

Theoretical Study of the Effect of Light on Nematic to Isotropic Phase Transition

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Optical response of liquid crystals is very important from the point of view of applications of liquid crystals in display and data storage devices. Experiments have shown that UV rays incident on nematic liquid crystals doped with photoactive azo compounds lower the nematic isotropic transition temperature (T_{NI}). This is attributed to the transformation of photoactive trans isomer to cis isomer due to UV rays. We have earlier developed a mean field model involving molecular explanation for two lengths in which the mutual orientation of near neighbor molecules changes from an antiparallel to a parallel configuration as the temperature lowered. In this paper, this model is extended to include the length change from trans to cis isomer. The calculated values of change in T_{NI} qualitatively agree with experimental trends.

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1. Introduction

Liquid crystals are fluids characterized by long-range orientational order without long-range three-dimensional translational molecular order [1, 2]. They have some properties of liquids (for example, they can flow) as well as some of those of crystals (for example, birefringence). They consist of molecules having pronounced shape anisotropy (rod-like, disc-like or with a bent core). Liquid crystals obtained by heating the solid crystals are called thermotropic liquid crystals.

Mainly, there are two fundamentally different types of liquid crystals made of rod-like molecules namely, the nematic and the smectic.

The extent of orientational order of the uniaxial nematic liquid crystal is represented by the so-called *scalar* order parameter S defined as [1]:

$$S = \frac{1}{2} \langle 3 \cos^2 \theta_i - 1 \rangle,$$

where θ_i is the angle between the long axis of the i -th molecule and the director. The order parameter takes a maximum value equal to 1 when all the rods are perfectly aligned and is zero when all the orientations of the long axes are equally probable (in the isotropic phase).

When a typical mesomorphic compound is cooled from the isotropic (I) phase, the usual sequence of phase transitions is (with K for solid crystal): I \rightarrow N \rightarrow K. The T_{NI} is the transition temperature at which the nematic to isotropic transition occurs.

In recent years, a field of research that is growing steadily is the photoinduced phenomenon in which the

incident light itself brings about molecular ordering/disordering of the liquid crystalline system [3]. Photonics, in which light can be controlled by light as a stimulus, is being proposed as the future technology for high-speed information processing [4]. It is well known that liquid crystals are convenient to control light because they exhibit large optical effects owing to reorientation of the molecules with the application of low-magnitude electric fields. It has been shown [5] that even in nonphotoabsorbing liquid crystals, optical fields, albeit large, can be used to cause a similar reorientation. However, an addition of chromophores, such as azo groups, has been found to lower the required optical field significantly [6]. Furthermore, the photoinduced birefringence has extremely high long-term stability and holograms recorded show hardly any degradation. This feature has made the photochromic materials, in particular the azo compounds, very promising candidates for optical data storage. An illustration of nature utilizing photoinduced effects is that of the biological photochrome bacterio-rhodopsin found in the eye. Apart from their biological and technological importance, these systems exhibit photodriven phase transitions, thus providing a new tool to study phase transitions and the associated critical phenomena. Several groups have done extensive work in this field [7].

Photoinduced effects reported in the literature are on liquid crystals in which the azo group is either chemically attached to the molecule or is used as a dopant in a liquid crystal host material. If the material exhibits a nematic-isotropic (N-I) transition and the UV irradiation is done in the nematic phase, the lowering of the transition temperature (T_{NI}) could induce an isothermal N-I transition. It is this photochemically induced transition that is promising for the optical image-storing systems. One of the requirements for such an application

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is that the lowering of T_{NI} is appreciable [8]. Although, large shifts in T_{NI} can be obtained if the host material itself is photoactive [9]. From the operational point of view, it is obviously better to dope small quantities of guest photoactive material into a host liquid crystalline system which has been optimized for temperature range, viscosity, etc. Molecules containing azo groups are well known to show reversible isomerization transformations upon irradiation with UV and visible light.

One salient feature observed is the drastic decrease by 15°C in the value of T_{NI} on UV exposure. $\Delta T [= T_{NI}(\text{without UV}) - T_{NI}(\text{with UV})]$ is also affected by pressure [10]. The experimental results are as shown in Fig. 1.

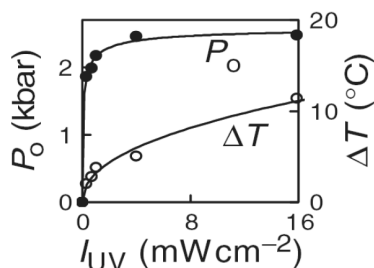


Fig. 1. The intensity dependence of ΔT and that of the pressure at which ΔT goes to zero for a given intensity [10].

Molecular interpretation of this is as follows. Upon UV irradiation around 365 nm, the energetically more stable trans configuration, with an elongated rod-like molecular form changes into a bent or cis configuration (Fig. 2). The reverse transformation can be brought about by illuminating with visible light (in the range 400–500 nm).

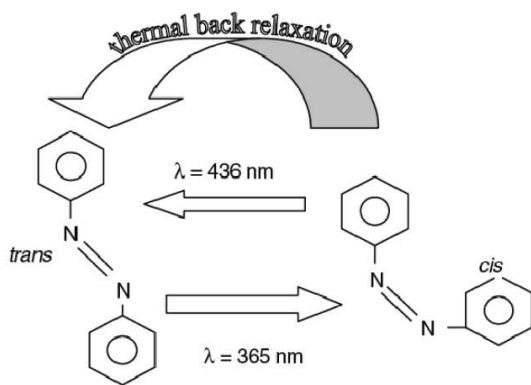


Fig. 2. Schematic diagram illustrating the trans-cis and cis-trans isomerizations [10].

The latter change also occurs in the “dark” by a process known as “thermal back relaxation” in a period ranging from minutes to tens of hours depending on the system [11]. In the case of the photoactive guest–non-photoactive host systems, the trans form of the azo dopant, as it is rod-like, is favourable for the stabilization of the liquid-crystalline phase. On the other hand, the cis

form, which is in bent form, acts like an “impurity” and therefore destabilizes the liquid-crystalline phase. Hence, photoisomerization from the trans to the cis form causes, in general, a lowering of the transition temperature.

2. Molecular model

The host medium has molecules with polar cyano end group. Such a medium has intrinsic ability to show re-entrant phenomena. This is explained considering the medium to be consisting of “two lengths”. The trans to cis change of the guest molecules in the medium also results in a system consisting of “two lengths”. Thus, the medium is assumed to have “two lengths”, with the fraction of shorter molecules varying with irradiation of UV and also with temperature.

A simple model to explain the *molecular origin* of the “two lengths” assumed in the Prost *phenomenological* model was proposed by Madhusudana and Jyothsna Rajan [12]. The basic concept in this model is that the molecular pairs can change over from antiparallel (A) to parallel (P) configuration as the intermolecular separation (r) is reduced due to cooling or due to increase of pressure. The medium is treated as an equilibrium *mixture* of the A and P types of pairs. Experiments [13] showing the presence of *polar* short range order at low temperatures support this model. In the model proposed by Madhusudana and Jyothsna Rajan [12], the origin of the two incommensurate lengths is explained as follows: the permanent dipolar interaction favours an antiparallel arrangement between the neighbouring mesogenic molecules [14]. However, the aromatic part of the antiparallel neighbours overlap due to the strong dispersion interaction between them leading to the partial bilayer arrangement (see Fig. 3a). In this configuration, the alkyl chains of the two molecules, which lie on opposite sides of the core region, do not have a significant interaction. On the other hand, if the molecules are parallel, the permanent dipolar interaction is repulsive. However, the aromatic cores have strong polarizabilities and the induced dipole moment due to a neighbouring polar molecule would weaken the *net* dipole moment of any given molecule in this configuration (see Fig. 3b).

Further, the chains of the two neighbours are now in close proximity and the dispersion interaction between them would favour this arrangement. The repulsive dipolar interaction is $\propto 1/r^3$ where r is the intermolecular separation, while both the dipole-induced dipole and the dispersion interactions are $\propto 1/r^6$ and are attractive in nature. Hence there can be a change from the antiparallel to the parallel configuration as the intermolecular separation is decreased below some value as the density is increased due to a lowering of temperature or an increase of pressure.

The calculated values [15] of $\Delta E = E_A - E_P$ for various intermolecular separations are shown in Fig. 4. This clearly shows favouring of P type at lower intermolecular separations.

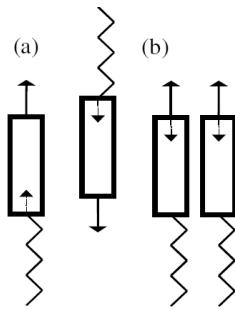


Fig. 3. Schematic diagram showing (a) the antiparallel configuration of two molecules favoured at intermediate molecular separations and (b) the parallel configuration favoured at relatively low values of intermolecular separation. The arrow with solid line represents the permanent dipole moment and the one with dotted line, the induced one. (For the sake of clarity, the relative separation in (a) is exaggerated.)

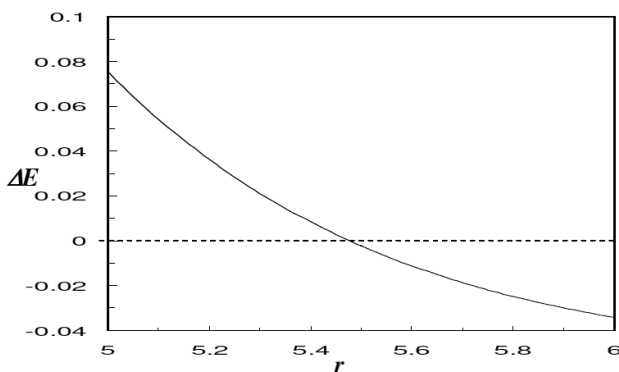


Fig. 4. The pairing energy difference $\Delta E = E_A - E_P$ (in 10^{-19} J) between the antiparallel and parallel configurations plotted as a function of the intermolecular separation r (in Å).

This concept has already been used by Govind and Madhusudana to explain $N_1 - N_d$ transition, double and quadruple re-entrance, effect of electric field etc. [16].

We extend this molecular theory [17] of highly polar compounds to include the effect of light. Many of the assumptions made in this model have already been discussed in the earlier papers [16]. We recall the assumptions relevant for the present theory.

2.1. Assumptions

As explained above, the medium is assumed to consist of “pairs” of molecules having either antiparallel (A) or parallel (P) configurations. The difference between the pairing energy of the A-type (E_A) and the P-type (E_P) configurations is written as

$$\Delta E = E_A - E_P = R_1 k_B T_{NI}, \quad (1)$$

where R_1 is an interaction parameter and R_2 is the reduced temperature at which the density of the medium is such that ΔE becomes zero and $T_R = T/T_{NI}$.

The orientational potential for A-type of pairs (U_{AA}) and P-type of pairs (U_{PP}) are assumed to be different

$$U_{PP} = YU_{AA} \quad (2)$$

and the mutual interaction potential

$$U_{AP} = U_{PA} = P\sqrt{U_{AA}U_{PP}},$$

where $P \neq 1$ indicates a deviation from the geometric mean (GM) approximation.

The following are the additional assumptions made to incorporate the effect of light.

As explained in Sect. 1, the molecular configuration changes from cis to trans upon irradiation. Their respective lengths [18] are about 2.41 nm and 1.5 nm. Thus, in our model, the A-type pairs are of the size of cis molecules and the P-type pairs match with the trans molecules. For simplicity in calculations we consider pairs of cis and trans molecules in the equations. Hence, irradiation of UV increases the number of molecular pairs of cis type, which is equivalent to increase of mole fraction of P-type pairs (X_P). The same effect would have occurred upon increase of E_P . An increase of E_P results in the decrease of ΔE . This is equivalent to shifting the graph downwards in Fig. 4. In other words, effectively R_2 decreases. Thus, R_2 with light ($R_2(L)$) is less than R_2 without light ($R_2(0)$).

In view of this, we can write

$$R_2(L) = R_2(0) - \delta, \quad (3)$$

where δ represents the change in R_2 because of light.

We calculate δ as follows:

Let dE be the amount of light energy incident on the sample in a time dt . Due to this, some trans molecules change to cis. Let the number of trans (i.e., A type) molecules change from N_A to $N_A - dN_A$.

Thus,

$$-\frac{dN_A}{N_A} \propto dE,$$

$$-\frac{dN_A}{N_A} = K_1 dE,$$

where K_1 is a constant to be estimated later.

As mentioned earlier, the reverse transformation of the cis isomer into the trans isomer (thermal back relaxation) takes a very long time. Thus, the fraction of cis changing back to trans is negligibly small. Hence, this change during UV irradiation is ignored.

Solving this, we get,

$$N_A = N_A(0)e^{-K_1 E},$$

where $N_A(0)$ is the number of trans pairs in the absence of light.

The number of cis (i.e., P type) molecules resulting is

$$N_P = N_A(0) - N_A = N_A(0)[1 - e^{-K_1 E}].$$

We assume that the change in $R_2 \propto N_P$. Thus, $\delta = K_2(1 - e^{-K_1 E})$, or

$$R_2 = R_2(0) - K_2(1 - e^{-K_1 E}). \quad (4)$$

Thus,

$$\frac{\Delta E}{kT} = R_1 \left[\frac{R_2(0)K_2(1 - e^{K_1 E})}{T_R} - 1 \right]. \quad (5)$$

The values of K_1 and K_2 are estimated as explained later in Sect. 2.3.

2.2. Free energy and order parameters

Extending the Maier–Saupe theory for mixtures, the potential energy of the i -th A-type of pair can be written as

$$U_{Ai} = -U_{AA}X_A S_A P_2(\cos \theta_{Ai}) - U_{AP}X_P S_P P_2(\cos \theta_{Ai}), \quad (6)$$

where X_A , X_P , S_A , S_P are the mole fractions, orientational of A and P types of pairs, respectively. Similarly for a P-type pair, U_{Pj} is obtained by interchanging suffixes A and P in Eq. (6). The internal energy of one mole of pairs can be written as

$$2U = \frac{NX_A}{2} \langle U_{Ai} \rangle + \frac{NX_P}{2} \langle U_{Pj} \rangle - NX_P \Delta E,$$

where the angular brackets indicate statistical average, the factor 2 on the left hand side reminds that we have a mole of pairs, the factor 1/2 appears in the first two terms since each pair is counted twice while averaging over the *mutual* interactions and we have also added the concentration dependent part of the configurational energy. The molar entropy is given by

$$2\zeta = -Nk_B \left[X_A \frac{1}{d} \int_{-d/2}^{+d/2} dz_{Ai} \int_0^1 d(\cos \theta_{Ai}) f_{Ai} \ln f_{Ai} + X_P \frac{1}{d} \int_{-d/2}^{+d/2} dz_{Pj} \int_0^1 d(\cos \theta_{Pj}) f_{Pj} \ln f_{Pj} \right] - Nk_B (X_A \ln X_A + X_P \ln X_P),$$

where the last term is the entropy of mixing and f_A and f_P are the normalised distribution functions of A and P types of pairs, respectively. The Helmholtz free energy is given by

$$F = U - T\zeta.$$

The orientational distribution functions of the A-type of pairs f_A and f_P are found by minimising F .

We have

$$f_A = \frac{1}{Z_A} \exp \left(\left(\frac{U_{AA}}{k_B T} [X_A S_A + P\sqrt{Y} X_P S_P] \right) \times P_2(\cos \theta_A) \right),$$

$$f_P = \frac{1}{Z_P} \exp \left(\left[\frac{U_{AA}}{k_B T} (Y X_P S_P + P\sqrt{Y} X_A S_A) \right] \times P_2(\cos \theta_P) \right),$$

where Z_A and Z_P are the appropriate normalising integrals. Hence the order parameters are given by

$$S_A = \int_0^1 d(\cos \theta_{Ai}) P_2(\cos \theta_{Ai}) f_A, \quad (7)$$

where S_P is obtained by interchanging the suffixes A and P in Eq. (7). The free energy per mole of pairs can now be written in the simplified form

$$2F = + \frac{NU_{AA}}{2} \left[X_A^2 S_A^2 + Y X_P^2 S_P^2 + 2P\sqrt{Y} X_A X_P S_A S_P \right] - Nk_B T X_A \ln \left(\frac{Z_A}{X_A} \right) - Nk_B T X_P \ln \left(\frac{Z_P}{X_P} \right) - NX_P \Delta E.$$

The equilibrium value of the mole fraction of the A-type of pairs (X_A) is found by minimising F with respect to X_A . We get, with $X_P = 1 - X_A$,

$$\frac{X_P}{X_A} = \frac{Z_P}{Z_A} \exp \left(\frac{\Delta E}{k_B T} \right).$$

2.3. Calculations

Calculations have been made as for $R_2(0) = 0.85$ with $R_1 = 10$, $P = 0.6$ and $Y = 0.8$ which are reasonable as explained in Ref. [19]. We evaluate all the necessary integrals using a 32 point Gaussian quadrature method in double precision. We look for the following types of solutions:

1. $S_A, S_P \neq 0$ leading to nematic phase and
2. $S_A, S_P = 0$ leading to isotropic phase.

The stable phase is the one having lower free energy. The temperature at which these two solutions have the same free energy gives T_{NI} .

The experiments show that trans to cis changing efficiency is quite high over a large temperature range, with the maximum occurring in the vicinity of the T_{NI} of the irradiated case. In fact [10] the efficiency remains within 20% of the maximum over a range of 10 °C.

The change in ΔE due to light corresponds to the energy difference between trans and cis configurations. This corresponds to the energy difference between 365 nm and 435 nm. This is about $22k_B T$ at $T = 300$ K. However, all the light energy incident is not used for trans to cis conversion because the photo absorbing material is doped to about 5% and the maximum photo efficiency is about 20%. Thus average energy per molecule reduces to (1/100)-th of $22k_B T$, i.e., $0.22k_B T$. For a pair of molecules, it is $0.44k_B T$. Hence, we have used $0.5k_B T$.

Thus, the change in ΔE due to light is

$$\frac{\delta(\Delta E)}{k_B T} = 0.5.$$

In Eq. (5), the change in ΔE due to change in R_2 is

$$\frac{\delta(\Delta E)}{k_B T} = \frac{R_1 K_2 (1 - e^{-K_1 E})}{T_R}.$$

Here, K_2 represents the maximum change in R_2 for light energy $E \rightarrow \infty$. This is assumed to be 0.1. We are investigating the change in T_{NI} due to light. Thus, our calculations are for T_R close to 1. For $R_1 = 10$ and $T_R = 1$, we have

$$K_2(1 - e^{-K_1 E}) = \frac{0.5T_R}{R_1} = 0.05,$$

$$e^{-K_1 E} = 1 - \frac{0.05}{0.1} = 0.5,$$

$$K_1 E = \ln 2 = 0.7.$$

For $E = 1 \text{ mJ cm}^{-2}$ and the magnitude of $K_1 = 0.7$ with E in mJ cm^{-2} , Eq. (3) becomes

$$R_2(L) = R_2(0) - 0.1(1 - e^{-0.7E}). \quad (8)$$

3. Results and discussions

The incidence of UV rays change the trans isomer (longer) to cis isomer (shorter). This is equivalent to an increase in shorter “P” type of pairs. The “P” type pairs which are shorter have lower orientational potential than “A” type pairs. Thus we have used $Y = 0.8$ in Eq. (2), as in earlier papers [19]. Thus, the medium with larger X_P has lower T_{NI} . Hence, UV irradiation results in lowering of T_{NI} . This is indirectly brought about by variation of R_2 . As mentioned earlier, the thermal back relaxation is very slow and the relaxation of cis to trans and hence the decrease of X_P is ignored. As the intensity of UV radiation is increased, the fraction of trans available reduces. Thus, the variation of ΔT_{NI} with intensity is not linear. The slope decreases indicating that the cis isomers are gradually reaching saturation. The total energy received also depends on the time of illumination. Thus we have plotted ΔT_{NI} with respect to energy not power.

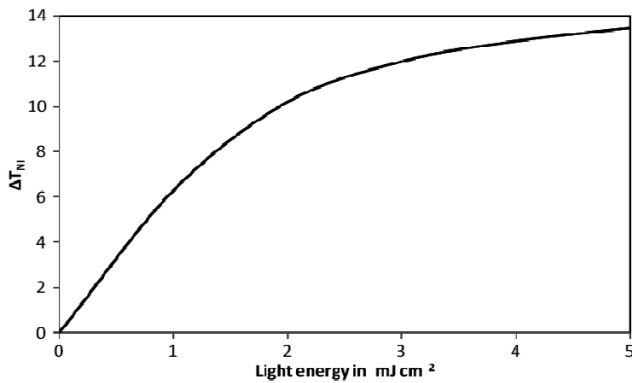


Fig. 5. Variation of calculated values of ΔT_{NI} in K as a function of incident light energy in mJ cm^{-2} .

Assuming the time duration of illumination to be same, it can be compared with the experimental graph of ΔT_{NI} with respect to intensity shown in Fig. 1. The trends agree qualitatively.

4. Conclusions

Response of liquid crystals to light is very important for applications of liquid crystals in display and memory devices. Recently experiments have been carried out on liquid crystals doped with photoactive azo compounds. It is seen that UV rays incident on such systems can lower the nematic isotropic transition temperature T_{NI} . This is attributed to the change in trans (longer) isomer to cis (shorter) isomer of photoactive dopant. We have earlier developed a molecular mean field model assuming the medium to consist of inter-converting antiparallel and parallel pairs to explain the origin of “two lengths”. The model was used to explain double re-entrance, effect of electric field on T_{NI} etc. This model is modified to include the change of trans to cis isomer which is equivalent to an increase of fraction of parallel (shorter) pairs. The calculated variation of ΔT_{NI} with respect to incident UV radiation energy shows a qualitative agreement with experimental trends. The model is being further extended to include the smectic interaction and further work is under progress.

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