis* isomer concentration of the starting material. Such a phenomenon has not been reported for azobenzene compounds. This may indicate that there is a conformation of the azoxybenzene compound that does not respond to short wavelength visible light, only relaxing to the *trans* isomer thermally. Finally, the liquid crystal phase is very sensitive to the relative concentrations of the two isomers. In fact, the nematic–isotropic transition is depressed from $70°C$ to room temperature by an increase in the *cis* isomer concentration from zero to about 12%.

2. Theoretical considerations

2.1. *Isomerization fundamentals*

A method to determine the relative concentration of *cis* isomers upon irradiation with light was developed by Fischer almost 40 years ago [19]. The specific system under study here is characterized by a thermal relaxation rate of the *cis* isomer that is much smaller than the photoisomerization rates of both the *trans* and *cis* isomers. In this case the time rate of change of the concentration of *cis* isomers is given by

$$\frac{\mathrm{d}[c]}{\mathrm{d}t} = B\left(\varepsilon_t^i \phi_t^i [t]^i - \varepsilon_c^i \phi_c^i [c]^i\right), \qquad (1)$$

where $[t]^i$ and $[c]^i$ are the time-dependent concentrations of the *trans* and *cis* isomers, respectively, ε_t^i and ε_c^i are the extinction coefficients at the irradiation wavelength of the *trans* and *cis* isomers, respectively, and ϕ_t^i and ϕ_c^i are the quantum yields at the irradiation wavelength of the *trans–cis* and *cis–trans* photoisomerizations, respectively. The parameter B depends on the incident photon flux of the irradiation light and the absorbance of the sample. The photostationary state achieved after a sufficient time of irradiation is therefore characterized by a ratio of isomer concentrations given by

$$\frac{[t]^i}{[c]^i} = \frac{\varepsilon_c^i \phi_c^i}{\varepsilon_t^i \phi_t^i} = \frac{A_c^i \phi_c^i}{A_t^i \phi_t^i}, \qquad (2)$$

where A_t^i and A_c^i are the absorbances at the irradiation wavelength of samples of the same chromophore concentration and thickness, in which all of the molecules are *trans* and *cis* isomers, respectively. The concentrations $[t]^i$ and $[c]^i$ now represent the time-independent photostationary state isomer concentrations.

The ratio of photostationary concentrations $[t]^i/[c]^i$ depends on the wavelength of the irradiation light. If the ratio of quantum yields ϕ_c^i/ϕ_t^i does not depend on wavelength, then the ratio of the photostationary state concentration ratios at two different irradiation wavelengths depends only on the ratios of absorbances at the two wavelengths,

$$\frac{[t]^{[1]}\Big/[c]^{[1]}}{[t]^{[2]}\Big/[c]^{[2]}} = \frac{A_c^{[1]}\Big/A_t^{[1]}}{A_c^{[2]}\Big/A_t^{[2]}}. \tag{3}$$

The superscripts in brackets denote the wavelength of irradiation, wavelength 1 or wavelength 2.

If the sample is irradiated with light of wavelength i and the absorbance of the sample is measured with light of wavelength m, then the absorbance is given by

$$A^m = \varepsilon_t^m [t]^i l + \varepsilon_c^m [c]^i l, \tag{4}$$

where the superscript m denotes quantities corresponding to the wavelength of the absorption measurement (just as the superscript i denotes quantities corresponding to the wavelength of the irradiation light) and l is the thickness of the sample. If $A_t^m = \varepsilon_t^m \left([t]^i + [c]^i\right) l$ and $A_c^m = \varepsilon_c^m \left([t]^i + [c]^i\right) l$ are the absorbances if all of the molecules are in the *trans* and *cis* form, respectively, which is consistent with the definitions in equation (2), then the measured absorbance is

$$A^m = \frac{[t]^i A_t^m + [c]^i A_c^m}{[t]^i + [c]^i}. \tag{5}$$

The ratio of photostationary state concentration ratios depends on the isomer absorbances at the irradiation wavelengths (equation 3), while the absorbance of the sample depends on the isomer absorbances at both the wavelength of the irradiation light and the wavelength of the measurement light (equation 5).

Equation (5) can be written for each of two irradiation wavelengths and combined with equation (3). In the resulting equation, a ratio of the relative photostationary state *cis* concentrations at the two irradiation wavelengths appears. This ratio can be determined by measuring the relative change of absorbances at a third

wavelength (normally chosen where the absorption changes are the greatest) when each of the irradiation wavelengths is used. Quantities measured at this wavelength are denoted with the superscript [*peak*]. The final equation is best written with some additional definitions. If irradiation is done at a wavelength denoted by i and absorbance is measured at a wavelength denoted by m, then let

$$\Delta_i^m = A^m - A_t^m = A^m - \varepsilon_t^m \left([t]^i + [c]^i\right) l \tag{6}$$

$$\delta_i^m = \frac{\Delta_i^m}{A_t^m} = \frac{A^m - \varepsilon_t^m \left([t]^i + [c]^i\right) l}{\varepsilon_t^m \left([t]^i + [c]^i\right) l}. \tag{7}$$

The relative photostationary state concentration of *cis* isomer when irradiated with light of a wavelength denoted by the index 2 is then given by

$$\frac{[c]^{[2]}}{[t]^{[2]} + [c]^{[2]}} = \frac{\delta_{[1]}^{[1]} - \delta_{[2]}^{[2]}}{1 + \delta_{[1]}^{[1]} - \left(\Delta_{[1]}^{[peak]}\Big/\Delta_{[2]}^{[peak]}\right)\left(1 + \delta_{[2]}^{[2]}\right)}. \tag{8}$$

All quantities on the right-hand side of equation (8) can be measured. Thus, acquiring absorption spectra in the photostationary state after irradiation with light of two different wavelengths allows the photostationary state *cis* concentration to be determined for each irradiation case.

2.2. Clearing point depression

When a small amount of an impurity, liquid crystalline or not, is added to a nematic liquid crystal, the temperature of the nematic–isotropic transition (clearing point) decreases and the width of the two-phase region increases. It has been shown that the relationship derived by van't Hoff for the depression of the freezing point works well for the nematic–isotropic transition [20]. If T_0 is the nematic–isotropic transition temperature of the pure material and T_X is the transition temperature with a molar concentration of impurity equal to X, then

$$T_0 - T_X = \frac{RT_0^2(X_I - X_N)}{L}, \tag{9}$$

where X_I and X_N are the molar concentrations of the impurity in the isotropic and nematic phase, respectively, L is the latent heat of the nematic–isotropic transition, and R is the gas constant. Experiments are usually done by raising the temperature of a sample with a known molar concentration of impurity and noting at what temperature the two-phase region

appears and at what temperature the two phase region disappears. If the width of the two-phase region is denoted by δT and if the midpoint of the two phase region is used for T_X, then the latent heat can be expressed in terms of measurable quantities,

$$L = \frac{RT_0^2 X \delta T}{(T_0 - T_X)^2 - (\delta T/2)^2}. \tag{10}$$

The second term in the denominator is often small enough to be ignored. If the latent heat is known but the molar concentration of the impurity is not, then performing such an experiment can determine the impurity concentration.

2.3. *Birefringence and order parameter*

Perhaps the most important fundamental properties of a nematic liquid crystal when used as a host material are its birefringence and order parameter. These two quantities are closely related and determine the nature of many of the effects used in devices. The birefringence Δn can be determined by measuring the optical retardation angle ψ of light passing through a sample. The relation is

$$\Delta n = n_\parallel - n_\perp = \frac{2\pi \lambda_0 \psi}{d}, \tag{11}$$

where λ_0 is the vacuum wavelength of the light and d is the thickness of the sample. The index of refraction for light polarized parallel and perpendicular to the direction of preferred orientation (called the director) is denoted by $n_\parallel$ and $n_\perp$, respectively.

There are many methods to measure the birefringence. A convenient one is to place the sample between two parallel linear polarizers and measure the transmitted intensity as the sample is rotated around the axis defined by the light propagation direction. The only parameters needed to fit the theoretical function of intensity vs. angle to the experimental data are the initial intensity of the light and the optical retardation angle [21]. Another method involves shining linearly polarized light on the sample with the polarization direction of the light at 45° to the director of the liquid crystal. The light then passes through a quarter wave plate with its fast axis oriented parallel to the direction of initial light polarization. The result is that the light is linearly polarized but at an angle to the initial polarization direction equal to half the optical retardation angle of the sample. The angle between the initial linearly polarized light and the final linearly polarized light is easily measured with a linear polarizer.

In a nematic liquid crystal, the molecules are oriented preferentially along one direction. The degree to which they are ordered is best given through an orientational distribution function, but it is customary to define a single quantity as an order parameter. If θ is the angle the long axis of a molecule makes with the director, than an order parameter S can be defined as

$$S = \langle P_2(\cos \theta) \rangle = \langle \frac{3}{2}\cos^2 \theta - \frac{1}{2} \rangle, \tag{12}$$

where P_2 is the second Legendre polynomial and the brackets denote an average over many molecules. Many methods to measure the order parameter actually determine the order parameter for a specific bond on the molecule rather than the molecular long axis. If this bond is parallel to the long axis of the molecule, then its order parameter can be close to the order parameter of the long axis of the molecule. If it is not exactly parallel to the molecular long axis, then in general the measured order parameter is less than the molecular order parameter. Alternatively, a small amount of a guest molecule can be dissolved in the liquid crystal, and the order parameter of its long axis (or a bond parallel to its long axis) can be measured. It has been shown that if the guest molecule is roughly the same size and shape as the liquid crystal molecule, the order parameters of both are very similar.

For example, if just about all of the absorption of a molecule occurs for light polarized parallel to one bond, which is true for the N=N bond of azobenzene and azoxybenzene compounds, measuring the absorption of light polarized parallel and perpendicular to the director allows the order parameter to be determined,

$$S = \frac{n_\parallel A_\parallel - n_\perp A_\perp}{n_\parallel A_\parallel + 2n_\perp A_\perp}, \tag{13}$$

where $A_\parallel$ and $A_\perp$ are the absorbances for light polarized parallel and perpendicular to the director, respectively [22]. Notice that the indices of refraction for light polarized parallel and perpendicular to the director must also be known.

3. Experiments

3.1. *Dilute solutions*

The absorption spectra of the *trans* isomers of azobenzene and azoxybenzene compounds differ slightly. As shown in figure 1, the typical absorption spectrum for the *trans* isomer of an azobenzene compound (di-pentylazobenzene) possesses a strong absorption around 340 nm with a much weaker absorption peak around 440 nm. The wavelength of maximum absorption shifts depending on the compound, reaching a minimum of 315 nm for azobenzene itself [23] and moving above 350 nm when alkoxy-groups are
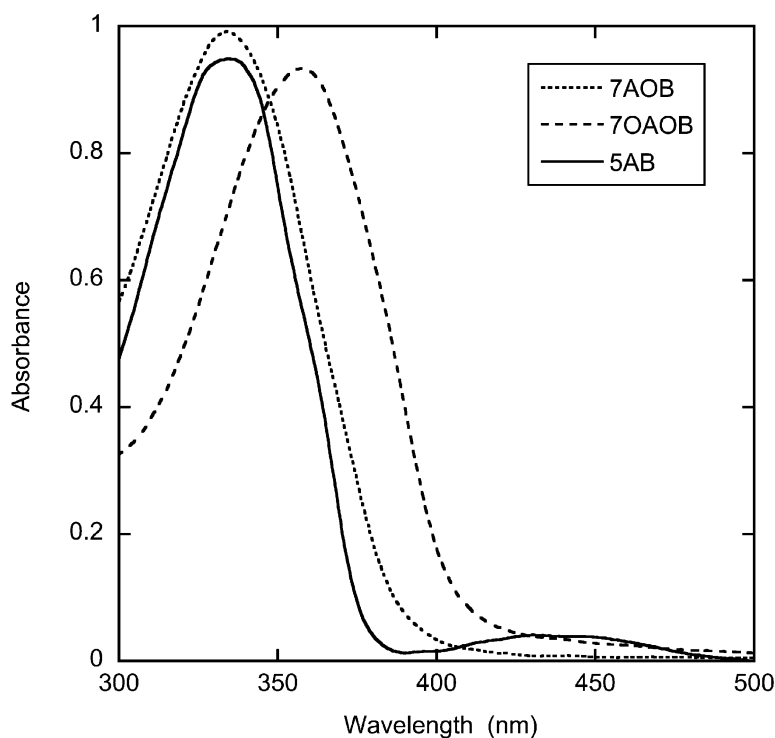
Figure 1. Absorbances of dilute solutions (about 0.03 mM in methanol) of the *trans* isomers of one azobenzene compound (5AB: di-pentylazobenzene) and two azoxybenzene compounds (7AOB: di-heptylazoxybenzene, 7OAOB: di-heptoxyazoxybenzene). The path length is 1 cm.

attached [2]. The absorption spectra for the *trans* isomer of azoxybenzene compounds also have a strong absorption at similar wavelengths to azobenzene compounds, but lack the weak absorption peak around 440 nm. The spectra of the *trans* isomers of two azoxybenzene compounds (di-heptylazoxybenzene and di-heptoxyazoxybenzene) are also shown in figure 1, demonstrating the shift from compound to compound and the lack of a weak absorption peak at visible wavelengths. The *trans* isomers of azoxybenzene compounds do absorb slightly in the 400–450 nm wavelength range, but less than azobenzene compounds.

ZhK-440 (NIOPIK) is a mixture of two-thirds *p-n-*butyl-*p*-methoxyazoxybenzene and one-third *p-n*-butyl-*p*-heptanoylazoxybenzene. If the molecules are *trans* isomers, ZhK-440 possesses a nematic liquid crystal phase from 0 to 70°C. The transition temperature from the nematic liquid crystal phase to the isotropic liquid phase decreases if molecules change from *trans* isomers to *cis* isomers, eventually reaching room temperature and probably eliminating the liquid crystal phase entirely. The *trans* and *cis* isomers of each of the compounds are shown in figure 2.

The absorption spectra of a dilute solution of ZhK-440 in methanol, both after being in the dark for over 12 hours and after irradiation with 366 nm light with an intensity of approximately 2 mW/cm^2 until the spectrum did not change further (about 2 minutes), are shown in figure 3. In the first case the concentration of *trans* isomers is maximized at nearly 100%, while in the second case the concentration of *cis* isomers is maximized. As explained later, the maximum concentration of *cis* isomers was approximately 50%. Notice that the *cis* isomer absorption is greater at the 230 nm peak, less at the 340 nm peak, and greater at visible wavelengths compared to the *trans* isomer absorption. The reduction in absorption at 340 nm and increase in absorption in the visible are similar to what is observed with azobenzene compounds [2, 23].

In the experiments just described and in all of the experiments utilizing the Jasco 500 uv-vis spectrophotometer, one must ask whether the intensity of light in the spectrophotometer is high enough to cause a change in the *trans* and *cis* isomer concentrations. To check this, a dilute solution of the ZhK-440 mixture was placed in the spectrophotometer with constant illumination at a wavelength of 341 nm, the wavelength of maximum absorption (and maximum sensitivity of *trans* to *cis* isomerization). The absorption of the solution was monitored for nearly 3 hours under these conditions and over this time period the absorption decreased only by 0.1%. Clearly, the intensity of the light in the
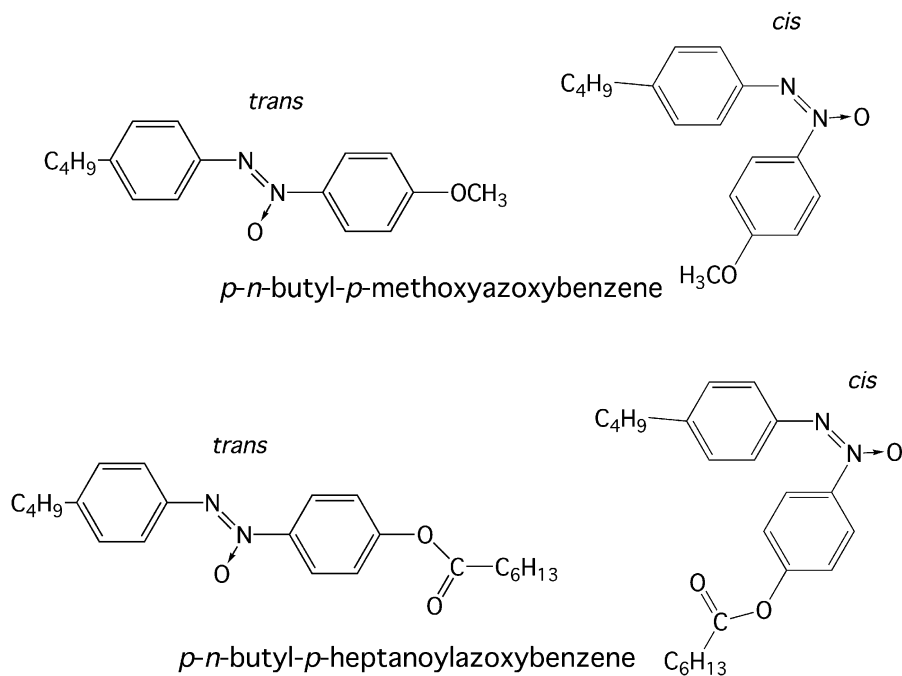
Figure 2. ZhK-440 is two-thirds *p-n*-butyl-*p*-methoxyazoxybenzene and one-third *p-n*-butyl-*p*-heptanoylazoxybenzene. The *trans* and *cis* isomers of each molecule are shown.
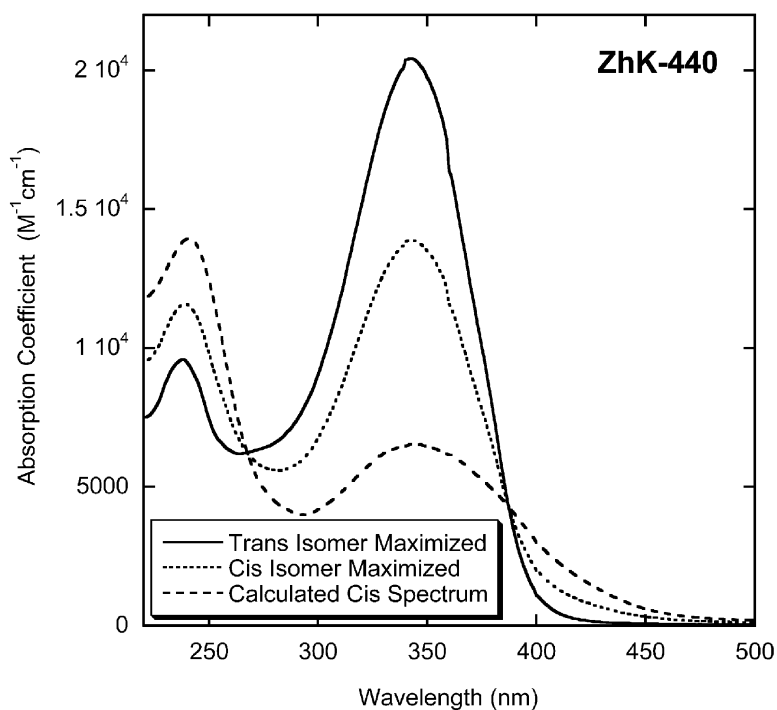

Figure 3. Absorption spectrum for a 0.31 mM solution of ZhK-440 in methanol (average molecular weight is 313.7 g/mol). If the sample has been in the dark for many hours, the concentration of *trans* isomers is maximized near 100%. If the sample has been illuminated with 366 nm light for several minutes, the concentration of *cis* isomers is maximized near 50% (see text). Once the *cis* isomer concentrations of the two spectra are known, the spectrum of the *cis* isomers can be calculated (see text).

spectrophotometer is quite weak. Since a spectro-photometer scan takes less than a minute, absorption measurements, even absorption measurements repeated 15–20 times, do not affect the *trans* and *cis* isomer concentrations.

In the following experiments, the solution was irradiated with light of a specific wavelength and an intensity of about $2\,mW/cm^2$ for 30 seconds, after which it was immediately placed in the spectrophotometer and an absorption scan performed, after which it was taken out of the spectrophotometer for irradiation for another 30 seconds, after which another absorption spectrum was taken. This process was repeated until there was no change in the absorption spectrum, which took at most about 30 minutes. Given the rate constant for thermal *cis* to *trans* isomerization of $0.25\,hr^{-1}$, this means that the rate at which the absorption changed might have been affected by up to 10%. These rates are not important for this study and they are not reported. The photostationary state absorption values (when the absorption spectrum no longer changes with continued irradiation) should not be affected to any great extent by thermal relaxation from *cis* to *trans* isomers during the intervals of no irradiation. These absorption values are important to the investigation and are reported.

Figure 4 displays the results when a dilute solution of ZhK-440 is irradiated with light of different wavelengths. The relative amounts of *trans* and *cis* isomers are monitored by measuring the absorption of the solution at 341 nm, the wavelength of maximum absorption of the *trans* isomer. If the sample contains almost entirely *trans* isomers, notice that light with a wavelength of either 335 or 366 nm is much more effective than 405 nm light in promoting the concentration of *cis* isomers, just as is expected since the absorption at the lower wavelengths is much greater for the *trans* isomer compared to the *cis* isomer. Thus the photostationary state after irradiation with light of the two lower wavelengths contains a significantly higher concentration of *cis* isomers than the photostationary state produced by 405 nm light. Alternatively, if the starting concentrations of *trans* and *cis* isomers are about equal, light with a wavelength of 405 and 436 nm are both effective in increasing the concentration of *trans* isomers, with the photostationary state for the 436 nm light containing a slightly higher concentration of *trans* isomers.

In order to calculate the concentration of *cis* isomers in the photostationary states, the data of figure 4 (a) were fit to exponential functions to determine the absorbances of the photostationary states at 341 nm. The fits are shown as lines in the figure. Similar data were obtained for the wavelength of irradiation, and fits to these data produce absorbances of the photostationary state. Table 1 contains the results of this procedure, where the absorbances at 341 nm are denoted by the superscript [*peak*].

The measurements at 405 nm can be combined with the measurements at either 335 or 366 nm in
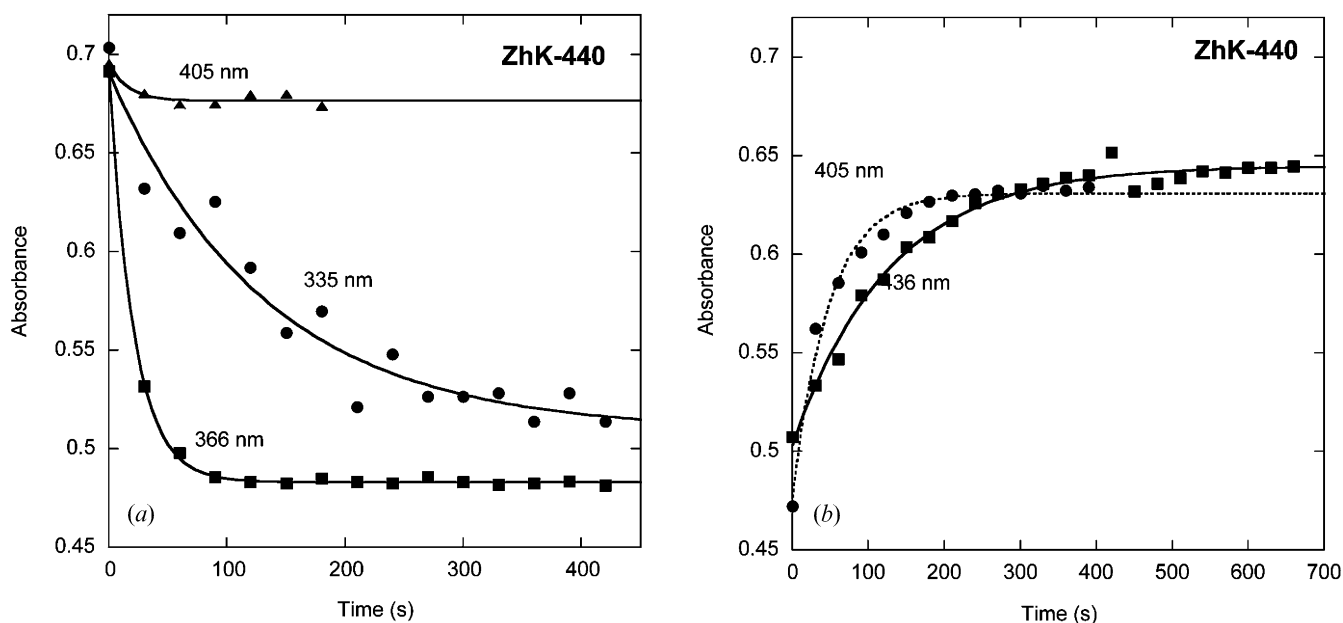

Figure 4. Absorbance at 341 nm of a 0.31 mM solution of ZhK-440 in methanol when irradiated with light of different wavelengths. The horizontal axis is the accumulated irradiation time, not the elapsed time (since irradiation was interrupted for absorption measurements). The path length is 1 mm and the intensity of the irradiating light is approximately $2\,mW/cm^2$. The starting concentration of *trans* isomers is near 100% in (a) and about 50% in (b).

Table 1. Absorbance measurements before and after irradiation.

i	λ(nm)	$A_t^{[i]}$	$A^{[i]}$	δ_i^i	$A_t^{[peak]}$	$A^{[peak]}$	$\Delta_i^{[peak]}$
1	335	0.672	0.501	−0.255	0.703	0.512	−0.191
2	366	0.524	0.394	−0.248	0.691	0.483	−0.208
3	405	0.030	0.041	0.370	0.695	0.681	−0.014

equation (8) to determine the concentration of *cis* isomers in the photostationary states. The result of this procedure is a *cis* concentration of $(47 \pm 2)\%$ for 335 nm light and $(47 \pm 1)\%$ for 366 nm light. The same procedure can be used twice to determine the *cis* concentration with irradiation with 405 nm light, combining the measurements at 405 nm with either those at 335 nm or those at 366 nm. In both cases the *cis* concentration is determined to be $(3 \pm 1)\%$. With this estimate of the *cis* isomer concentration for the photostationary state using 366 nm light, the spectrum of the *cis* isomer can be calculated from the spectra before and after irradiation (assuming the *trans* and *cis* spectra are additive). The result of this calculation is shown in figure 3.

3.2. *Liquid crystal phase*

To investigate the effect of irradiation on the liquid crystal phase, measurements of the birefringence and order parameter as a function of temperature for a sample of nearly 100% *trans* isomers were first performed. The method utilizing two parallel polarizers and rotating the sample described earlier was employed and the results are displayed in figure 5. The liquid crystal sample was contained in either a 2 or 5 μm commercial glass cell with rubbed polyimide layers, mounted in a temperature controlled oven ($\pm 0.1°C$). The order parameter was determined by measuring the absorbance for light polarized parallel and perpendicular to the director as described earlier. When a small amount (a few percent) of the dye Disperse Red 1 was added, measurements were possible using a wavelength of 488 nm. The results are shown in figure 5. Since the liquid crystal molecules are slightly longer than the dye molecules, the order parameter for the ZhK-440 molecules may be slightly higher than shown in the figure. A similar measurement was performed on
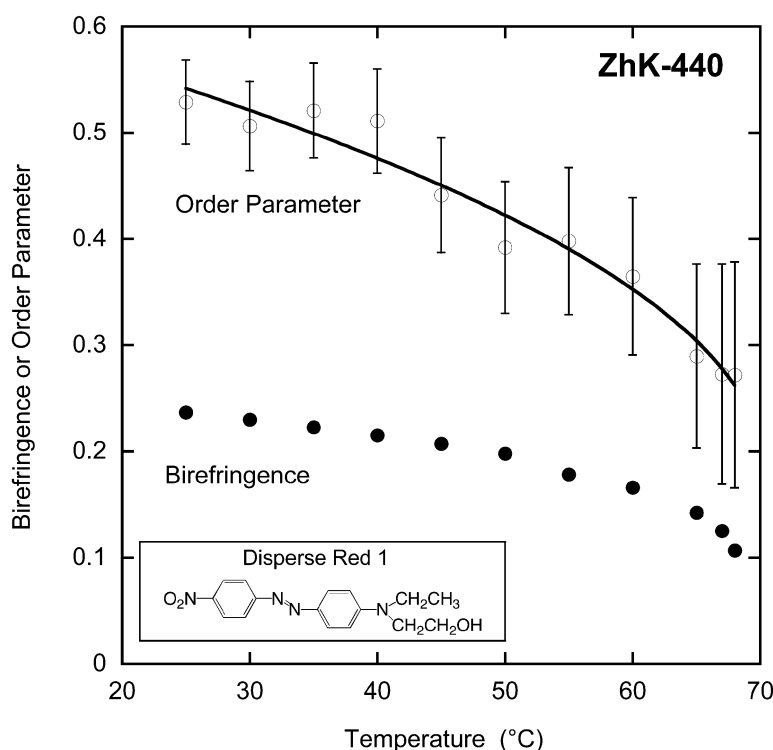

Figure 5. Birefringence and order parameter of ZhK-440 when nearly all the molecules are *trans* isomers. The wavelength for the birefringence measurements is 633 nm. The order parameter is measured for dye molecules that are dissolved in the liquid crystal. The molecular structure of the dye (Disperse Red 1 with a peak absorbance at 503 nm) is shown.

ZhK-440 with no added dye, but using 436 nm light, a wavelength at which there is some absorption. These order parameter data are consistent with the dye data at higher temperatures, but are slightly smaller at lower temperatures. Possibly the 436 nm light causes some isomerization, less at higher temperatures where the thermal relaxation rate is faster and more at the lower temperatures where the thermal relaxation rate is slower.

Just as the concentration of *cis* isomers can be tracked by measuring the peak absorption of dilute solutions, in the liquid crystal phase the concentration of *cis* isomers can be monitored by observing the birefringence. As the concentration of *cis* isomers increases, the temperature at which the nematic phase transforms into the isotropic liquid phase decreases. This shifts the birefringence curve in figure 5 to lower temperatures, resulting in a decrease in birefringence at a particular temperature. To demonstrate this, a sample of ZhK-440 at room temperature was irradiated with 366 nm light with its birefringence measured periodically. The sample was irradiated for either 20 or 30 seconds, after which the irradiating light was blocked so the birefringence could be measured with 633 nm light, which took about 1 minute. This procedure was repeated for a accumulated irradiation time of over 4

minutes, after which the wavelength of the irradiating light was changed to 436 nm and the birefringence was again measured periodically. The birefringence as a function of time during this procedure is plotted in figure 6, where the decrease in birefringence as the concentration of *cis* isomers builds up followed by the increase in birefringence as the *cis* isomer concentration decreases is clearly evident.

The thermal relaxation of *cis* isomers to *trans* isomers in the liquid crystal phase was monitored by irradiating the sample with light from a 100 W mercury lamp and uv bandpass filter for 10 seconds and then taking birefringence measurements for over an hour. This was done at many temperatures in the liquid crystal phase and the results are shown in figure 7. By fitting exponential functions to these data, the relaxation rate at each temperature could be determined. These relaxation rates are plotted versus inverse temperature in the insert in figure 7, and a fit of Arrhenius behaviour to these data produces a value for the activation energy of (66 ± 7) kJ/mol. This is less than the activation energies measured for azobenzene in ethanol and heptane, 104 and 81.1 kJ/mol, respectively [24].

In order to estimate the concentration of *cis* isomers from the decrease in the nematic–isotropic transition temperature, the latent heat of the transition must be
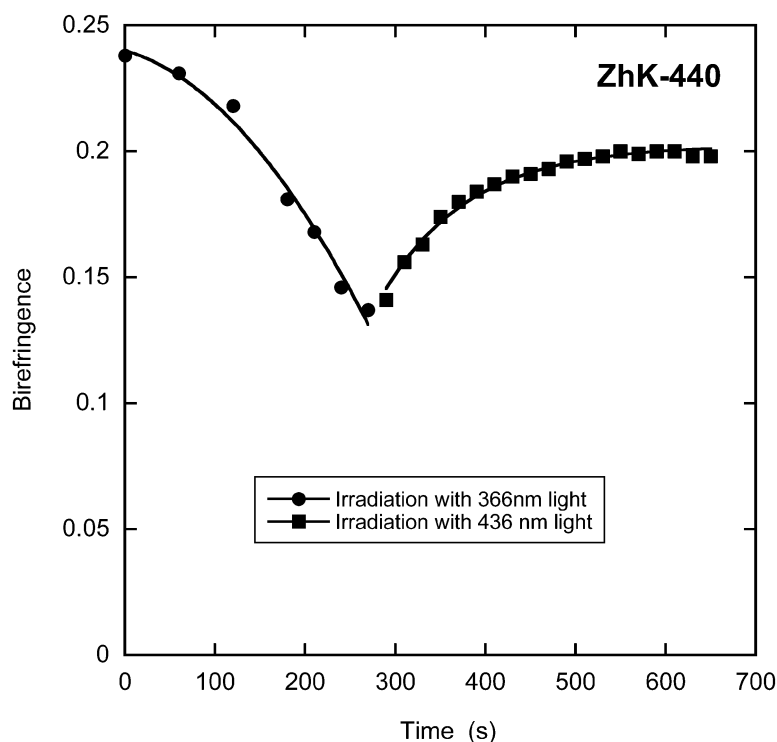

Figure 6. Birefringence at 633 nm of ZhK-440 at room temperature during irradiation with both 366 nm and 436 nm light. The horizontal axis is the accumulated irradiation time, not the elapsed time (since irradiation was interrupted for birefringence measurements).
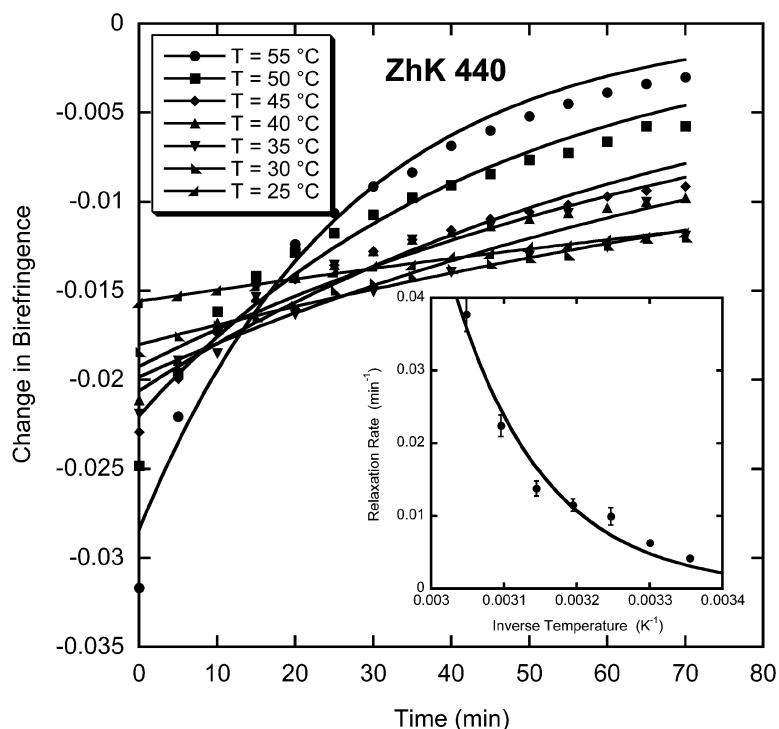
Figure 7. Change in birefringence at 633 nm of ZhK-440 at various temperatures after irradiation with light from a mercury lamp and uv bandpass filter. The lines are fits of exponential functions to the data. The inset shows a plot of the relaxation rates (from the exponential fits) versus inverse temperature. The line in the inset is a fit of Arrhenius behaviour to the data, yielding a value for the activation energy of (66 ± 7) kJ/mol.

known. To measure the latent heat, known amounts of triphenylene were added to ZhK-440 and the decrease in the transition temperature from pure ZhK-440, ΔT, and the width of the coexistence region, δT were determined. The results are shown in table 2, from which a latent heat value of (21.3 ± 0.9) J/mol was calculated using equation (10).

A sample of ZhK-440 was then irradiated with 366 nm light until its transition temperature had decreased significantly. Both the transition temperature and width of the coexistence region were then measured. The coexistence region occurred between 32 and 50°C, which utilizing equation (10) yields a value for the impurity concentration (in this case *cis* isomers) of (8 ± 1)%. A slightly higher concentration (perhaps

around 12%) would be required to depress the transition temperature all the way to room temperature.

4. Discussion

The main absorption feature for azobenzene and azoxybenzene compounds is very similar, namely a strong absorption feature somewhere between 315 and 360 nm, the exact location of which depends on the attached chemical groups. The main difference between the two types of compounds is that both isomers of azobenzene compounds possess an absorption peak around 450 nm, whereas both isomers of azoxybenzene compounds show a slowly decreasing absorption with increasing wavelength in this region. Just as the *cis* isomer of azobenzene compounds possess a stronger peak around 450 nm than the *trans* isomer, the absorption of the *cis* isomer of azoxybenzene compounds is greater than the *trans* isomer around 450 nm. In addition, the thermal relaxation from *cis* to *trans* isomers is governed by similar activation energies, resulting is a slow relaxation at room temperature for both types of compounds. As expected, irradiation by light in the main absorption region increases the concentration of *cis* isomers for both types of

Table 2. Nematic–isotropic transition parameters of ZhK-440 with triphenylene as an impurity.

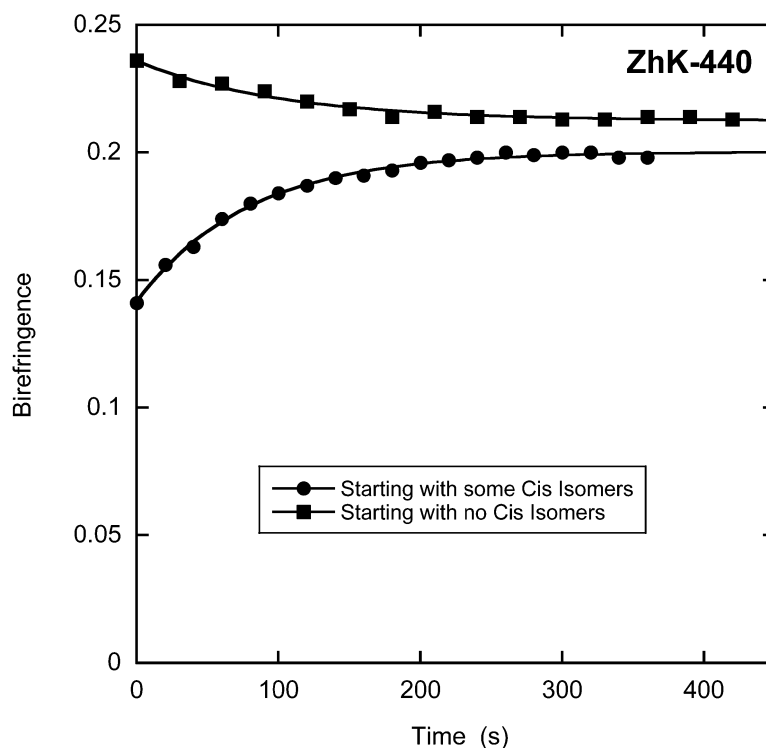| Triphenylene mole fraction	$\Delta T(°C)$	$\delta T(°C)$	Latent heat (J/mol)
0.0239	5.20 ± 0.05	0.64 ± 0.06	20.4 ± 2.9
0.0500	8.69 ± 0.06	0.99 ± 0.10	21.3 ± 2.5
0.0595	11.36 ± 0.07	1.61 ± 0.11	22.2 ± 2.5

Figure 8. Change in birefringence at 633 nm of ZhK-440 when irradiated with 436 nm light. The horizontal axis is the accumulated irradiation time, not the elapsed time (since irradiation was interrupted for birefringence measurements). In one case, denoted by solid squares, the starting concentration of *cis* isomers is close to 0%. In the other case, denoted by solid circles, there are some *cis* isomers present initially (approximately 8%). The lines are fits of exponential functions to the data.

compounds. For the azoxybenzene mixture studied, a modest intensity of light in the main absorption region produces a photostationary state with about equal concentrations of *trans* and *cis* isomers. Finally, for both types of compounds, irradiation with light between 400 and 450 nm creates a stationary state with a low concentration of *cis* isomers. This means irradiation of a sample with a high concentration of *cis* isomers with light of this wavelength lowers the *cis* isomer concentration at a rate similar to the rate *cis* isomers are created by irradiation of light with a wavelength in the main absorption band.

The experiments on the liquid crystal phase of ZhK-440 reveal that azoxybenzene compounds respond to light when in the nematic phase in the same way as when in dilute solutions. Thus the concentration of *cis* isomers can be controlled by irradiation with light either in the main absorption region or in the short wavelength visible range. A revealing finding is how sensitive the liquid crystal phase is to the presence of *cis* isomers. A *cis* isomer concentration of only about 12% is enough to depress the nematic–isotropic transition temperature from 70°C to room temperature. Such a concentration is easily produced with only a modest

intensity of light of the appropriate wavelength. This sensitivity can be described in another way. A property of the liquid crystal phase, birefringence at a fixed temperature for example, changes significantly due to irradiation with a modest intensity of ultraviolet light.

While the determination that a *cis* isomer concentration of only 12% is enough to decrease the transition temperature to room temperature was done by considering the *cis* isomers as impurities, other findings in this investigation are consistent with this estimate. From the experiments on dilute solutions, it is known that irradiation with 366 nm light is capable of producing a *cis* isomer concentration of nearly 50%. When the liquid crystal phase of ZhK-440 was irradiated with 366 nm light, the nematic–isotropic transition rapidly decreased to room temperature, with the birefringence showing no signs of reaching a photostationary value. In addition, the absorption measurements on dilute solutions indicates that irradiation with 436 nm light produces less than 3% *cis* isomers, since 405 nm light created a *cis* concentration of about 3%. When the liquid crystal phase is irradiated with 436 nm light, the nematic–isotropic transition decreases by about 10°C. It would therefore take approximately five times the *cis* concentration to bring

the transition down 50°C to room temperature, or a concentration of about 15%. So the estimate of 12% *cis* concentration to lower the nematic–isotropic transition to room temperature is consistent with both of these results.

There is one more point worthy of note. Notice in figure 4 that the photostationary states during irradiation with 405 nm light are not the same when the starting concentrations of *cis* isomers are different. If the starting concentration of *cis* isomers is nearly 0%, then the absorbance of the photostationary state is 0.667 ± 0.002. If the starting concentration of *cis* isomers is close to 50%, then the absorbance of the photostationary state is 0.631 ± 0.002. A similar phenomenon occurs in the liquid crystal phase. With none of the molecules originally *cis* isomers, repeated irradiation with 436 nm light for 20 or 30 seconds followed by a birefringence measurement with the irradiating light blocked results in a photostationary state birefringence of 0.212 ± 0.001. Starting with a higher concentration of *cis* isomers and irradiating similarly with 436 nm light yields a birefringence of 0.200 ± 0.001 in the photostationary state. These results are shown in figure 8 where the effect is clear. So in both dilute solution and the liquid crystal phase, the same photostationary state is not achieved when the only difference is the initial concentration of *cis* isomers. Yet in both cases, if the sample is left to thermally relax over a period of many hours, the absorbance and birefringence return to their values when nearly 100% of the isomers are *trans*. As noted before, the experimental procedure of irradiating for a certain period of time followed by an absorption or birefringence measurement with the irradiation blocked does introduce an error of up to 10% in observed isomerization rates. But the photostationary state should not be affected much at all, since each absorbance and birefringence measurement takes only a minute. In short, it is difficult to think of a way this effect is due to the experimental procedures used and not the actual behaviour of the azoxybenzene compounds. Such an effect does not seem to be present in azobenzene [23], but the isomerization rearrangement in azoxybenzene compounds is more complicated than in azobenzene compounds [25, 26]. Perhaps there is an intermediate state in the isomerization of azoxybenzene compounds that is not photo-responsive, so the only way for this state to de-excite even when illuminated with visible light is thermally.

5. Conclusions

Azoxybenzene compounds afford many of the advantages of azobenzene compounds as the photo-active agent in optically addressed applications. Modest intensities of ultraviolet and short wavelength visible light are capable of switching a considerable fraction of the molecules from *trans* isomers to *cis* isomers and vice versa. A very slow thermal relaxation rate at room temperature means that refresh rates do not have to be high. When used as the liquid crystal host material, the optical properties are very sensitive to the relative isomer concentrations, indicating that very low light levels can be used. In short, azoxybenzene compounds should be just as useful in optical applications as azobenzene compounds.

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