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New pyrimidine-based photo-switchable bent-core liquid crystals[†]

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The first examples of liquid crystalline pyrimidine-based photo-switchable bent-core monomers incorporating azobenzene as side arms linked with terminal double bonds as polymerizable functional groups are synthesized and characterized. Polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction analysis reveal that the bent-shaped lower homologue compounds are crystalline in nature whereas higher homologue compounds display the stable enantiotropic B₆ phase. They exhibit fast photoisomerization effects in solution and relatively slow photoisomerization effects in liquid crystal cells. In solution both *trans–cis* and *cis–trans* occur at around 3 s and 200 s, respectively, whereas in solids they occur at around 10 s to 200 min. These are some of the first examples of azobenzene liquid crystals which exhibit very fast switching properties in solutions.

Introduction

Pyrimidine and its derivatives have been widely used as biologically active compounds.¹ They have also been used in materials science to generate calamitic and discotic liquid crystals.² However, to the best of our knowledge, use of pyrimidine as a core molecule for the generation of bent-core liquid crystalline materials has so far not been explored. Here, we report the first examples of pyrimidine-based photo-switchable bent-core liquid crystalline molecules.

Bent-core or banana-shaped liquid crystals comprise five, six and seven aromatic rings, whereby aromatic rings are connected through a wide variety of connecting groups to the central rigid core, such as benzene and naphthalene derivatives. A large number of bent shaped molecules containing 1,3/1,5-substituted benzene as a central unit have been extensively investigated as "Banana" phases.^{3,4} In general the mesophases formed by the banana-shaped compounds are termed as "Banana" (Bn) phases, designated B_1-B_8 phases, the B_3 and B_4 phases are crystalline, while the others are mesomorphic.⁵ The nomenclature used is SmCP (polar tilted smectic) for B_2 ,

^b Raman Research Institute, C. V. Raman Avenue, Sadashivanagar, Bangalore 560080, India Col_{r} (rectangular columnar)or Col_{ob} (columnar oblique lattice) for B₁ and Sm_{intercal} (intercalated smectic) for the B₆ phase.⁵ The bent shaped molecules exhibit the Bn phases in addition to normal smectic or nematic phases.^{6–9} There are numerous studies accomplished on the effect of different lateral substituents on the arms of the five-ring bent-core molecules and a lateral fluorine substituent *ortho* to the terminal *n*-alkoxy chain induces interesting electro-optical switching properties to the mesophases.^{10–12}

In recent years, a field of research that has been growing steadily is the photo-induced phenomenon in which the incident light brings about the molecular ordering/disordering of the liquid-crystalline system.13,14 The typical thermally accompanied process of cis-trans transformations leads to dramatic changes in the electronic spectra of the azobenzene molecules to favour photochromism.¹⁵ This particular aspect of photonics, in which molecular geometry can be controlled by light, is being proposed as the future technology for optical storage devices.¹⁶ Molecules containing the azobenzene moiety are well known to show reversible isomerization transformations upon irradiation with UV and visible light.¹⁷ Upon absorption of UV light (\sim 365 nm) the energetically more stable trans configuration transforms into a cis configuration. Photoinduced effects reported in the literature are on liquid crystals in which the azobenzene group is either chemically attached to the molecule of interest or used as a dopant in a liquid crystal host material.^{18–20} The time taken for the phase transition to takes place following the isomerization of the photoactive molecules is not only of significant interest from a basic point of view, but is also of concern for applications.

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The azobenzene liquid crystals are among the most promising materials for photo-switchable devices. These highly stable molecules are promising materials for the photochromic applications. Therefore, a number of monomeric and polymeric bent-core molecules containing an azo (-N=N-) linkage have been reported for the possibility of photochromism and photoisomerization.^{21,22} Polymerization of the appropriate bent-core liquid crystals has also been received significant attention in the last several years.^{23–25} The cross-linked liquid crystal polymers derived from acrylate monomers containing banana liquid crystals have also been reported.^{26,27} Bent core liquid crystalline monomers with double bonds at both ends were used for polymerization to obtain main chain LC polymers.^{28,29} Several oligomeric/polymeric compounds are reported.³⁰ with vinyl-terminated side chains and a bent core mesogenic unit of polysiloxane-based liquid crystals.³¹

The present investigation focuses on the synthesis and photoisomerization behaviour of new bent-shaped monomers derived from 2,6-pyrimidinediol as a central unit and rod shaped azobenzene units with terminal chains having double bonds as the side arms. In addition, we have created the optical storage device using a guest–host system where the bent-core azo dye (guest) is mixed with the liquid crystalline material E7 (room temperature liquid crystals acting like host) for measuring the thermal back relaxation. In the light of this, guest–host effects in liquid crystals with azo dyes could provide a path for the exploration of systems for obtaining long-term optical storage devices.

Experimental

Synthetic procedures

Ethyl 4-[(4-hydroxyphenyl)diazenyl]benzoate (1). Compound 1 was synthesized according to the reported procedure^{32a} from ethyl 4-aminobenzoate (10.18 g, 0.0616 mol), conc. hydrochloric acid (14 ml), sodium nitrite (4.257 g, 0.0616 mol) and phenol (5.79 g, 0.0616 mol) in 600 ml methanol. Yield: 8.01 g, 50.7% as red crystals and m.p. 160 °C. IR, ν_{max}/cm^{-1} 3322 (OH), 1724 (C=O, ester), 1604, 1480 (C=C, aromatic), 1249, 1142 (C-O), 828 (C-H). $\delta_{H}(500$ MHz; acetone-d₆; Me₄Si) 8.16 (2H, d, *J* = 8.0 Hz, Ph), 7.90 (2H, d, *J* = 6.8 Hz, Ph), 7.88 (2H, d, *J* = 7.8 Hz, Ph), 7.0 (2H, d, *J* = 8.9 Hz, Ph), 5.57 (1H, s, OH), 4.42 (2H, q, *J* = 6.9 Hz, *-CH*₂CH₃), 1.47 (3H, -CH₂CH₃). $\delta_{C}(125$ MHz; acetone-d₆; Me₄Si) 14.58, 61.40, 116.10, 122.59, 125.58, 130.70, 131.62, 147.19, 155.41, 159.21, 166.41. Elemental analysis, found: C, 66.56; H, 5.26; N, 10.27. Calc. for C₁₅H₁₄N₂O₃: C, 66.69; H, 5.22; N, 10.36%.

Ethyl4-{2-[4-(prop-2-enyloxy)phenyl]hydrazinyl}benzoate

(2a). Compound 2a was synthesized according to the reported procedure^{32b} from compound 1 (2.0 g, 7.4 mmol) in dry acetone (60 ml), allyl bromide (1.1 g, 9.0 mmol), potassium carbonate (1.24 g, 9.0 mmol) and a catalytic amount of potassium iodide (20 mg) was refluxed for 24 h under an argon atmosphere. Yield of 2a: 1.44 g (63%), m.p. 101 °C. A similar procedure was adopted for synthesis of other higher members of homologues with odd and even numbers of alkyl carbons such as butene, pentene, hexene, heptene and octene (2b–f).

2a: IR, $\nu_{\text{max}}/\text{cm}^{-1}$ 3076 (=CH₂), 2928 (CH₂), 2862 (CH₂), 1728 (C=O, ester), 1642 (C=C, vinyl), 1605, 1497 (C=C, aromatic), 1240, 1136, 1064 (C-O), 829 (C-H). $\delta_{\text{H}}(500 \text{ MHz; CDCl}_3; \text{ Me}_4\text{Si})$ 8.18 (2H, d, J = 8.6 Hz, Ph), 7.97 (2H, d, J = 6.8 Hz, Ph), 7.91 (2H, d, J = 6.9 Hz), 7.01 (2H, d, J = 6.8 Hz), 6.05 (m, 1H, CH=), 5.42 (d, 1H, J = 16.2 Hz, =CH₂), 5.31 (d, 1H, J = 10.2 Hz, =CH₂), 4.61 (d, 2H, J = 4.8 Hz, OCH₂-), 4.18 (q, 2H, OCH₂CH₃), 1.43 (t, 3H, -CH₂CH₃). $\delta_{\text{C}}(125 \text{ MHz; CDCl}_3; \text{ Me}_4\text{Si})$ 14.48, 61.34, 69.25, 115.22, 118.25, 122.61, 125.29, 130.22, 131.36, 132.33, 147.22, 155.45, 161.79 and 166.48.

4-{2-[4-(Prop-2-enyloxy)phenyl]hydrazinyl}benzoic acid (3a). Compound **2a** (1.30 g, 4.19 mmol) was prepared according to the reported procedure.^{32b} A solution of potassium hydroxide (0.94 g, 16.76 mmol) in water (10 ml) was added and the solution was refluxed for 4 h. Yield: 0.45 g (38%) and m.p. 221 °C. A similar procedure was adopted for synthesis of other higher members of homologues such as **3b-f** from compounds **2b-f**.

3a: IR, $\nu_{\text{max}}/\text{cm}^{-1}$ 3072 (=CH₂), 2922 (CH₂), 2864 (CH₂), 1684 (C=O, acid), 1644 (C=C, vinyl), 1597, 1496 (C=C, aromatic), 1249, 1136, 1064 (C=O), 829 (C-H). $\delta_{\text{H}}(500 \text{ MHz; CDCl}_3; \text{ Me}_4\text{Si})$ 8.18 (2H, d, J = 8.2 Hz), 7.94 (2H, d, J = 7.1 Hz), 7.93 (2H, d, J = 6.7 Hz), 7.05 (2H, d, J = 8.9 Hz), 6.04 (m, 1H, CH=), 5.45 (d, 1H, J = 16.6 Hz, =CH₂), 5.31 (d, 1H, J = 10.2 Hz, =CH₂), 4.60 (d, 2H, J = 4.1 Hz, OCH₂-). $\delta_{\text{C}}(125 \text{ MHz; CDCl}_3; \text{Me}_4\text{Si})$ 69.13, 115.18, 118.25, 122.41, 125.24, 130.64, 131.66, 132.73, 147.23, 155.38, 161.69 and 166.98.

2,6-Pyrimidine bis[4-{[4-(allyl-en-1-yloxy)phenyl]diazen-yl}**benzoate**] (4a). Compound 3a (0.290 g, 1.02 mmol) and 2,6-pyrimidinediol (0.0570 g, 0.510 mmol) were dissolved in 50 ml of dry dichloromethane. Then DCC (0.226 g, 1.10 mmol) and DMAP (0.013 g, 0.11 mmol) were added and the mixture was stirred for 48 h. The precipitate was removed by filtration and the solvent was removed. The product was dissolved in dichloromethane and water. The organic phase was washed with diluted acetic acid and water and the solvent was removed under reduced pressure. The compound was purified on silica gel by column chromatography using dichloromethane/hexane as an eluent. Solid was recrystallized from ethanol and chloroform to obtain the target compound 4a. Yield: 0.112 g, 34%. A similar procedure was adopted for synthesis of other higher members of homologues with odd and even numbers of alkyl carbons such as 4b–f from compounds 3b–f.

4a: IR, $\nu_{\text{max}}/\text{cm}^{-1}$ 3090 (=CH₂), 2923 (CH₂), 2858 (CH₂), 1749 (C=O ester), 1642 (C=C, vinyl), 1594, 1496 (C=C, aromatic), 1248, 1129, 1052 (C-O), 852 (CH, aromatic). $\delta_{\text{H}}(500 \text{ MHz; CDCl}_3; \text{ Me}_4\text{Si})$ 8.30 (4H, d, J = 8.9 Hz, Ph), 8.02 (1H, d, Py), 7.97 (4H, d, J = 6.8 Hz, Ph), 7.92 (4H, d, J = 6.9 Hz, Ph), 7.03 (4H, d, J = 5.6 Hz, Ph), 6.95 (1H, t, Py), 6.07 (2H, m, CH=), 5.46 (2H, dd, J = 17.2 Hz, =CH₂), 5.32 (2H, dd, J = 10.3 Hz, =CH₂), 4.63 (4H, t, J = 6.5 Hz, OCH₂-). $\delta_{\text{C}}(125 \text{ MHz}; \text{ CDCl}_3;$ Me₄Si) 69.19, 115.11, 115.21, 122.31, 122.91, 124.15, 125.48, 131.76, 132.64, 138.55, 147.17, 156.42, 161.92, 165.55 and 168.67. Elemental analysis, found: C, 67.16; H, 4.22; N, 13.02. Calc. for C₃₆H₂₈N₆O₆: C, 67.49; H, 4.40; N, 13.11%.

Instrumentation

The structures of the intermediates and desired products were confirmed by spectroscopic methods: IR spectra were recorded

using a Perkin Elmer (670) FTIR spectrometer. ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra were recorded using a Bruker (DMX500) spectrometer. The transition temperatures and their enthalpies were measured using differential scanning calorimetry (Perkin DSC 7) at heating and cooling rates of 5 °C min⁻¹. Optical textures were obtained by using an Olympus BX51 polarizing optical microscope equipped with a Mettler Toledo FP82HT hot stage and a FP90 central processor unit. X-ray diffraction measurements were carried out using Cu-K α radiation (λ = 1.54 Å) generated from a 4 kW rotating anode generator (Rigaku Ultrax-18) equipped with a graphite crystal monochromator. The sample was filled into Hampton research capillaries (0.5 mm diameter) from the isotropic phase, sealed and held on a heater. X-ray diffraction was carried out in the mesophase obtained on cooling the isotropic phase and diffraction patterns were recorded.

Sample preparation for the photo-switching study

UV/Vis absorption spectra were recorded using a UV-Visible spectrophotometer obtained from Ocean Optics (HR2000+). For photo-switching studies in solutions, pyrimidine-based photoswitchable bent-core liquid crystals were dissolved in dimethylformamide at suitable concentrations. Photo-switching behaviour of the azobenzene containing pyrimidine moiety was investigated by illuminating with an OMNICURE S2000 UV source equipped with a 365 nm filter. For photoswitching studies in solids, pyrimidine-based photoswitchable bentcore liquid crystals were mixed with room temperature liquid crystals E7 to make a guest-host system. Concentration used for room temperature nematic liquid crystals to bent core liquid crystals is around 1:20 ratio (5% of the bent core azo dye is dissolved in 95% E7). Room temperature nematic liquid crystals E7 are used as host materials along with bent core liquid crystals as guest materials. The mixture is capillary filled into the previously prepared ITO + polyimide coated, unidirectionally rubbed, sandwiched cell at isotropic temperature (\sim 70 °C). Qualities of the cells were observed under an optical polarizing microscope.

Results and discussion

Materials synthesis

The synthesis of the new materials is depicted in Scheme 1. Compound 1, compounds 2a-f and 3a-f were synthesized according to the earlier papers.^{32b} In the final step, acid compounds 3a-f were coupled with 2,6-pyrimidinediol by DCC and DMAP to achieve corresponding desired molecules 4a-f (Scheme 1). Compounds were purified on silica gel by column chromatography and recrystallized from ethanol/chloroform and are characterized by ¹H, ¹³C NMR and elemental analysis. Analytical data confirmed the structures and purity of all the samples (see detailed synthetic procedures and data in ESI[†]).

Mesomorphic properties

Thermal behaviour of all the compounds was studied using polarized optical microscopy (POM) and differential scanning calorimetry (DSC). The homologous series of symmetric bent-core



Scheme 1 Synthesis of **4a–f**. Reagents and conditions: (i) K_2CO_3 , KI, BrC_nH_{2n–1} (n = 1-6), reflux; (ii) KOH, MeOH, reflux; (iii) 2,6-pyrimidinediol, DCC, DMAP.

compounds (4a-f) consist of five-ring aromatic compounds including pyrimidine as a central core and terminal chains having double bonds as polymerizable functional groups as the side arms both sides with odd and even numbers of carbon atoms (1-8). Phase transition temperature and associated transition enthalpies are given in Table 1. DSC thermograms of the compound were measured at a rate of 5 $^{\circ}$ C min⁻¹. Compounds 4a and 4b did not exhibit any mesomorphism, both compounds showed only one peak upon heating and cooling cycles. Compounds 4c and 4e with odd numbers of carbon atoms in the side chains showed enantiotropic phase sequences of Cr-B₆-I (Table 1). Compounds 4d and 4f having an even number of carbons in the alkyl chain showed enantiotropic phase sequences of Cr1-Cr2-B6-I with higher isotropic temperature compared to those having odd numbers of carbon alkyl chains (Table 1). The isotropic temperatures are slightly increased with longer alkyl chains which is consistent with reported paper.34

Polarized optical microscopy (POM) was used for textural observations of the six compounds (4a-f) in order to identify the mesophase type. Among these homologous series of compounds, the shorter alkyl chains as 4a and 4b showed no

Table 1 Phase transition temperature (T/°C) and associated enthalpies [$\Delta H/J g^{-1}$] in parentheses of DSC scan for 4a–f

Comp.	n	Scan	Phase transitions
4a	1	Heat	Cr 98.7 [45.2] I
		Cool	I 93.9 [41.1] Cr
4b	2	Heat	Cr 91.1 [54.6] I
		Cool	I 88.7 [51.4] Cr
4c	3	Heat	Cr 71.1 [68.7] B ₆ 96.5 [11.0] I
		Cool	I 92.7 [10.7] B ₆ 67.1 [57.8] Cr
4d	4	Heat	Cr ₁ 64.0 [20.4] Cr ₂ 72.3 [29.4] B ₆ 102.8[18.3] I
		Cool	I 101.3 [18.0] B ₆ 68.2 [48.8] Cr
4e	5	Heat	Cr 65.7 [24.8] B ₆ 100.4 [20.6] I
		Cool	I 98.2 [9.9] B ₆ 62.8 [25.5] Cr
4f	6	Heat	Cr ₁ 62.1 [8.6] Cr ₂ 100.6 [28.8] B ₆ 113.8 [12.9] I
		Cool	I 111.2 [14.4] B ₆ 81.8 [49.4] Cr

Abbreviation: Cr = crystal, N = nematic, B_6 = smectic A, I = isotropic phase.

mesophase texture, instead showing a clear transition from crystalline solid to isotropic liquid or isotropic to crystalline form. This could be due to very short flexible aliphatic chains in these molecules. Under POM, a typical fan shaped texture which is a smectic A phase corresponding to the B_6 phase was observed for compounds **4c** and **4d** (Fig. 1) upon cooling from the isotropic state, which upon further cooling transformed into a crystalline phase. Broken fan shaped and pseudo fan shaped textures were found for **4e** and **4f**, respectively, as a B_6 phase (Fig. 1). Compounds **4c–f** showed the enantiotropic phase which is in good agreement with DSC data. Overall, higher homologues of the series show mesophase behaviour (**4c–f**), therefore, the alkyl chain influences the mesophase character rather than double bonds on the terminals as expected.

X-ray diffraction studies: X-ray diffraction was carried out in the mesophase obtained upon cooling from the isotropic phase of compound 4f (n = 6) for further examination of mesophase structure. For example, the powder XRD profile of compound 4f showed two reflections in the small angle region with spacing d1 = 26.27 Å, d2 = 13.12 Å and a diffuse peak in the wide angle region with spacing d3 = 4.25 Å. These small angle peaks at d1and d2 can be indexed as (01) and (02) indicating a smectic type ordering. In addition, a diffused peak in the wide-angle region with *d*-spacing of 4.25 Å is due to a liquid like in-plane ordering of molecules in the layers. In the small angle region, two reflections at d1 = 26.27 Å and d2 = 13.12 Å with the ratio of spacing as $1:\frac{1}{2}$ indicate a smectic type ordering with a layer spacing of 26.27 Å.33a The XRD pattern observed which is typical of a B₆ intercalated mesophase due to a sharp reflection is half of the molecular length (50.13 Å).^{33b} The X-ray diffraction profile of compound 4f at 105 °C is shown in Fig. 2.

Photo-switching study

All bent-core molecules showed similar absorption spectra due to their similar molecular structures, the only difference being in the alkyl chain (n = 1-6), which does not alter the electronic transitions, and the absorption spectra of compounds **4c**-**f** are shown in ESI[†] (Fig. S2). Consequently, compounds **4c** and **4d** were considered for a photoisomerization study.^{33*a*-*c*} Photoswitching studies were initially performed on solutions and then on liquid crystal cells. It gives an idea of the behaviour of materials with respect to UV light and also these results are indispensable for creating optical storage devices.

Fig. 3 depicts the absorption spectra of 4d (n = 6) before and after UV illumination. The absorption spectra of compound 4d show absorbance maxima at 392 nm. The absorption spectra of compound were carried out in dimethyl formamide (DMF) solution having concentration $C = 1.2 \times 10^{-5}$ mol L⁻¹. The strong absorbance in the UV region at 392 nm corresponds to π - π * transition of the *E* isomer (*trans* isomer) and a very weak absorbance in the visible region at around 450 nm represents n- π * transition of the *Z* isomer (*cis* isomer).

The photo-switching property of **4d** was investigated in DMF using UV/visible spectroscopy in the absence and the presence of UV light illumination. Compound **4d** was illuminated with



Fig. 1 Polarized optical micrographs obtained from cooling of isotropic phases of (a) B_6 phase of **4c** at 82 °C, (b) B_6 phase of **4d** at 88 °C, (c) B_6 phase of **4e** at 84 °C, (d) B_6 phase of **4f** at 96 °C.

UV light having a 365 nm filter at different time intervals and immediately the absorption spectra were recorded. The absorption maximum at 392 nm decreases due to E/Z photoisomerization,



Fig. 2 The intensity versus 2 θ graph derived from the X-ray diffraction for the B₆ phase of compound **4f** at 105 °C.



 $\label{eq:Fig.3} Fig. 3 \quad \mbox{Absorption spectra of $4d$ with different exposure time of UV light. Before UV corresponds to the 0 seconds UV light illumination (absence of UV light).$

which leads to the *E* isomer being transformed into the *Z* isomer. After ~ 10 s illumination, there is no change in the absorption spectrum which confirms the saturation of the *E*/*Z* isomerization process.

Fig. 4 shows the E-Z absorption of compound 4d as a function of exposure time. Data were extracted from Fig. 3 and 392 nm peak wavelength was fixed and absorption values at 392 nm at different exposure times were recorded. The curve



Fig. 4 Time dependence photoisomerization curve of E isomer (**4d**) showing effect of UV illumination.



Fig. 5 Thermal back relaxation process for the compound **4d** shows that to relax from *cis* to *trans* takes around 200 seconds. 0 seconds corresponds to the UV off, after illuminating the material for 20 seconds (photostationary state).

shows that photosaturation occurs within 2 seconds which is very fast as compared with nematic to isotropic phase involved photoisomerization.³⁵ The reverse transformation from Z to E can be brought by two methods, one by keeping the solution in dark and other by shining white light of higher wavelength. The earlier process is well known as thermal back relaxation.

Fig. 5 shows the thermal back relaxation process where the solution is illuminated continuously for 20 seconds (photo-stationary state) and kept in the dark and then at subsequent time intervals, spectral data were recorded.

Fig. 6 shows the time dependence of the *Z*–*E* absorption of compound **4d**. Peak wavelength at 392 nm as obtained from Fig. 5 is plotted as a function of recovery time. The curve shows that thermal back relaxation occurs within 200 seconds which is reasonably fast as compared with nematic to isotropic phase involved thermal back relaxation.³⁵

A possible reason for observing faster thermal back relaxation as well as the UV ON process could be that the phases involved on both sides of transition possess a layer structure and that the change that occurs is confined to in-plane rotation of the molecules. The argument is supported by the fact that a similar feature was observed in another case wherein the two phases involved have a layer structure.³⁶



Fig. 6 Time dependence photoisomerization curve of Z isomer (4d) showing thermal back relaxation time.



Fig. 7 Time dependence photoisomerization curve of *E* isomer (**4c**) showing UV ON process (a) and time dependence photoisomerization curve for the thermal back relaxation to *E* isomer (b).

Spectral investigations on solid films were also recorded as a function of UV illumination. Here the guest-host effect is employed where E7, room temperature nematic liquid crystals, act as a host system and pyrimidine based bent core liquid crystals act as guest systems. Previously prepared polyimide coated, unidirectionally rubbed sandwiched cells were filled with the guest-host mixture at isotropic temperature of the mixture (\sim 70 °C). UV/Vis spectral data were recorded using a spectrophotometer.

Fig. 7(a) and (b) show the UV ON and the UV off (thermal back relaxation) process for the compound **4c**. Peak wavelength is ~360 nm and data are generated from peak absorbance at 360 nm as a function of exposure time. One can clearly observe that E-Z conversion takes around 10 seconds whereas recovery to the original state *i.e.*, thermal back relaxation takes around 200 minutes. In Fig. 7(b), the No UV point is given to make it clear that the system has already reached its original value.

Fig. 8(a) and (b) shows the UV ON and the UV off (thermal back relaxation) process for compound **4d**. Peak wavelength is \sim 360 nm and data are generated from peak absorbance at 360 nm as a function of exposure time. One can clearly observe



Fig. 8 Time dependence photoisomerization curve of *E* isomer (**4d**) showing UV ON process (a) and time dependence photoisomerization curve for the thermal back relaxation to *E* isomer (b).

that *E–Z* conversion takes around 10 seconds whereas recovery to the original state *i.e.*, thermal back relaxation takes around 250 minutes.

In Fig. 8(b), the No UV point is given to make it clear that the system has already reached its original value. As compared to the liquid state, the solid state behaviour is very slow, which may be due to the tightly packed molecules in cells, whereas in solutions, molecules have more freedom to move around.

As a demonstration of the efficacy of the materials, an optical storage device is shown here (see Fig. 9) that is realized by using the above mentioned method. The guest–host mixture was illuminated with UV light of 10 mW cm⁻² intensity through a standard mask for 5 minutes. Bright regions are the areas masked with UV radiation and the dark regions are the areas illuminated with UV radiation.

As expected material transforms from the ordered to the disordered state with the illumination of light giving high contrast between bright and dark states. Research is in progress to stabilize these materials to use it as permanent optical storage devices by incorporating polymeric chains to photopolymerize the structure.



Fig. 9 Demonstration of optical pattern storage capability of the device based on the principle described in this article observed under the crossed polarizers. The sample was kept at room temperature and illuminated with UV radiation through a photo mask. The dark regions are e the molecules are exposed to UV radiation and the bright regions are where the radiation is masked. P and A were the polarizer and analyser.

Comparison of mesophase and photoisomerization behaviour

Although the comparison of mesomorphic properties of the compounds 4c-f with other compounds is difficult because the core molecule used in this study is pyrimidine which is the first example, at least compounds 4c-f can be compared with our previously reported bent-core compounds derived from the resorcinol core with variable alkyl groups and double bonds at both terminals.^{32,33} Several bent-shaped monomers containing azobenzene as a side arm, resorcinol as a central unit and terminal double bonds as polymerisable functional groups were reported as SmA_{intercal} mesophases.^{33a} Six new bentshaped monomers were reported to have substituted or non-substituted azobenzene moiety in the periphery and substituted or non-substituted resorcinol as a central unit with polymerisable double bonds linked at both ends of all the molecules. Four members of the family showed an intercalated smectic phase and two were crystalline in nature.^{33b}

Although the pyrimidine-based bent-core is considered to be a new molecule, this molecule is open to comparison with other bent-shaped compounds exhibiting excellent photoisomerization behaviour. The photo-isomerization behaviour in solution of compound 4d can be compared with similar fivearomatic ring containing bent-core compounds derived from the resorcinol core which was reported earlier.^{33a,b} The photoisomerization studies reveal that compound 4d intensifies isomerization properties in which E to Z and Z to E isomerizations take place only at 3 s and 200 s, whereas our previously reported resorcinol based compounds were recorded at about 50 s.^{33*a,b*} It was observed that photoisomerization described in a very recent paper takes place in 30 s for *E* to *Z* transformation.^{33c} We have anticipated that the time taken for the photoisomerization depends on the core molecules though a previous report was based on the nature of the linking group (electron withdrawing group/donating group) and size of the substituent in the azobenzene moiety.^{33c} The faster isomerization process is a key factor for optical switching applications.

Conclusion

A new series of bent core monomers derived from pyrimidine as a core and azobenzene as a side arm were synthesized. POM, DSC and X-ray studies showed that four compounds exhibited the B₆ phase and other two were crystalline in nature. The compounds can be used for preparation of polymers or silvlfunctionalized bent-core mesogens, whereas the presence of the azo linkage in these liquid crystal monomers is suitable for photochromism studies and trans-cis-trans isomerization cycles under UV irradiation. The photoswitching properties of compound 4d of this series show trans to cis isomerization at around 3 s, whereas the reverse process takes place at around 200 s in solutions and in solids E-Z photoisomerization takes around 10 s and reverse back to original Z-E takes around 200 min. Thus, the photoswitching behaviour of these materials may be suitably exploited in the field of optical data storage devices and in molecular switches which need fast switching as well as for permanent optical storage devices. Indeed, so far, hardly any azo compound has been reported which exhibits such a fast switching property in solutions.

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Notes and references

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