Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thermochimica Acta 440 (2006) 205–211

thermochimica acta

www.elsevier.com/locate/tca

# High pressure investigations of the photo-stimulated orientational ordering transition in a liquid crystal with photoactive dimeric molecules

Vivek Kumar Gupta[1], D.S. Shankar Rao, Chethan V. Lobo, S. Krishna Prasad*,
Uma S. Hiremath, Channabasaveshwara V. Yelamaggad

*Centre for Liquid Crystal Research, Jalahalli, Bangalore 560 013, India*

Received 8 October 2005; received in revised form 7 November 2005; accepted 10 November 2005

## Abstract

High pressure investigations have been carried out on the photo-stimulated phase transition exhibited by a guest–host system, where the host is a non-photoactive liquid crystal. As guest molecules we chose successive homologues of a dimeric photoactive azobenzene liquid crystalline molecule to understand the influence of the length and parity of the alkylene spacer on such a transition. Our studies show that application of pressure as well as the parity of the spacer has a drastic influence both on the static and dynamic characters of the photo-stimulated phase transition.

*Keywords:* Photo-isomerization; Photoinduced transition; High pressure studies

## 1. Introduction

The phenomenon of a beam of light, of a proper wavelength, inducing isothermal phase transitions in liquid crystalline materials was first realized in 1963 [1]. However, this phenomenon is attracting significant interest only in recent times [2–9]. Such photo-stimulated phase transitions have been reported in a variety of systems including spin-crossover complexes [10] and π-conjugated polymers [11]. The photo-isomerization and the associated shape change of certain molecules, e.g. azobenzene is a convenient but powerful mechanism that has been exploited for such studies. The molecules containing the azobenzene moiety show reversible isomerization transformations upon irradiation with UV and visible light [12]. Upon absorption of UV light (typically 365 nm) the energetically more stable E configuration with an elongated rod-like molecular form, changes its shape to a bent banana-like Z configuration. The reverse transformation of the Z isomer into the E isomer can be brought about by irradiation of visible light (in the range of 400–500 nm) or spontaneously through a process termed "thermal back relaxation" even when the system is kept in the "dark". When the azobenzene entities are integrated into a liquid crystalline medium, either by physical mixing with a non-photoactive host system or by chemical bonding, the photo-isomerization can lead to interesting effects. For example, owing to its rod-like shape the E form stabilizes the liquid crystalline phase but the photoinduced Z isomer with its bent shape acts like an "impurity" destabilizing the phase. Such a destabilization can even cause a photoinduced transition from a liquid crystalline phase, say, the nematic phase to the isotropic phase. The attractive feature of this light-driven transition is that it is isothermal, which has been investigated, not only from a basic point of view, but also for possible applications in optical switching, image storage and opto-mechanical devices [13–17]. Photoinduced effects across different liquid crystalline transitions involving the nematic [2,4,6], and polymorphic forms of the smectic phase, [5,8,18,19] have been studied at atmospheric pressure. Recently, we have investigated the effect of pressure on the phase diagram [20] and the dynamics [21] of the photoinduced nematic-isotropic phase transition. In this paper we report the influence of the spacer and parity of a photoactive guest dimeric material on the pressure behaviour of guest–host systems in which the host molecule is non-photoactive.

---

* Corresponding author. Tel.: +91 80 2838 1119; fax: +91 80 2838 2044.
*E-mail address:* skpras@gmail.com (S.K. Prasad).

[1] Present address: P.G. Department of Physics, University of Jammu, Jammu 180 004, India.

0040-6031/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2005.11.012

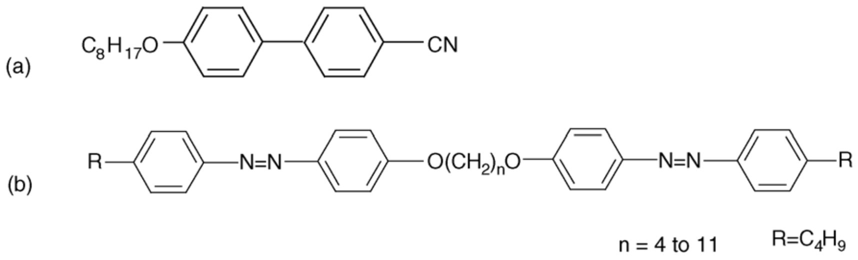

Fig. 1. Molecular structures of the (a) host and (b) photoactive guest molecules used in this study.

## 2. Experimental

The liquid–crystalline host material is 4-*n*-octyloxy cyano biphenyl (8OCB, for short), procured from E-Merck and exhibiting nematic and smectic A mesophases. The UV-active guest compounds used are the C = 4–11 homologues of the series, $\alpha$,$\omega$-bis(4′-*n*-butylazobenzene-4-oxy) alkane [22]. The molecular structures of the host and the guest molecules are given in Fig. 1. Notice that the guest compounds are dimeric in nature with two mesogenic units linked via a flexible spacer. The presence of two azo groups symmetrically disposed about the center of these molecules is expected to enhance any photoinduced effect. The actual materials used for the pressure studies were mixtures of 8OCB with the UV-active compound doped at a low concentration of 5% by weight. In the rest of the paper these mixtures are designated as Mn ($n = 4$–11) where $n$ indicates the number of methylene units in the spacer of the photoactive compound. The nematic-isotropic (N-Iso) transition temperatures ($T_{\text{N-Iso}}$) obtained by polarizing microscopy observations for the various mixtures are shown as a function of the spacer length in Fig. 2.

A schematic diagram of the optical transmission high pressure set-up [20] employed for the experiments is shown in Fig. 3. It essentially consists of the sample sandwiched between two optically polished sapphire rods enclosed in an elastomeric tube, serving not only as a container but also to isolate the sample from the liquid pressure-transmitting medium. The phase transition is detected by monitoring the intensity of a He–Ne laser beam transmitted through the sample. The UV apparatus used for inducing photo-isomerization consisted of an intensity stabilized UV source with a fiber-optic guide (Hamamatsu L7212-01, Japan) in conjunction with a UV-bandpass filter and an IR-block filter. The actual power $I_{\text{UV}}$ of the radiation passing through the filter combination, the sapphire rod pair, and falling on the sample was measured to a precision of 0.1 mW/cm$^2$ with a UV power meter (Hamamatsu C6080-03) kept in the sample position. The precision in the applied pressure measured using a Heise gauge is reckoned to be ±2 bar and that of the temperature measured with a thermocouple mounted close to the sample is 0.1 °C.

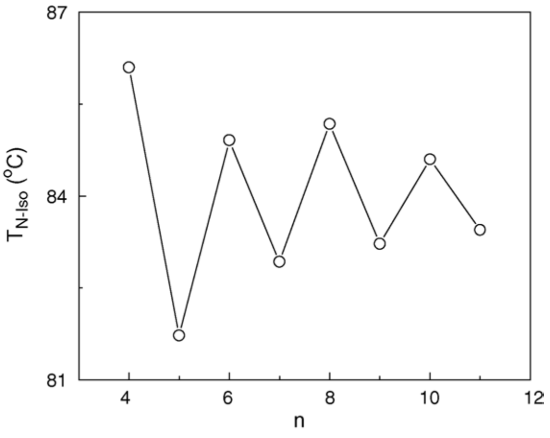

Fig. 2. Spacer length ($n$) dependence of the nematic-isotropic transition temperature $T_{\text{N-Iso}}$ for the mixtures M4–M11. Notice that $T_{\text{N-Iso}}$ alternates with the parity of the spacer.

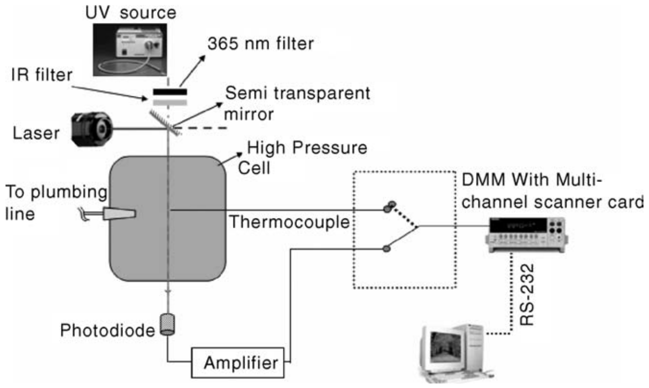

Fig. 3. Schematic diagram of the high pressure apparatus employed for the investigations.

## 3. Results and discussion

### 3.1. Phase diagram

For the different mixtures (M4, M5 and M6), Fig. 4 shows traces of the transmitted laser intensity $I_{\text{laser}}$ as a function of temperature at room pressure, obtained when there is no UV and when the sample is irradiated with UV illumination of 3.5 mW/cm$^2$. In the illuminated as well as the non-illuminated case the N-Iso transition is signified by an abrupt change in the intensity. The first feature to note is that for all the mixtures $T_{\text{N-Iso}}$ exhibits a significant diminution upon illumination with UV radiation. Such a UV-induced lowering in the transition temperature is a consequence of the photo-isomerization of the photoactive molecules from their rod-like E form to the bent Z form [1–6]. In fact, in certain cases, UV light of very low intensities (100 μW/cm$^2$) is sufficient to lower the transition temperature by as much as 15 °C [6]. The second feature to

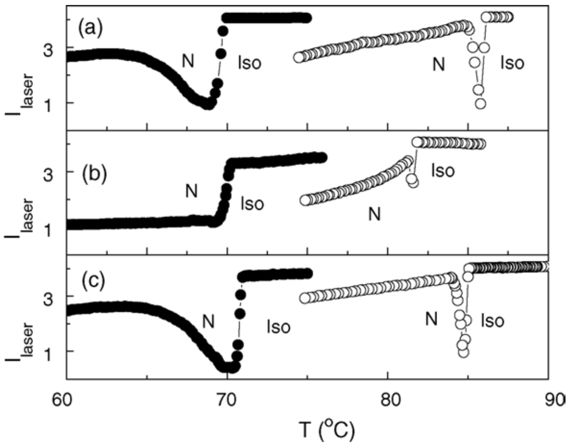

Fig. 4. Temperature dependence of the probe laser beam intensity ($I_{\text{laser}}$) with (○) and without (●) the UV radiation for the mixtures (a) M4, (b) M5 and (c) M6 at atmospheric pressure, showing the photoinduced shift in $T_{\text{N-Iso}}$.

be noted is that $\Delta T$, the shift in the transition temperature, does not seem to have a monotonic variation with the spacer length, but exhibits an odd–even alternation with the parity of the spacer (see Fig. 5), with the mixture having an odd-spacer guest compound showing a lower $\Delta T$ and the one with even parity spacer a higher value of $\Delta T$. Further as the length of the spacer increases the magnitude of the odd–even effect diminishes. For example, the shift is 16, 12 and 14 °C for M4, M5 and M6, respectively. Such behaviour was indeed seen for another dimeric guest–host system and has been explained by considering the equilibrium (in the E form) shape of the molecule and the extent of change in the Z form due to the photo-isomerization. The odd-spacer dimers possess ($n = 5$ in Fig. 6) a substantially bent form even under equilibrium conditions and the change upon shining the UV radiation is minimal. On the contrary, the even-spacer dimer exhibits a nearly rod-like shape in the E-form and alters significantly in the presence of UV ($n = 4$ in Fig. 6). This results in the alternation in the magnitude of $\Delta T$. Previous studies [20,21] have shown that upon application of pressure the magnitude of $\Delta T$ decreases finally reducing to zero at a certain pressure $P_o$.

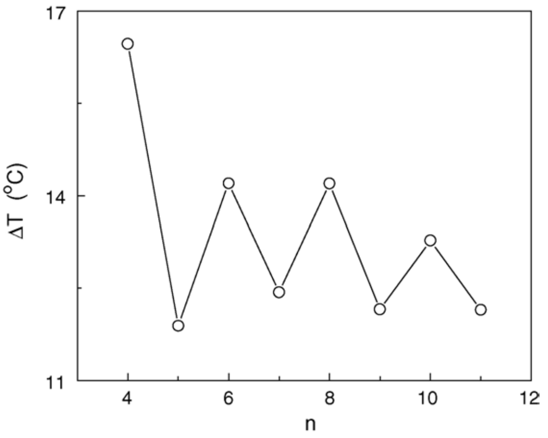

Fig. 5. Effect of the spacer length of the dopant dimeric molecule on $\Delta T$, the photoinduced shift in $T_{\text{N-Iso}}$. Notice that both the parity and the length of the spacer influence the value of $\Delta T$.

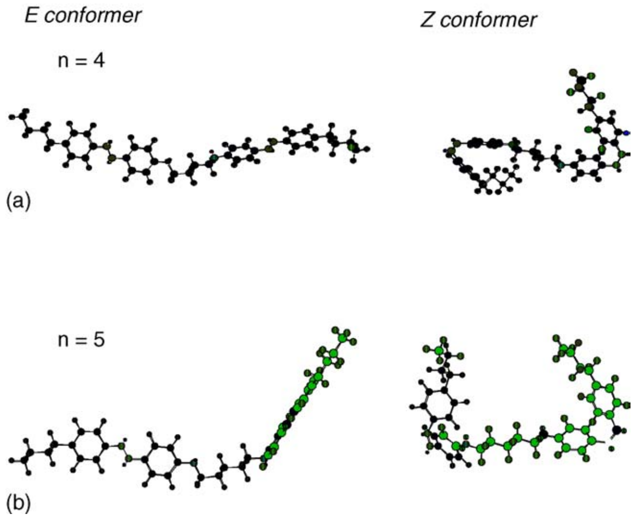

Fig. 6. Minimum energy configurations in the E and Z conformer states for representative (a) even ($n = 4$) and (b) odd ($n = 5$) spacer dimer molecules.

The aim of the present study is to investigate the influence of the length and parity of the dimeric photoactive molecule on the photoinduced behaviour under pressure.

The pressure–temperature phase diagrams obtained for all the mixtures M4–M11 are shown in Fig. 7(a)–(h). A common feature in all these diagrams is that the N-Iso boundary appears to be linear in the absence of UV, whereas the boundary obtained with UV is, even on a qualitative level, non-linear for M4, M5, M6 and M9 mixtures. According to classical thermodynamics the pressure-dependence of the transition temperature of a first order transition (like, for example, the N-Iso) can be described by the Clausius–Clapeyron equation:

$$\frac{dT}{dP} = T\frac{\Delta V}{\Delta H}$$

The drawback of this simple expression is that unless the pressure dependence of $\Delta V$ and $\Delta H$ are known, this expression describes only a linear $P$–$T$ boundary. In the past, non-linear phase boundaries in the $P$–$T$ plane have been described by different empirical relations including higher degree polynomial expressions. Among these the Simon–Glatzel (SG) law [23],

$$\frac{P}{A} = \left(\frac{T}{T_o}\right)^m - 1$$

containing only two constants, $A$ and $m$, has been quite popular. More recently a modified form of this has been proposed by Rein and Demus [24], and Kechin [25] that is especially suitable for strongly non-linear curves including situations where a maximum in the transition temperature is seen, like, for example, in phase diagrams with a reentrant phase. In the present case, although non-linear behaviour is seen for the UV-induced transition boundary, no maximum is observed and therefore we describe the phase boundaries using the SG equation. The solid lines in Fig. 7(a)–(h) show that the SG equation describes quite well the data for all the mixtures.

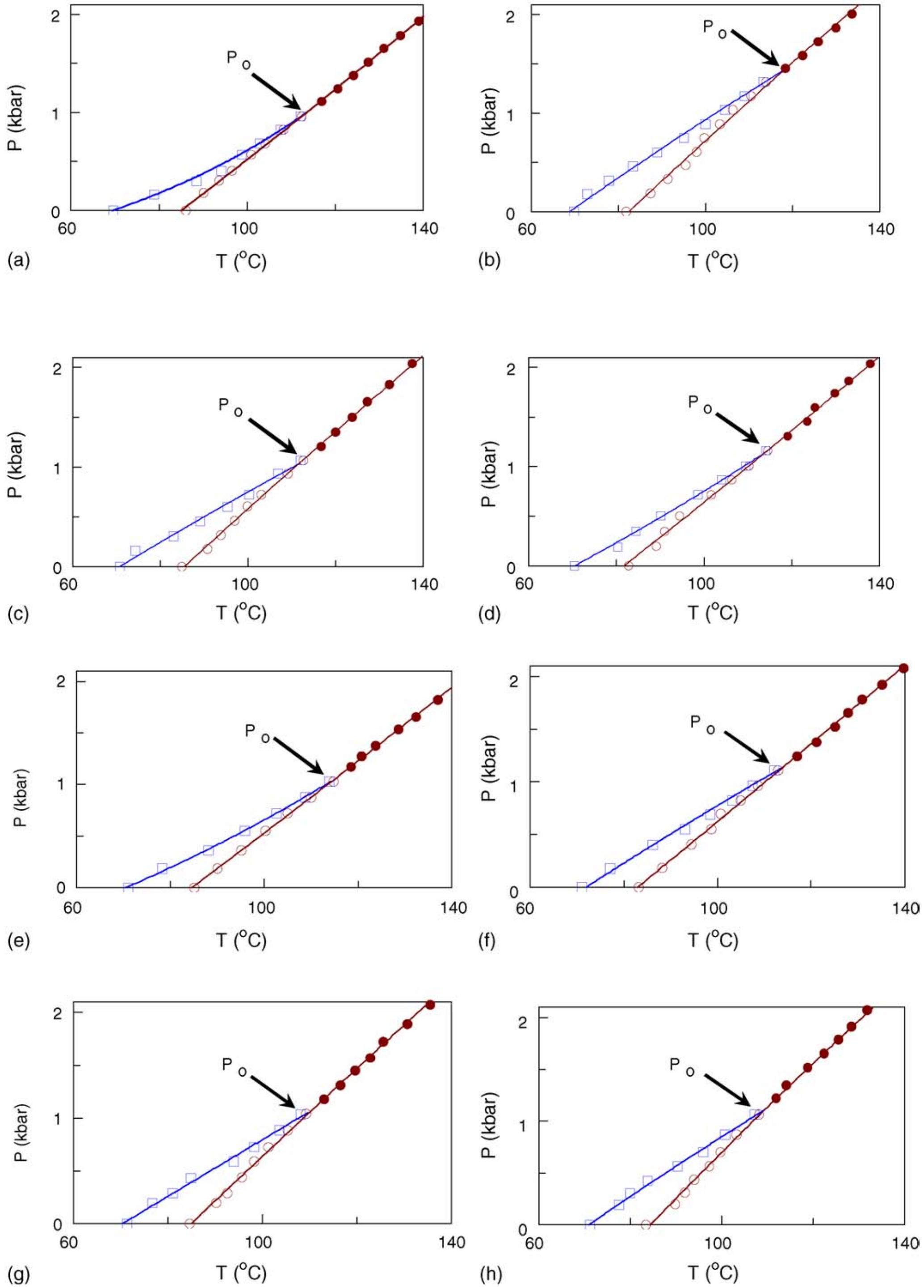

Fig. 7. Pressure–temperature phase diagrams showing the nematic-isotropic (N-Iso) boundary obtained when there is no UV radiation (open circles) as well as in the presence of 3.5 mW/cm$^2$ UV radiation (open squares), for the mixtures M4–M11 (panels (a)–(h), respectively). The photoinduced shift in $T_{\text{N-Iso}}$ decreases with increasing pressure becoming zero at a pressure of $P_o$, whose value depends on the length of the spacer. The data beyond $P_o$ are shown as solid circles. The solid lines in all the cases are the result of fitting the data to Simon–Glatzel law.

An important feature to be noted in Fig. 7(a)–(h) is that the magnitude of $\Delta T$, the UV-induced shift in the transition temperature decreases with increasing pressure, a feature observed in our earlier similar studies [20,21]. The diminution results in $\Delta T$ becoming zero, i.e. UV illumination does not shift the transition temperature, above a certain pressure $P_o$. Based on the concept in which the pressure dependence of volume and the energy of the UV radiation counteract each other, we proposed [20] the following argument to explain the existence of a pressure $P_o$ at which $\Delta T$ goes to zero leading to the meeting of the thermal and photoinduced N-Iso boundaries. Measurements at constant temperature have established that there is a

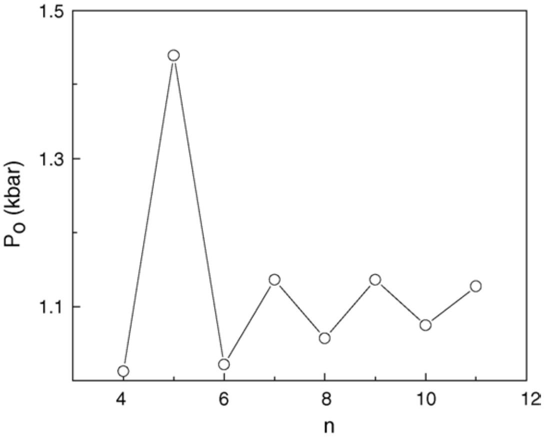

Fig. 8. Odd–even behaviour of the pressure $P_o$ at which the photoinduced shift in the transition ceases to exist as a function of the spacer length $n$.

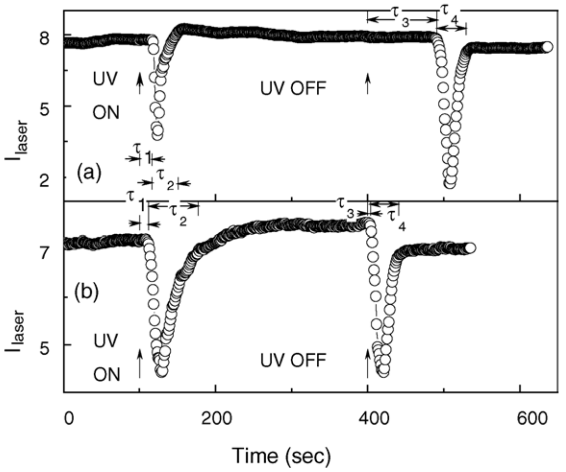

Fig. 9. Representative traces of the temporal variation of $I_{laser}$ upon UV illumination and subsequent switch off at a constant reduced temperature ($T_{red}$ = 5 °C) and two pressures (a) 0.19 kbar and (b) 0.55 kbar for the mixture M6. The notations used to determine the corresponding delay and response times are also shown.

decrease in the specific as well as transition volumes with higher transition pressures and temperatures [26]. Consequently, the intermolecular space available for the photoactive molecule to take a bent conformation decreases with increasing pressure. To accommodate such a feature, the system opposes the formation of the Z isomers. Hence a finite $\Delta T$ caused by the Z isomer becomes smaller with increasing pressure and finally vanishes.

It is also seen that the value of $P_o$ depends on both the length and the parity of the spacer (Fig. 8) displaying a pronounced odd–even effect—mixtures exhibiting a higher value of $\Delta T$ at room pressure have a lower value of $P_o$ and vice versa with the magnitude of the effect diminishing as the length of the spacer is increased. This is somewhat puzzling because one would expect that if $\Delta T$ is large, it would take a much higher pressure to suppress the UV-induced effect. The answer for the anomaly can be found if we extend the argument given above to explain the alternation of $\Delta T$ with the parity of the spacer. The UV illumination causes a significant change in the equilibrium shape of the even parity photoactive molecules but not of the odd parity ones. Therefore even quite low pressures can annul the effect of UV in the case of even parity members resulting in lower values of $P_o$. Thus, the spacer length dependence of $P_o$ should also mimic that of $\Delta T$ except it has the opposite sign.

### *3.2. Dynamics*

As stated in Section 1, the E isomer of the photoactive molecule is the equilibrium form and the Z form realized by UV illumination will relax back to the E form when the illumination is stopped. The temporal variation of $I_{laser}$ upon turning the UV on and subsequently off, at a constant pressure and temperature is shown in Fig. 9(a). When UV is turned on, the consequent photoinduced N-Iso transition takes place on a much faster scale compared to the recovery of the system when the UV is turned off. For both conditions we define the delay time ($\tau_1$ for ON and $\tau_3$ for OFF conditions) as the period between the instant when the UV is turned on (or off) and the instant at which there is a significant change in the $I_{laser}$ value. Also defined is the response time ($\tau_2$ for ON and $\tau_4$ for OFF conditions) which is the period over which the entire change in $I_{laser}$ takes place; these notations are indicated in Fig. 9(a). Increasing the pressure has different effects on the delay and response times. The delay time for the on process ($\tau_1$) hardly changes whereas for the off process ($\tau_3$) it decreases drastically. The response times for the two processes show opposite behaviour with $\tau_2$ (for the on process) increasing and $\tau_4$ having a small decrease upon application of pressure. For one of the mixtures, M4, we have determined the delay and response times at a constant pressure of 0.55 kbar as a function of the reduced temperature, $T_{red}$ (=$T_{N\text{-}Iso} - T$) (see Fig. 10(a) and (b)), and when pressure is varied and $T_{red}$ is kept constant (Fig. 11(a) and (b)). At a constant pressure, as the system moves deeper into the nematic phase ($T_{red}$ increasing), the dynamics of the photoinduced transition gets slowed down, i.e. the corresponding delay and response times ($\tau_1$ and $\tau_2$) increase. In contrast, the thermal back relaxation process ($\tau_3$ and $\tau_4$) becomes faster. In the case where $T_{red}$ is kept constant and the pressure is varied (Fig. 11) the data corresponds to a constant distance from the phase boundary at all pressures (in other words, on an imaginary line which is parallel to the phase boundary). Thus the data shown will have only the effect of pressure without the influence of the temperature at which the data is taken. Hence the data in Fig. 11 suggests that the two sets of pressure constant; $T_{red}$ varying and $T_{red}$ constant; pressure varying, behave qualitatively in a similar fashion: the UV on dynamics gets slower and UV off dynamics becomes faster. In fact the pressure dependence of the delay ($\tau_3$) and response time ($\tau_4$) values can be written in terms of an activation volume as $\Delta U \sim \partial \ln\tau/\partial P$; as expected the activation volume does not depend on the magnitude of $I_{UV}$ used to excite the system. These features can perhaps be understood as follows. The UV ON response is a stimulated one, taking place under the influence of the UV radiation, whereas the time durations for the recovery to the original state through the thermal back relaxation process

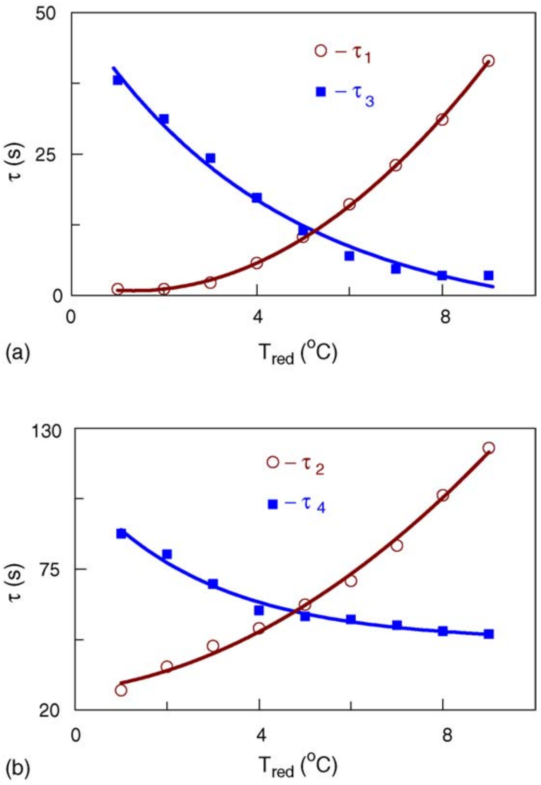

Fig. 10. Dependence of the (a) delay ($\tau_1$ and $\tau_3$) and (b) response times ($\tau_2$ and $\tau_4$) on the reduced temperature for the mixture M4. The data has been obtained at a constant pressure of 0.55 kbar.

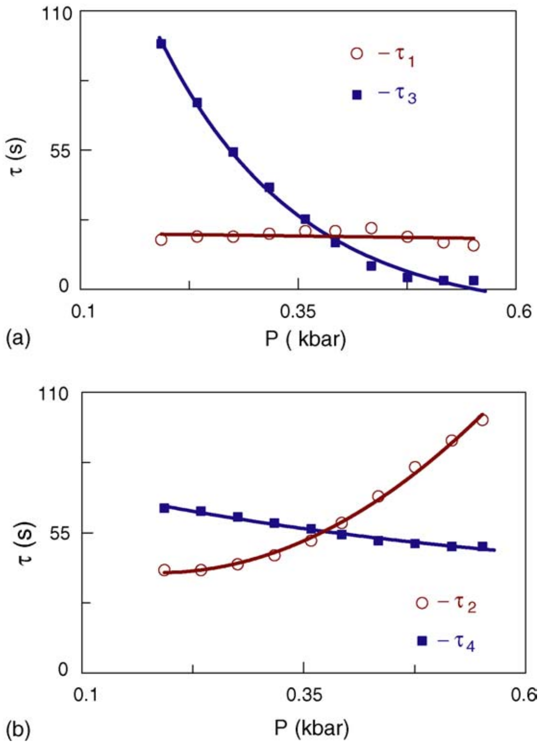

Fig. 11. Dependence of the (a) delay ($\tau_1$ and $\tau_3$) and (b) response times ($\tau_2$ and $\tau_4$) on the applied pressure at a constant reduced temperature of $T_{red} = 5\,^{\circ}C$ for the mixture M4.

happens in the absence of the UV and is thus controlled by the viscous forces of the medium.

In summary we have carried out detailed high pressure investigations of the influence of the length and parity of the spacer group in successive homologues of azobenzene dimers. It is observed that pressure has significant influence on both the phase boundary and the dynamics of the photoinduced nematic-isotropic transition. The shift in the N-Iso transition temperature, induced by light, decreases with increasing pressure finally vanishing at a certain pressure. The pressure at which this happens is found to increase with increasing magnitude of the UV intensity and exhibits a strong odd–even effect connected with the parity of the spacer. The dynamics studied as a function of pressure shows that the delay and response of the system in inducing the isotropic phase is slowed down as pressure increases. In contrast, the time scales associated with the thermal back relaxation become shorter (system relaxes faster) as the pressure is increased.

## Acknowledgements

The work described here has been carried out under an Indo-Italian collaborative project [INT/ITALY/POC(2005–2007)MST-03/05] and a SERC project (Grant no. 93357) of the Department of Science and Technology, New Delhi.

## References

[1] W.E. Haas, K.F. Nelson, J.E. Adams, G.A. Dir, J. Electrochem. Soc. 121 (1974) 1667–1669.
[2] C.H. Legge, G.R. Mitchell, J. Phys. D: Appl. Phys. 25 (1992) 492–499.
[3] H.J. Coles, H.G. Walton, D. Guillon, G. Poetti, Liq. Cryst. 15 (1993) 551–558.
[4] T. Ikeda, O. Tsutsumi, Science 268 (1995) 1873–1875.
[5] S. Servaty, F. Kremer, A. Schonfeld, R. Zentel, Z. Phys. Chem. (Leipzig) 190 (1995) 73–82.
[6] G.G. Nair, S.K. Prasad, C.V. Yelamaggad, J. Appl. Phys. 87 (2000) 2084–2089.
[7] N. Tamaoki, Adv. Mater. 13 (2001) 1135–1147.
[8] V.A. Mallia, M. George, S. Das, Chem. Mater. 11 (1999) 207–208.
[9] For recent reviews on this article see S.K. Prasad, G.G. Nair, G. Hedge, K.L. Sandhya, D.S.S. Rao, C.V. Lobo, C.V. Yelamaggad, Phase Trans. 78 (2004) 443–455;
T. Ikeda, J. Mater. Chem. 13 (2003) 2037–2057;
A.Y. Bobrovsky, N.I. Boiko, V. Shibaev, J. Springer, Adv. Mater. 12 (2000) 1180.
[10] T. Tayagaki, K. Tanaka, Phys. Rev. Lett. 86 (2001) 2886–2889.
[11] M. Pientka, V. Dyakonov, D. Meissner, A. Rogach, D. Talapin, H. Weller, L. Lutsen, D. Vanderzande, Nanotechnology 15 (2004) 163–170.
[12] H. Rao, in: J.F. Rabek (Ed.), Photochemistry and Photophysics, vol. II, CRC Press, Boca Raton, 1990, pp. 119–141.
[13] H. Knobloch, H. Orendi, M. Buchel, T. Seki, S. Ito, W. Knoll, J. Appl. Phys. 77 (1995) 481–487.
[14] L.M. Blinov, M.V. Kozlovsky, M. Ozaki, K. Skarp, K. Yoshino, J. Appl. Phys. 84 (1998) 3860–3866.
[15] A. Stracke, J.H. Wendorff, D. Goldmann, D. Janietz, Liq. Cryst. 27 (2000) 1049–1057.
[16] Y. Yu, M. Nakano, T. Ikeda, Nature 425 (2003) 145–148.
[17] M. Camacho-Lopez, H. Finkelmann, P. Palffy-Muhoray, M. Shelley, Nat. Mater. 3 (2004) 307–310.
[18] G.G. Nair, S.K. Prasad, U.S. Hiremath, C.V. Yelamaggad, J. Appl. Phys. 90 (2001) 48–52.

[19] S.K. Prasad, K.L. Sandhya, Y.S. Negi, Phys. Rev. E 65 (2002) 031718.
[20] S.K. Prasad, D.S.S. Rao, P. Jeyagopal, Phys. Rev. E 64 (2001) 011706.
[21] S.K. Prasad, V.K. Gupta, D.S.S. Rao, C.V. Lobo, Phys. Rev. E 72 (2005) 021705.
[22] These compounds were synthesized using a procedure similar to that reported by A.E. Blatch, G.R. Luckhurst, Liq. Cryst. 27 (2000) 775–787.
[23] F.E. Simon, G. Glatzel, Z. Anorg. Allg. Chem. 178 (1929) 309–316; also see L. Salter, Philos. Mag. 45 (1954) 369.
[24] C. Rein, D. Demus, Cryst. Res. Technol. 28 (1993) 273–281.
[25] V.V. Kechin, J. Phys.: Condens. Matter 7 (1995) 531–535.
[26] R.V. Transfield, P.J. Collings, Phys. Rev. A 25 (1982) 2744–2749.