CHAPTER-2

REVIEW OF EXPERIMENTAL RESULTS ON PHOTO INDUCED TRANSITION PHENOMENA
2.1 Introduction

Over the past two decades, liquid crystals [1] have attracted ever-increasing interest because of their ability, due to their self-assembling nature, to dramatically alter the properties of light reflected from or transmitted through them. Traditionally, low-magnitude electric fields have been used to control/alter the molecular ordering of these systems resulting in the highly successful electro-optic display applications. In such devices an applied electric field induces a change in the material properties, which in turn affects the birefringence of the sample. More recently, a field of research that is growing steadily is the photo-induced phenomenon in which the incident light itself brings about molecular ordering/disordering of the liquid crystalline system. This particular aspect of photonics, in which light can be controlled by light as a stimulus, is being proposed as the future technology for high-speed information processing [2]. It has been shown [3] that even in non-photo absorbing liquid crystals, optical fields, albeit large, can be used to cause a reorientation of the molecules. However, addition of chromophores, such as azo groups, has been found to significantly lower the required optical field [4]. Furthermore, the photo-induced birefringence has extremely high long-term stability, and holograms recorded show hardly any degradation [5]. This feature has made the photochromic materials, in particular the azo compounds, promising candidates for optical data storage. An illustration of nature utilizing photo-induced effects is that of the biological photochrome bacteriorhodopsin found in the eye. In fact, the photosensitive nature of this material has found uses in the construction of spatial light modulators and optical storage devices [6]. Apart from their biological and technological importance, these systems exhibit photo-driven phase transitions, thus providing a new tool to study phase transitions and the associated critical phenomena [7,8,9,10]. In this chapter, we review some of the experimental results [11,12,13,14,15,16,17,18,19,20] to the field of photo-induced isothermal phase transitions in various liquid crystalline systems. We concentrate here on the photo-induced effects observed in systems having the photochromic azo (–N=N–) group. The azo group is either chemically attached to the molecule or is used as a dopant in a liquid crystal host material. The heart of the phenomenon in such systems is the reversible photo induced shape transformation of the molecules containing the photochromic azo groups. Upon UV irradiation (around 360 nm, corresponding to the \( p - p^* \) band of the azo group), the energetically more stable trans configuration, with an elongated rod-like molecular form,
changes into a bent cis configuration. The reverse transformation can be brought about by illuminating with visible light (in the range 400–500 nm, corresponding to the $n-p^*$ band). This latter change can also occur spontaneously in the ‘dark’ by a process known as thermal back relaxation. 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 bent cis 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. If, for instance, 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, $T_{\text{NI}}$, could induce an isothermal N–I transition. It is this photochemically induced transition that is promising for the optical image storing systems.
2.2 Photo-isomerization

Photo-isomerization is the transformation of a chemical compound between two conformations having different absorption spectra. Light–induced isomerization of azobenzene derivatives are well-known phenomena that has been extensively used in the past. Azobenzene is the parent molecule of the large group of azo compounds. This group is very important in practical use as its members are dye stuffs of high light fastness. Azobenzene derivatives may exist as two geometric isomers, the Trans and the cis form, also referred to as E and Z forms respectively. These two configurations differ in the direction of the central bonds as shown in the figure 2.1.

![Figure 2.1 Schematic diagram of the azobenzene molecule in the E and Z forms.](image)

In the energetically more stable (by about 50kJ/mol) E state the two bonds linking the azo group to the aromatic rings are parallel, resulting in an elongated shape of the molecule. In the metastable cis state the angle between the two bonds is 120 degrees and the molecule adopts a bent banana-like confirmation. The two isomers also differ in their absorption spectra. The absorption spectrum of Trans azobenzene exhibits a maximum in the range 350-370nm, due to the $\pi-\pi^*$ transition (see Figure 2.2).
Figure 2.2 Absorption spectrum of the azobenzene derivative showing two peaks marked as 1 and 2.

Upon absorption of UV light (~365nm) the energetically more stable E configuration, transforms into the Z configuration. The reverse transformation of the Z isomers into the E isomers can be brought about by irradiation with visible light (in the range of 400-500nm). The latter change can also occur 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[21]. A schematic representation of this E-Z isomerization process is given in figure 2.3.
Figure 2.3 A schematic representation of the E-Z (trans-cis) isomerization [21].

Effects brought about by the E-Z isomerization in viscous solutions of azo dye was discovered by Weigert nearly a century ago and has been studied widely since then. The actual mechanism of photoisomerization in azobenzene systems is being understood only recently. The usual approach of Photoisomerization suggests an initial excitation of the dye molecules (path 1, of figure 2.4) from their stable R (T) form to the excited singlet (T*) states. These molecules relax very rapidly and nonradiatively via the so-called internal conversions to the lowest excited state (path 2) of the same isomer. The rate of this relaxation is high, of the order of 10-12 sec.
Recent resonance Raman studies indicate that the time scale of the dynamics is in the femtosecond range. The lifetime of lower singlet state of the E molecule relaxes to the metastable isomeric Z (C) form. This reaction is usually reversible with different E-Z and Z-E quantum yields. The direct transition model is considered via path 3, and the non-direct transition via the long living triplet state (path4). The type of molecule and the host environment play a crucial role in the character of dye isomerization. Thus, the quantum yields can change strongly depending on the dye structure, its environmental condition (for example, host matrices, temperatures, etc.) and, in particular, the excitation wavelength.

The most important property that changes as a result of the photo-driven isomerization is the shape of the molecule. While the E isomers has a rod-like shape, the Z isomers is bent or V-shaped(see figure 2.5) Associated with this shape change the geometrical dimension of the azobenzene molecule also changes. For example, in the case of EPH (azobenzene), it has been found that the length of the E isomers is 2.2nm, whereas the cis isomers is substantially smaller being about 1.6nm as shown in figure 2.5. It is this combination of dramatic change in the shape and length of the molecule in conjunction with the high photochemical stability of azobenzene that lies at the heart of the phenomenon of photo induced transitions.

**Figure 2.4.** Schematic energy diagram of dye photo excitation. T and C are the Fundamental E and Z states’ T* and C*, excited state of E and Z forms; Tt and Ct, Possible triplet states in E and Z isomeric forms.
Liquid crystals are elastically soft materials. If a small portion of LC molecules changes their orientation on response to an external stimulus, the other LC molecules also follow the change. When a small amount of photochromic molecules such as azobenzene are incorporated into a liquid crystalline system, and the host mixture is irradiated with actinic light, it may lead to even phase transitions, although isothermally. The mechanism of the photo induced phase transitions is given in figure 2.6.
In the absence of UV radiation, the photoactive molecules are rod-like in shape and therefore support, if not enhance the orientational order of the host molecules and the material, say in the liquid crystalline nematic phase, appears birefringent under the microscope. When the UV is switched ON, the photoactive molecules undergo shape transformation to bent form and therefore introduce a local region of higher orientational entropy (disorder) compared to the regions of the host molecules. If the increase is large enough, it may result in the formation of isotropic (Iso) domains at the irradiated sites which appears as dark regions under the microscope. The sphere of influence of the azobenzene molecules could very large making the entire sample undergo the photo induced transition from the nematic to the isotropic phase. Therefore the E-Z change generally leads to a lowering of the phase transition temperature. Photo-induced isothermal transitions have been observed for a variety of systems exhibiting different phases. The photo induced phase will have point group symmetry although exceptions have been reported.
Photo induced effects have been well studied in systems exhibiting nematic-isotropic (N-Iso), smectic-A-nematic, smecticC*- smecticA, and smectic-Cα*-smectic-A, and also from the reentrant nematic to smectic-A system. The last of these is a rare example of a photo induced disorder to order phase transition. One of the requirements for optical storage applications is that the lowering of $T_{N-Iso}$ be applicable. Although, large shifts in $T_{N-Iso}$ can be obtained if the host material itself is photoactive, 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.

As explained earlier upon irradiation with light of suitable wavelength, photochromic molecules, such as azobenzene derivatives, exhibit a shape transformation due to trans±cis photoisomerization. The principle involved in the following figure 2.7.

![Figure.2.7. Schematic representation of the photo-induced N-I phase transition due to trans-to-cis photoisomerization of the guest azo molecules. In the absence of the UV irradiation, the azo molecules are in the trans state and therefore have a rod shape, thus stabilizing the liquid crystalline nematic phase of the host molecules. On irradiating with the UV radiation the azo molecules undergo a shape change, assuming a bent shape in the cis form. This destabilizes the N phase with the host molecules pointing in random directions. As the trans form is energetically more stable, turning the radiation OFF results in the azo molecules converting back from the cis-ti-trans form and the N phase is recovered.](image-url)
While the trans form of the azobenzene derivatives is rod-like, thus stabilizing the LC phase, the cis form has a bent shape and therefore destabilizes the LC phase. Hence, if the sample is in the nematic phase, the photoinduced trans-to-cis conversion can lead to an isothermal nematic-isotropic (N-I) transition, in the process causing large birefringence changes. This feature is being extensively investigated for possible image storage applications. The dynamics of the photo-induced N-I transition has also been well-studied. For instance, if the material consists of non-photoactive host molecules and a small amount of photoactive guest molecules, then the photo-induced transition occurs in two steps. Upon irradiation, photoisomerization and the resulting shape transformation of the guest molecules takes place. Next, owing to the presence of the bent guest molecules, which act as an impurity, the rod-like host molecules undergo the transition from the nematic to the isotropic phase. The former is a very fast process and for the azobenzene derivatives occurs within 10 ns. The latter process of the disappearance of the LC phase can in principle also occur within 10 ns, but the fastest observed hitherto is in the range of 100 ns. The origin of this fast transition lies in the fact that in LC phases the optical anisotropy comes from the anisotropy due to the orientational ordering alone, as the center of gravity of each molecule is distributed randomly. Therefore, the transition can be brought about by just randomizing the direction of the molecular orientation without involving any diffusion of the molecules, which would have required a translation process. This mechanism assumes significance due to the recent observations of photo-induced transitions from the lamellar Sm A phase to the nematic phase. In fact, to explain this transition, using molecular dynamics simulations, a new mechanism termed nanophase segregation has been proposed. In this chapter we discuss a new type of photoinduced transition which can be taken as direct evidence for the existence of such a mechanism. Time-resolved measurements near this transition provide further confirmation of this.
2.3 Experimental Study

The host material used for the measurements was a 24 wt.-% mixture of 4-cyanophenyl 4-octyloxybenzoate in 4-octyloxy 4-cyanobiphenyl. The photoactive guest compound was p-(p-ethoxyphenylazo) phenyl hexanoate doped at a low concentration of 2.9 wt.-% to the host mixture. The transition temperatures of the resultant guest-host mixture are isotropic 80.6°C, nematic 48.8°C, smecticA 34.8°C, re-entrant nematic (I → N → SmA → N_re). The lower temperature N phase is termed re-entrant because of its re-appearance on the temperature scale [13].

When irradiated in the SmA and high-temperature N phases, the material transforms into N and I phases respectively. This is not surprising and, in fact, is in agreement with the results in the literature that the UV irradiation can lead to a melting of the phase, or in other words, a transition to a less ordered state. But when the experiment is done in the N_re phase, a novel feature is observed. The N_re phase transforms into the SmA phase, i.e., to a more ordered state.

2.3.1 Photo-induced effects in nematic liquid crystals

Photo-induced 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 photo-chemically induced transition that is promising for the optical image-storing systems. One of the requirements for such an application is that the lowering of T_{NI} be appreciable [22]. Although, large shifts in T_{NI} can be obtained if the host material itself is photoactive [23], 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 150°C in the value of T_{NI} on UV exposure. \( \Delta T = T_{NI} \) (without UV) – T_{NI} (with UV) is also affected by pressure [21]. The experimental results are as shown in fig 2.8.
2.3.2 Photo-induced effects in Smectic phase and Nematic to Smectic Phase Transition

In other experiments [24] with light, the host LC material was chosen to be the binary system formed by the eighth (C8) and tenth (C10) homologues of the series 4-(2-cyanoethyl)phenyl-4-(alkoxy)benzoate. While C10 exhibits the isotropic (I)-smectic A (SmA)-smectic C (SmC) sequences, C8 shows only an I-N transition. The photoactive azobenzene based guest compound, 4-(4-ethoxyphenylazo) phenyl hexanoate (EPH in short), is also liquid crystalline, having a nematic phase, a feature which facilitates homogenous mixing with the host LC system. The experimental temperature–concentration (T-X; where X is the concentration in wt.-% of C10 in C8) phase diagram obtained for 4% (by weight) of EPH in the host system is shown in figure 2.10. The interesting feature of the phase diagram is the existence of the N phase both above and below the SmA phase for concentrations in the range of X= 70 to 85 wt.-%. The low-temperature N phase is referred to as the re-entrant nematic (N\textsubscript{R}) phase [25].
Figure 2.9. T-X diagram of the guest-host system used in the study, containing 4% of EPH as the photoactive component. Notice that for X>70 the phase sequence on cooling (iso) I-N-SmA-N$_R$, whereas for X<70 it is simply I-N. The concentration X=60m (on which the main investigations were done) is indicated by a vertical line. The dashed line indicates a virtual SmA-N$_R$ transition (N$_R$: re-entrant nematic phase) [25].

The experiment performed[24] on the X=60 mixture, which exhibits only the I-N sequence on the temperature scale, shows two additional transitions in the presence of the UV radiation. The phase sequence now is I-N-SmA-N$_R$, which means that irradiation with UV light introduced a phase (SmA phase) which does not exist in the normal temperature scale. The temperature range of the induced phase is seen to be (Figure 2.10) strongly dependent on the magnitude of the UV intensity.
Figure 2.10. The He-Ne laser transmitted intensity in the absence of (O) and upon shining UV light of different magnitudes in $\mu$W cm$^{-2}$: 2(Δ), 8(□), 50(○), and 100(□). The sharp fall and steep rise in the transmitted intensity for the last three sets indicates the onset of the transition from the N phase and to the NR phase respectively [24].

What is more surprising is that unlike the temperature-concentration phase diagram (Figure 2.9), which has a parabolic shape of the SmA region, the temperature-intensity diagram is asymmetric in shape (Figure 2.11) [24].
Figure 2.11. Temperature-UV intensity phase diagram. Notice that it is asymmetric rather than symmetric as in the temperature-concentration plane [24].

The figure 2.12 represents the critical intensity required to induce the SmecticA phase.

Figure 2.12. Concentration ($X$) dependence of the critical intensity ($I_c$) required to induce the sm-A phase. The critical intensity $I_c$ diverges as the concentration moves away from the tip of the parabola in the T-X diagram [26].
2.4 Dynamic Effects

To observe the dynamic effects, measurements were made by irradiating the sample with a UV intensity of 2mW/cm$^2$ from the conventional source. The time dependence of the transmitted probe beam intensity, $I_{\text{probe}}$, when the sample is kept in the $N_{\text{re}}$ phase and UV irradiated is shown in Figure 2.13. On turning the UV on, an abrupt and almost instantaneous decrease in $I_{\text{probe}}$ is observed, signifying that the $N_{\text{re}}$-Sm A transition has taken place. As mentioned earlier, this transition is caused by the trans-to-cis photoisomerization of the guest azo molecules. Also shown in this figure is the reverse Sm A-$N_{\text{re}}$ transition occurring as a consequence of the azo molecules converting back from the cis to the thermally more stable trans form when the UV radiation is switched off. A significant feature is that the time required to recover 90% of the initial intensity due to this thermal back relaxation, $\tau_{\text{back}}$, is unusually long, about 24 h. For comparison, the results of similar measurements in the high temperature nematic phase. While the time response for the UV ON condition is quite abrupt, just as in the case of the $N_{\text{re}}$ phase, $\tau_{\text{back}}$ is also fast, taking about 3 min. In other words, the back relaxation process is about three orders of magnitude slower in the case of the $N_{\text{re}}$ phase. In contrast, the photo-induced change from the Sm A phase to the higher temperature nematic phase relaxes back in about 17 min.

![Figure 2.13. Time dependence of the transmitted intensity of the probe laser beam across the photo-induced $N_{\text{re}}$-Sm A and $N$-I (shown in the inset) transitions, as well as through the thermal back relaxation process, when the UV radiation is turned on and off respectively.](image-url)
The second type of time-resolved investigation was done using the YAG laser source keeping the intensity at 10mw/cm². Typical time-dependence of $I_{\text{probe}}$ obtained in the $N_{re}$ and N phases by irradiating the sample with a single pulse of the laser are shown in Figure 2.14. In the N phase the value of response time $\tau_r$ (the time required for the intensity to change from 90% to 10% of the initial value) was extremely small (485)ns the fastest observed for any photochemical transition involving a liquid crystalline phase. Further, this number is only 40 times more compared to the value reported for the trans-to-cis conformational hange to take place[27]. In contrast, the $N_{re}$-Sm A transition was much slower taking about 100 ms.

![Image](image.png)

**Figure 2.14.** Time-resolved probe beam intensity measurements of the photo-induced a) $N_{re}$-Sm A and b) N-I transitions. The N-I transition takes place extremely fast, with about 485 ns as the response time. In comparison, the $N_{re}$-Sm A transition is slower requiring about 100 ms to complete.
2.5 Explanation

To explain the photo-induced effects, particularly in the N_{re} phase, usually, the photo controlled nanophase segregation mechanism mentioned earlier[28] is used. The principle behind this nanophase segregation (see Figure 2.17) is that when the UV radiation is absent the azo molecules are in their trans form which have a rod-like shape and are therefore easily accommodated into the smectic layers. But in the photo-induced cis form the molecules assume a bent shape and therefore get expelled from within the layers and occupy the region between the layers. This shows up as an increase in the overall layer spacing value. It may be mentioned that in the UV irradiated state neither in the studies of Krentzel et al [29] nor in our case, any additional reflections, which may be expected to originate from the phase separated regions, have been seen. This is perhaps because of the low concentration of the photochromic molecules used.

The frustrated spin-gas model developed by Berker and collaborators[30,31] has been found to describe the re-entrant transitions quite successfully. The model is essentially designed for molecules that have a strong polar group at one end like the ones in the host mixture used in the current study. In the Sm A phase of such systems, the model considers a two-body dipolar potential with ferroelectric and antiferroelectric interactions, and then looks for the effect on a third dipole, with the dipoles oriented parallel to the layer normal. When the dipolar forces between two particles cancel, the third dipole experiences no force and is therefore free to permeate or diffuse from one smectic layer to the next one, thus frustrating the smectic order. Consequently, the nematic phase re-enters. On the other hand, if the cancellation is not complete, the presence of the triplet is supposed to stabilize the smectic order through short-range dipolar interactions.

Now, consider the nanophase segregated SmA phase. The guest azo-rich regions (in cis form) and the Sm A layers of the host molecules are not favored to mix with each other. The permeation of the molecules from one layer to another is now less preferred. Consequently, the situation becomes less conducive for the formation of a re-entrant nematic phase. This argument should also apply for the transition to the high temperature nematic phase. However, increase in thermal fluctuations can help overcome the problem (albeit at temperatures not far from the transition temperature for the non-irradiated case) and the
system can transform to a nematic phase. Perhaps for this reason the shift in the SmA-N transition temperature is quite small compared to those for the N-I or the N_{re}-SmA transitions.

We propose a molecular mean field model to explain these results. This is discussed in the subsequent chapters.
2.6 References: