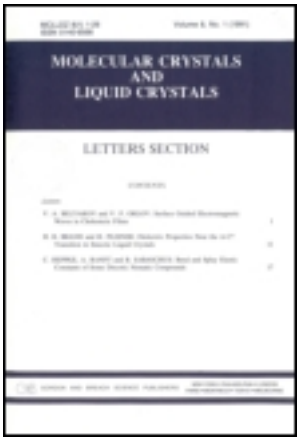

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Synthesis of Banana-Shaped Liquid Crystals for Photoswitching Properties

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Synthesis of Banana-Shaped Liquid Crystals for Photoswitching Properties

MD RAHMAN LUTFOR,[1,*] MASHITAH MOHD YUSOFF,[1] GURUMURTHY HEGDE,[1] MUHAMMAD NOR FAZLI,[1] ABDUL MALEK,[1] NURLIN ABU SAMAH,[1] AND H. T. SRINIVASA[2]

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Three banana-shaped monomers containing naphthalene as central units and azobenzene in side arms with terminal alkenes were synthesized and characterized. DSC, polarizing optical microscopy, and X-ray diffraction measurements prove that all compounds exhibit B_6 phase. The trans-azobenzene showed high-intensity π–π^* transition at about 365 nm and low-intensity n–π^* transition at about 450 nm. The strong photoisomerization behavior in solutions of the molecules displayed that trans to cis isomerization takes 45 sec whereas reverse process takes about 28 h and 30 min. This long thermal back relaxation is useful for creation of optical image storage.

Keywords Azobenzene; isomerization; naphthalene; optical image storage; photoswitching

Introduction

The electro-optic responses of some liquid crystals are examined by using electro-optic devices such as a flat-panel display, light scattering electro-optical switches, and electrically switchable color-tunable reflectors [1]. Azobenzene moiety is not only attractive photoactive groups but also efficient for many optical storage devices [2]. Due to their unique *cis-trans* isomerization properties, azobenzene moieties play important role when they are mixed with bent core liquid crystals (BCLCs). Bent core mesogens usually comprise of five or six member phenyl units connected by linking groups like azomethine groups. In most of the cases, bend of the molecular long axis results from 1,3-phenylene connection near the center of the molecule. When azobenzene moiety is inserted between these two phenyl rings, then banana-shaped liquid crystals become very sensitive to light. Lutfor et al. [3] reported bent-shaped azobenzene monomers and their photoisomerization properties when they used it as guest–host system along with liquid crystals. Synthesis of new azobenzene-containing bent-shaped monomers and their photochemical properties when mixed with calamitic liquid crystals in solutions were reported [3, 4]. Increase in the photo-induced

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thermal back relaxation was found, which could be useful for creation of permanent optical storage devices [3].

A field of research that is growing steadily is that of photo-induced phenomenon, in which the incident light brings about the molecular ordering/disordering of the liquid-crystalline system [5–8]. 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 [9–11]. The heart of the phenomenon in such systems is the reversible photo-induced shape transformation of the molecules containing the photo-chromic azo groups [12]. Upon UV irradiation (around 365 nm, corresponding to the π–π^* excitation of the azo group), the energetically more stable E or *trans* configuration, with an elongated rod-like molecular form, changes into a bent Z or *cis* configuration. The reverse transformation can be brought about by illumination with visible light (in the range 400–500 nm, corresponding to the n–π^* band). This latter change can also occur in the "dark" by a process known as thermal back relaxation. Several bent-core molecules containing an azo (–N=N–) linkage have been reported for the possibility of photoisomerization [13]. In this report, we emphasize on the synthesis and characterization of naphthalene-based liquid crystalline bent-shaped monomers with rod-shaped azobenzene units connected to the core. In addition, an investigation on the UV-induced absorption is carried out, which gives powerful insight on the influence of light on them.

Experimental

Materials

Ethyl 4-aminobenzoate (Fluka), sodium nitrite (BDH), phenol (Merck), potassium carbonate (Fluka), 9-bromonon-1-ene (Aldrich), 10-bromodec-1-ene (Aldrich), 11-bromoundec-1-ene (Aldrich), 2,7-dihydroxynaphthalene (Aldrich), 1,3-dicyclohexyl-carbodiimide (DCC; Fluka), 4-(*N*,*N*-dimethylamino)pyridine (DMAP; Fluka), and silica gel-60 (Merck) were used as received. Acetone was refluxed over phosphorus pentaoxide (Merck) and dichloromethane was refluxed over calcium hydride and both were distilled before use. Other solvents and chemicals were used without further purification.

Ethyl 4-[(4-hydroxyphenyl)diazenyl]benzoate (1)

Compound **1** was synthesized according to the reported procedure [14] 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 mp 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). ^{1}H NMR ($CDCl_3$) δ: 8.16 (2H, d, $J = 8.0$ Hz), 7.90 (2H, d, $J = 6.8$ Hz), 7.88 (2H, d, $J = 7.8$ Hz), 7.0 (2H, d, $J = 8.9$ Hz), 5.57 (1H, s, OH), 4.42 (2H, q, $J = 6.9$ Hz, $-CH_2CH_3$), 1.47 (3H, $-CH_2CH_3$). ^{13}C NMR ($CDCl_3$) δ: 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 $C_{15}H_{14}N_2O_3$: C, 66.69; H, 5.22; N, 10.36%.

Ethyl 4-{2-[4-(non-8-enyloxy)phenyl]diazenyl}benzoate (2a)

Compound **1** (1.20 g, 4.44 mmol) was dissolved in dry acetone (100 mL); 9-bromonon-1-ene (6.07 mmol), potassium carbonate (0.840 g, 6.08 mmol), and a catalytic amount of potassium iodide (20 mg) were added and the mixture was refluxed for 24 h under

argon atmosphere. Afterwards, it was poured into ice-cold water and acidified with dilute hydrochloric acid (pH < 3). The precipitate was filtered off and was crystallized from methanol/chloroform (10:2). Yield of **2a** was 57%. IR, ν_{max}/cm^{-1} 3076 ($=CH_2$), 2929 (CH_2), 2856 (CH_2), 1725 (C=O, ester), 1645 (C=C, vinyl), 1600, 1477 (C=C, aromatic), 1250, 1137, 1056 (C–O), 825 (C–H). ^{1}H NMR ($CDCl_3$) δ: 8.18 (d, 2H, $J = 8.5$ Hz), 7.98 (d, 2H, $J = 8.8$ Hz), 7.91 (d, 2H, $J = 8.5$ Hz), 7.02 (d, 2H, $J = 8.6$ Hz), 5.86 (m, 1H, CH=), 5.06 (dd, 1H, $J = 13.2$ Hz, $=CH_2$), 5.01 (dd, 1H, $J = 9.5$ Hz, $=CH_2$), 4.07 (t, 2H, $J = 6.7$ Hz, OCH_2–), 3.97 (s, 2H, OCH_2CH_3), 2.18 (m, 2H, –CH_2–), 1.88 (m, 4H, –CH_2–), 1.57 (m, 8H, –CH_2–), 1.49 (t, 3H, –CH_2CH_3). ^{13}C NMR ($CDCl_3$) δ: 14.44, 20.44, 25.56, 26.68, 27.55, 28.55, 29.68, 30.15, 62.22, 69.18, 116.23, 118.24, 122.88, 125.32, 130.68, 131.67, 132.79, 147.25, 155.38, 161.77, 166.22.

Ethyl 4-{2-[4-(dec-9-enyloxy)phenyl]diazenyl}benzoate (2b)

Compound **1** (1.30 g, 4.81 mmol), dry acetone 100 mL, 10-bromodec-1-ene (6.64 mmol), potassium carbonate (0.919 g, 6.65 mmol), and potassium iodide (20 mg) were refluxed for 24 h. Etherification was carried out by the same method as used for synthesis of **2a**.Yield: 64.5%. IR, ν_{max}/cm^{-1} 3070 ($=CH_2$), 2928 (CH_2), 2856 (CH_2), 1725 (C=O, ester), 1644 (C=C, vinyl), 1601, 1478 (C=C, aromatic), 1251, 1127, 1050 (C–O), 825 (C–H). ^{1}H NMR ($CDCl_3$) δ: 8.19 (d, 2H, $J = 8.4$ Hz), 7.98 (d, 2H, $J = 8.7$ Hz), 7.92 (d, 2H, $J = 8.5$ Hz), 7.02 (d, 2H, $J = 8.5$ Hz), 5.87 (m, 1H, CH=), 5.05 (dd, 1H, $J = 13.3$ Hz, $=CH_2$), 5.02 (dd, 1H, $J = 9.3$ Hz, $=CH_2$), 4.06 (t, 2H, $J = 6.7$ Hz, OCH_2–), 3.98 (s, 2H, OCH_2CH_3), 2.19 (m, 2H, –CH_2–), 1.87 (m, 6H, –CH_2–), 1.59 (m, 8H, –CH_2–), 1.47 (t, 3H, –CH_2CH_3). ^{13}C NMR ($CDCl_3$) δ: 14.43, 20.45, 25.66 26.78, 27.12, 28.51, 29.78, 30.25, 31.51, 62.22, 69.18, 116.22, 118.23, 122.78, 125.32, 130.78, 131.68, 132.77, 147.33, 155.44, 161.82, 166.32.

Ethyl 4-{2-[4-(undec-10-enyloxy)phenyl]diazenyl}benzoate (2c)

Compound **1** (1.10 g, 4.07 mmol), dry acetone 100 mL, 11-bromoundec-1-ene (5.07 mmol), potassium carbonate (0.700 g, 5.07 mmol), and potassium iodide (20 mg) were refluxed for 24 h. Etherification was carried out by the same method as used for synthesis of **2a**. Yield: 78.3%. IR, ν_{max}/cm^{-1} 3077 ($=CH_2$), 2926 (CH_2), 2862 (CH_2), 1724 (C=O, ester), 1642 (C=C, vinyl), 1600, 1467 (C=C, aromatic), 1248, 1136, 1052 (C–O), 824 (C–H). ^{1}H NMR ($CDCl_3$) δ: 8.18 (d, 2H, $J = 8.6$ Hz), 7.97 (d, 2H, $J = 8.8$ Hz), 7.94 (d, 2H, $J = 8.6$ Hz), 7.01 (d, 2H, $J = 8.5$ Hz), 5.86 (m, 1H, CH=), 5.05 (dd, 1H, $J = 13.5$ Hz, $=CH_2$), 5.02 (dd, 1H, $J = 9.5$ Hz, $=CH_2$), 4.06 (t, 2H, $J = 6.7$ Hz, OCH_2–), 3.95 (s, 2H, OCH_2CH_3), 2.16 (m, 2H, –CH_2–), 1.82 (m, 6H, –CH_2–), 1.55 (m, 10H, –CH_2–), 1.48 (t, 3H, –CH_2CH_3). ^{13}C NMR ($CDCl_3$) δ: 14.41, 20.44, 25.16 26.68, 27.32, 28.75, 29.78, 30.35, 31.77, 32.88, 62.21, 69.19, 116.33, 118.22, 122.78, 125.31, 130.78, 131.77, 132.55, 147.23, 155.24, 161.67, 166.29.

4-{2-[4-(non-8-enyloxy)phenyl]diazenyl}benzoic acid (3a)

Compound **2a** (2.46 mmol) was dissolved in 150 mL of methanol. A solution of potassium hydroxide (0.400 g, 7.13 mmol) in water (10 mL) was added and the solution was refluxed for 4 h. The mixture was poured into ice-cold water (200 mL) and the precipitate was acidified with conc. hydrochloric acid (10 mL). The precipitate was filtered off, washed with water, and crystallized from ethanol/chloroform (2:1) to give compound **3a**. Yield:

56.4%. IR, ν_{max}/cm^{-1} 3080 ($=CH_2$), 2928 (CH_2), 2852 (CH_2), 1684 (νC=O, acid), 1624 (C=C, vinyl), 1602, 1507 (C=C, aromatic), 1260, 1143, 1012 (C–O), 827 (C–H). ^{1}H NMR ($CDCl_3$) δ: 8.20 (d, 2H, $J = 8.8$ Hz), 7.97 (d, 2H, $J = 8.9$ Hz), 7.92 (d, 2H, $J = 8.7$ Hz), 7.04 (d, 2H, $J = 9.0$ Hz), 5.85 (m, 1H, CH=), 5.05 (dd, 1H, $J = 13.6$ Hz, $=CH_2$), 4.96 (dd, 1H, $J = 8.2$ Hz, $=CH_2$), 4.08 (t, 2H, $J = 6.5$ Hz, OCH_2–), 2.11 (m, 2H, –CH_2), 1.87 (m, 2H, –CH_2–), 1.51 (m, 2H, –CH_2–), 1.44 (m, 6H, –CH_2–). ^{13}C NMR ($CDCl_3$) δ: 21.50, 25.86, 26.12, 28,67, 29.67. 29.65, 69.88, 115.66, 118.34, 122.78, 125.33, 130.68, 131.69, 132.89, 147.27, 155.48, 161.78, 167.73.

4-{2-[4-(dec-9-enyloxy)phenyl]diazenyl}benzoic acid (3b)

The hydrolysis of **2b** was carried out according to the method described for **3a**. Yield of **3b**: 52.5%. IR, ν_{max}/cm^{-1} 3084 ($=CH_2$), 2925 (CH_2), 2852 (CH_2), 1684 (νC=O, acid), 1627 (C=C, vinyl), 1601, 1503 (C=C, aromatic), 1261, 1149, 1012 (C–O), 825 (C–H). ^{1}H NMR ($CDCl_3$) δ: 8.20 (d, 2H, $J = 8.8$ Hz), 7.96 (d, 2H, $J = 8.6$ Hz), 7.93 (d, 2H, $J = 8.6$ Hz), 7.05 (d, 2H, $J = 9.1$ Hz), 5.86 (m, 1H, CH=), 5.05 (dd, 1H, $J = 13.1$ Hz, $=CH_2$), 4.92 (dd, 1H, $J = 8.3$ Hz, $=CH_2$), 4.08 (t, 2H, $J = 6.5$ Hz, OCH_2–), 2.11 (m, 2H, –CH_2), 1.87 (m, 2H, –CH_2–), 1.53 (m, 2H, –CH_2–), 1.44 (m, 8H, –CH_2–). ^{13}C NMR ($CDCl_3$) δ: 22.56, 25.46, 26.22, 28,47, 29.61. 29.65, 30.31, 69.78, 115.46, 118.54, 122.68, 125.44, 130.61, 131.64, 132.83, 147.26, 155.46, 161.72, 167.63.

4-{2-[4-(undec-10-enyloxy)phenyl]diazenyl}benzoic acid (3c)

The hydrolysis of **2c** was performed in similar manner. **3c**: 55.3%. IR, ν_{max}/cm^{-1} 3081 ($=CH_2$), 2924 (CH_2), 2851 (CH_2), 1684 (νC=O, acid), 1624 (C=C, vinyl), 1604, 1502 (C=C, aromatic), 1260, 1144, 1011 (C–O), 826 (C–H). ^{1}H NMR ($CDCl_3$) δ: 8.20 (d, 2H, $J = 8.4$ Hz), 7.98 (d, 2H, $J = 8.9$ Hz), 7.91 (d, 2H, $J = 8.7$ Hz), 7.04 (d, 2H, $J = 9.0$ Hz), 5.85 (m, 1H, CH=), 5.05 (dd, 1H, $J = 13.2$ Hz, $=CH_2$), 4.91 (dd, 1H, $J = 8.4$ Hz, $=CH_2$), 4.05 (t, 2H, $J = 6.7$ Hz, OCH_2–), 2.18 (m, 2H, –CH_2), 1.88 (m, 2H, –CH_2–), 1.52 (m, 2H, –CH_2–), 1.44 (m, 10H, –CH_2–). ^{13}C NMR ($CDCl_3$) δ: 22.40, 25.86, 26.22, 27.32, 28.47, 29.62. 29.55, 30.44, 69.78, 115.56, 118.44, 122.73, 125.34, 130.66, 131.63, 132.79, 147.37, 155.55, 161.65, 167.79.

2,7-Naphthalene bis[4-{2-[4-(non-8-enyloxy)phenyl]diazenyl}benzoate] (4a)

Compound **3a** (0.358 mmol), resorcinol (0.179 mmol), 50 mL of dry dichloromethane, DMAP (0.04 mmol), and DCC (0.40 mmol) were stirred for 48 h. The mixture was filtered and filtrate was washed with acetic acid and water. The solvent was removed by reduced pressure and product was purified by column chromatography over silica gel 60 eluted with dichloromethane and hexane (10:1). Finally, product was recrystallized from ethanol/chloroform (2:1). Yield of **4a**: 35%. IR, ν_{max}/cm^{-1} 3080 ($=CH_2$), 2924 (CH_2), 2852 (CH_2), 1722 (C=O, ester), 1624 (C=C, vinyl), 1602, 1456 (C=C, aromatic), 1251, 1143, 1030 (C–O), 840 (C–H). ^{1}H NMR ($CDCl_3$) δ: 8.20 (d, 4H, $J = 8.4$ Hz), 7.97 (d, 4H, $J = 8.8$ Hz) 7.92 (d, 4H, $J = 8.4$ Hz), 7.76 (d, 2H, $J = 4.1$ Hz), 7.44 (dd, 2H, $J = 8.2$ Hz), 7.04 (d, 4H, $J = 8.8$ Hz), 5.85 (m, 2H, CH=), 5.05 (dd, 2H, $J = 15.5$ Hz, $=CH_2$), 4.96 (dd, 2H, $J = 9.7$ Hz, $=CH_2$), 4.07 (t, 4H, $J = 6.5$ Hz, OCH_2–), 2.10 (m, 4H, –CH_2–), 1.87 (m, 4H, –CH_2–), 1.71 (m, 4H, –CH_2–), 1.50 (m, 12H, –CH_2). ^{13}C NMR ($CDCl_3$) δ: 24.93, 25.25, 27.26, 28.16, 29.99, 30.34, 68.57, 114.64, 115.29, 118.38, 118.71, 119.21, 121.23,

122.79, 124.21, 125.35, 129.33, 130.57, 131.76, 132.65, 134.53, 147.34, 149.53, 155.72, 161.12, 164.23.

2,7-Naphthalene bis[4-{2-[4-(dec-9-enyloxy)phenyl]diazenyl}benzoate] (4b)

Compound **3b** (1.00 mmol), resorcinol (0.50 mmol), 80 mL of dry dichloromethane, DMAP (0.012 mmol), and DCC (1.20 mmol) were stirred for 48 h. Esterification was carried out according to the method described for **4a**. Yield of **4b**: 40%. IR, ν_{max}/cm^{-1} 3077 ($=CH_2$), 2928 (CH_2), 2862 (CH_2), 1732 (νC=O, ester), 1642 (C=C, vinyl), 1601, 1456 (C=C, aromatic), 1242, 1148, 1078 (C–O), 835 (C–H). ^{1}H NMR ($CDCl_3$) δ: 8.35 (d, 4H, J = 8.4 Hz), 8.01 (d, 4H, $J = 5.9$ Hz) 7.97 (d, 4H, $J = 6.8$ Hz), 7.75 (d, 2H, $J = 4.3$ Hz), 7.43 (dd, 2H, J = 8.1 Hz), 7.04 (d, 4H, J = 9.0 Hz), 5.90 (m, 2H, CH=), 5.23 (dd, 2H, J = 15.1 Hz, $=CH_2$), 5.10 (dd, 2H, $J = 9.2$ Hz, $=CH_2$), 4.10 (t, 4H, $J = 6.6$ Hz, OCH_2–), 2.32 (m, 4H, –CH_2–), 1.98 (m, 4H, –CH_2–), 1.73 (m, 6H, –CH_2–), 1.50 (m, 12H, –CH_2). ^{13}C NMR ($CDCl_3$) δ: 24.73, 25.21, 26.76, 27.36, 28.26, 29.49, 30.55, 67.59, 114.85, 115.44, 115.83, 118.45, 119.32, 122.57, 124.22, 125.33, 129.94, 130.15, 131.27, 132.51, 135.57, 146.94, 149.78, 151.46, 155.90, 162.38, 164.38.

2,7-Naphthalene bis[4-{2-[4-(undec-10-enyloxy)phenyl]diazenyl}benzoate] (4c)

Compound **3c** (0.355 mmol), resorcinol (0.177 mmol), 50 mL of dry dichloromethane, DMAP (0.04 mmol) and DCC (0.40 mmol) were stirred for 48 h. Esterification was carried out according to the method described for **4a**.Yield of **4c**: 37%. IR, ν_{max}/cm^{-1} 3081 ($=CH_2$), 2925 (CH_2), 2862 (CH_2), 1728 (C=O, ester), 1624 (C=C, vinyl), 1604, 1457 (C=C, aromatic), 1252, 1144, 1031 (C–O), 840 (C–H). ^{1}H NMR ($CDCl_3$) δ: 8.20 (d, 4H, $J = 8.5$ Hz), 7.98 (d, 4H, $J = 8.6$ Hz) 7.92 (d, 4H, $J = 8.6$ Hz), 7.75 (d, 2H, $J = 4.3$ Hz), 7.43 (dd, 2H, $J = 8.1$ Hz), 7.04 (d, 4H, $J = 8.6$ Hz), 5.85 (m, 2H, CH=), 5.03 (dd, 2H, J = 15.1 Hz, $=CH_2$), 4.96 (dd, 2H, $J = 9.3$ Hz, $=CH_2$), 4.07 (t, 4H, $J = 6.6$ Hz, OCH_2–), 2.10 (m, 4H, –CH_2–), 1.88 (m, 4H, –CH_2–), 1.71 (m, 8H, –CH_2–), 1.51 (m, 12H, –CH_2–). ^{13}C NMR ($CDCl_3$) δ: 24.93, 25.66, 26.71, 27.26, 28.16, 29.99, 30.32, 33.21, 68.77, 114.12, 114.78, 115.46, 111.34, 119.47, 123.17, 124.23, 125.43, 129.22, 130.25, 131.43, 132.67, 138.22, 146.62, 149.12, 151.25, 155.66, 162.12, 164.36.

Characterization

The products were confirmed by spectroscopic methods: IR spectra were recorded with a Perkin Elmer (670) FTIR spectrometer. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded with a Bruker (DMX500) spectrometer. The transition temperatures and their enthalpies were measured by differential scanning calorimetry (Perkin DSC 7), heating and cooling rates were 10°C min^{-1}, and melting point of the intermediate compounds was determined by DSC. Optical textures were obtained by using Olympus BX51 polarizing optical microscope equipped with a Mettler Toledo FP82HT hot stage and a FP90 central processor unit. Absorption spectra were recorded using a Perkin Elmer UV/VIS Spectrometer (Lambda 25). Absorption spectra for photochromic study were recorded using a Shimazdu 3101 PC UV-Vis spectrometer. All the solutions were prepared and measured under air in the dark at room temperature (21 ± 1°C) using 1 cm quartz cells. The cells were closed to avoid the evaporation of the solvent and the solutions were stirred during the irradiation time. The solutions were irradiated at $\lambda_{exc.} = 254$ nm, 365 nm, and 436 nm respectively, using a 200 watt high pressure Hg-lamp HBO 200 (NARVA, Berlin,

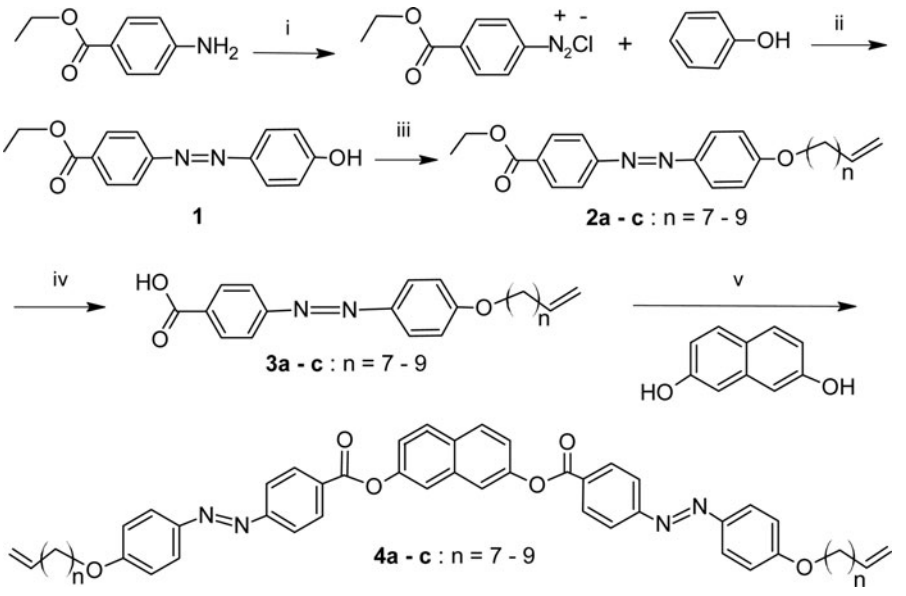
Germany) and filters IF 254, HgMon 365, HgMon 436 (Zeiss, Jena, Germany) generating monochromatic light as excitation source. Additional protection glass filters Code-No. 601 were used for irradiation at 365 nm and 254 nm and Code-No. 805 (both Schott, Jena, Germany) for irradiation at 436 nm was used.

Results and Discussion

Synthesis

The azobenzene containing rod-like side arms is synthesized from ethyl 4-aminobenzoate. The diazonuim salt was prepared with sodium nitrite in the presence of aqueous hydrochloric acid, which was coupled with phenol to give ethyl 4-[(4-hydroxyphenyl)diazenyl]benzoate **1**. The reaction and purification by crystallization was performed [15]. Compound **1** was alkylated with 9-bromonon-1-ene in the presence of potassium carbonate as base to give ethyl 4-{2-[non-8-enyloxy)phenyl]diazenyl}benzoate **2a**. Other compounds (**2b** and **2c**) were prepared with the same method as compound **2a**. These intermediate compounds **2a–c**, were found to be liquid crystalline and showed smectic A phase. Then compounds **2a–c** having ester groups were hydrolyzed under basic conditions to yield the acids **3a–c**. All the acid compounds showed nematic phase.

The liquid crystallinity in such compounds is induced due to hydrogen-bonded dimer formation, a phenomenon well documented in literature [4, 16–21]. The carboxylic acid groups are associated to form the H-bonded cyclic dimers either in crystalline or liquid crystalline phases, and most of the dimers exhibited enantiotropic mesophase behavior. In final step, two equivalents of acids **3a–c** were coupling with one equivalent of 2,7-dihydroxynaphthalene by DCC and DMAP to achieve desired molecules **4a–c** (Scheme 1).



Scheme 1. Synthesis of compounds **4a–c**. Reagent and conditions: (i) $NaNO_2$, 3 equiv HCl, 2°C; (ii) NaOH, pH 9, 2°C; (iii) K_2CO_3, KI, BrC_nH_{2n-1} (n = 7–9), reflux; (iv) KOH, MeOH; (v) DCC, DMAP.

Mesomorphic Properties

The mesomorphic behavior of the compounds was studied by polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction measurements at elevated temperature. The DSC curves were obtained during two successive heating–cooling scans at a heating/cooling rate of 5°C min^{-1}. The POM and X-ray measurements were performed for the confirmation of phase structure of the expected compounds. The thermodynamic parameters such as the phase transition temperatures (T/°C) and enthalpy changes ($\Delta H/Jg^{-1}$) associated with these phase transitions of all the synthesized banana-shaped monomers are listed in Table 1. Compound **4a** shows enantiotropic phase sequences of Cr–B_6–I transitions, which is confirmed by DSC and POM textural observation. On cooling, the isotropic-B_6 transition appears that crystallizes at 78.6°C (Table 1). The compounds **4b** and **4c** also showed two transition peaks on heating that are attributed to the Cr–B_6 and B_6–I transitions. On cooling, again two peaks corresponding to I–B_6 and B_6–Cr transitions were observed (Table 1).

Compounds **4a–c** exhibit enantiotropic mesophase identified by DSC and POM studies. A representative compound **4a** was confirmed by X-ray measurements. The thermal behavior of all these compounds **4a–c** is in accordance with literature [4, 15, 22–24]. Hence, increasing the terminal chain length (**4a** vs. **4c**), as expected, decreases the transition temperature (Table 1). In addition, the odd–even effect on the isotropic temperature was seen on compounds **4a–c** where even number of alkyl carbon has higher transition temperature than odd number of alkyl carbon chain [15, 22–24]. The enthalpy changes determined by DSC are in agreement with the values usually observed for typical crystalline–smectic, smectic–isotropic, and smectic–crystalline transitions that confirm the presence of smectic mesophases [25, 26]. The solid–liquid crystal or liquid crystal–solid transitions involved much more energy than the liquid crystal–isotropic liquid or liquid crystal–liquid crystal transitions [27].

Similar odd–even effects have been reported in other materials [28]. Increasing terminal chain length decreases the transition temperature as usual. A large number of bent-core liquid crystalline materials derived from 2,7-dihydroxynaphthalene unit has already been reported [29–34]. The structure–property relationship in bent-core liquid crystals derived from 2,7-dihydroxynaphthalene core has been extensively discussed by several researchers [28–34]. Several series of bent-shaped mesogens based on substituted naphthalene-2,7-diol having phenylbenzoate wings and a double bond at one or at both ends of the terminal

Table 1. Phase transition temperature (T/°C) and associated enthalpy values (ΔH/J g^{-1}) in parentheses given for the second heat and cooling of DSC scans for compounds **4a–c**

Compound	n	Scan	Phase transitions
4a	7	Heat	Cr 107.1 (22.7) B_6 150.5 (18.1) I
		Cool	I 147.3 (16.6) B_6 78.6 (22.3) Cr
4b	8	Heat	Cr 109.8 (20.2) B_6 152.1 (10.9) I
		Cool	I 150.4 (15.8) B_6 80.8 (24.4) Cr
4c	9	Heat	Cr 102.8 (21.0) B_6 146.6 (11.7) I
		Cool	I 144.1 (18.8) B_6 77.8 (23.4) Cr

Note. Cr = crystal; B_6 = smectic A phase; I = isotropic phase.

chains have been reported [29, 35]. These compounds were synthesized using the long chains, but only smectic phases were observed for the ester-based bent-core molecules. These comparisons indicate the stabilizing effect of azobenzene units on the nematic and smectic phases of the naphthalene-based banana-shaped compounds [29, 35].

Under the polarizing microscope, a fan-shaped texture as typical for smectic A phase corresponding to the B_6 phase for compound **4a** was observed upon cooling from the isotropic phase. Optical textures taken for compound **4a** ($n = 7$) at 110°C is shown in Fig. 1; no other phase transition on further cooling, except crystallization, was observed. On cooling from the isotropic phase, compound **4b** ($n = 8$) showed also fan-shaped texture and compound **4c** showed broken fan-shaped texture, which is a typical smectic A phase corresponding to the B_6 phase for **4b** and **4c**; there was no other phase transitions observed. All the transition temperatures observed under POM were matching with DSC data.

The X-ray diffraction was carried out for further phase structure conformation. The mesophase was obtained upon cooling of the isotropic phase of the compound **4a** ($n = 7$). The intensity versus 2θ plot derived from the diffraction pattern is shown in Fig. 2. The compound **4a** showed one sharp reflection at $d = 27.57$ Å in the lower-angle region and in addition, a diffused peak in the wide-angle region with d-spacing of 4.22 Å at 105°C is due to a liquid-like in-plane ordering of molecules in the layers. The XRD pattern, observed as typical of a B_6 intercalated mesophase due to sharp reflection, is half of the molecular length (55.92 Å).

Photoswitching Study

All banana-shaped molecules showed similar absorption spectra due to their similar molecular structure; the only difference is the alkyl chain ($n = 7$–9), which does not alter the electronic transitions, the absorption spectra of compounds **4a–c**. Consequently, compound **4a** was considered for photoisomerization study [3]. A solution of concentration 5×10^{-5} mol L^{-1} of **4a** was prepared in chloroform. The spectrum shows three absorption peaks with maximum absorbance at 261 nm, 365 nm ($\varepsilon = 34.940$ L.mol^{-1}.cm^{-1}), and 445 nm. Since peak around 261 nm is non-photoactive and it is not our interest, so we eliminate our discussions regarding this peak. Fig. 3 shows the spectral changes by irradiation at 365 nm. The absorbance at 365 nm decreases and after 45 sec the photostationary state of a *cis-trans* mixture is reached. By irradiation at 436 nm, the absorbance at 365 nm increases until a new photostationary state is reached. The photochemical back reaction by irradiation at 436 nm is shown in Fig. 4.

The thermal back reaction (*cis*→ *trans*) is shown in Fig. 5. After irradiation at 365 nm to photostationary state, the solution was kept in the dark and the back reaction was measured at $\lambda = 365$ nm after over 28 h and 30 min. The presence of the two isosbestic points indicates the absence of side reactions. A linear correlation of ln ($E_\infty - E_t$) as a function of time indicates a reaction of the first order (see Fig. 6).

After 1590 min, the conversion degree from *cis* to *trans* was 96%. Similar photochemical switching behavior has previously been reported to center-linked bent-core azobenzene liquid crystalline polymers in which two azobenzene groups are attached to a central resorcinol unit [36].

Using the materials described in this article, an optical pattern storage device is fabricated as shown in Fig. 7. Here, experimental cell is filled with the mixture of guest naphthalene bent-shaped molecules and the host liquid crystalline molecules (10% of guest mixed with 90% of guest 5CB). The region 1 represents UV-illuminated area and region 2 represents masked region that per se is not contributing in the isomerization phenomena.

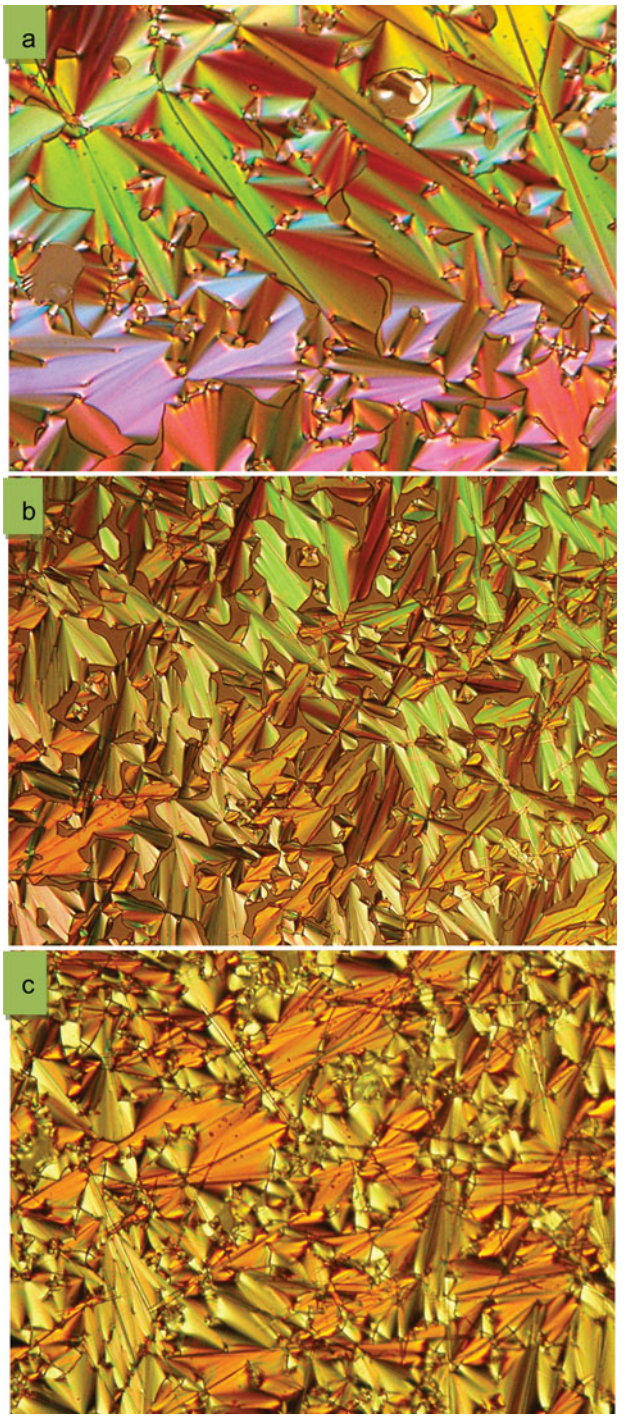


Figure 1. Optical micrograph of (a) compound **4a** taken at 110°C, (b) compound **4b** taken at 112°C, and (c) compound **4c** taken at 105°C from cooling cycle.

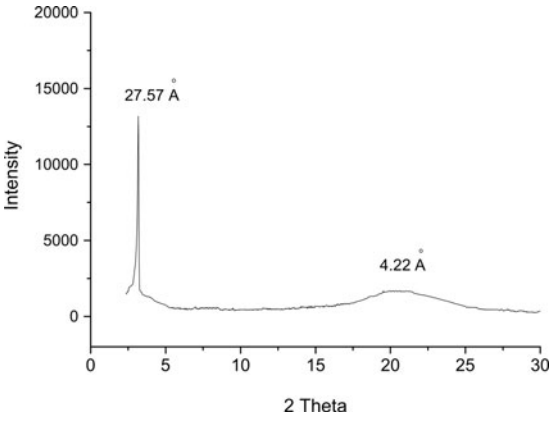


Figure 2. The intensity versus 2θ graph derived from X-ray diffraction for $SmA_{intercal}$ corresponding to B6 phase of compound **4a** at 105°C.

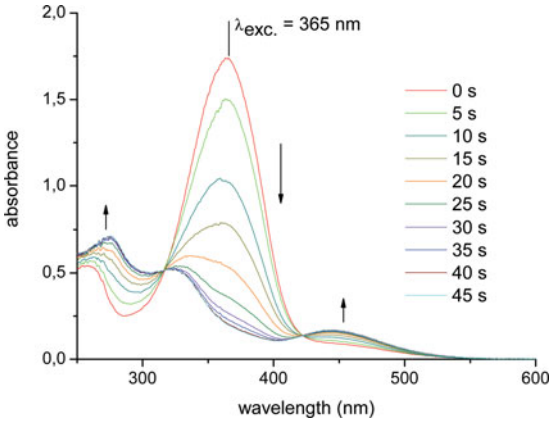


Figure 3. UV/Vis absorption spectra of **4a** in chloroform, $c = 5 \times 10^{-5}$ mol L^{-1}, irradiation at 365 nm.

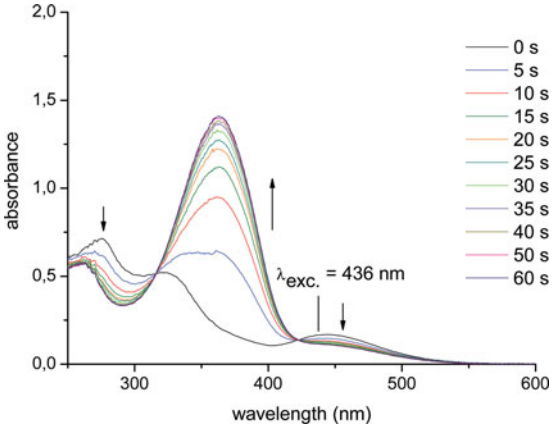


Figure 4. UV/Vis absorption spectra of **4a** in chloroform, $c = 5 \times 10^{-5}$ mol L^{-1}, irradiation at 436 nm (the sample was irradiated before at 365 nm).

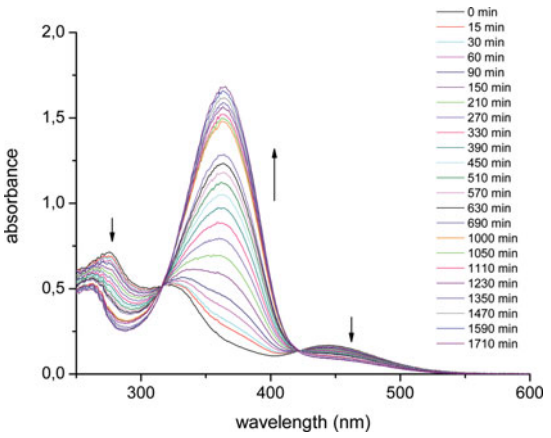


Figure 5. Thermal back reaction (*cis*→ *trans*) of **4a** in chloroform (the solution was irradiated before at 365 nm).

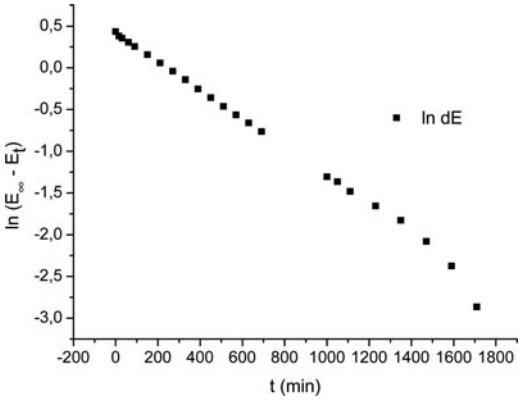


Figure 6. Thermal back reaction (*cis*→ *trans*) of **4a** in chloroform. Plot of ln ($E_\infty - E_t$) at λ = 365 nm as a function of time. After 1590 min (26 h and 30 min), the conversion of *cis*→ *trans* was 96%.

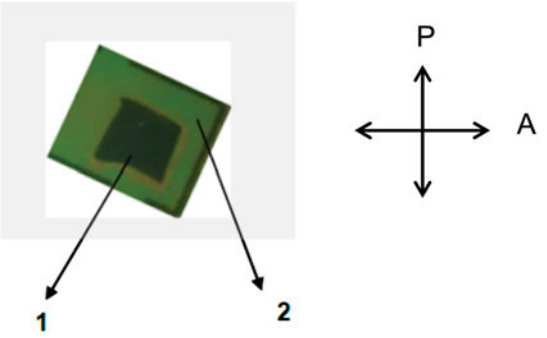


Figure 7. Demonstration of optical pattern storage capability of the device based on the principle described in the article observed under the crossed polarizers (marked as P and A). The sample was kept at room temperature and illuminated with UV radiation through a mask. The dark region marked as 1 is where the molecules are in isotropic state caused by illuminating UV and the bright region marked as 2 is where the radiation is masked.

Pattern is illuminated with 365 nm UV light at room temperature through photomask to create the pattern shown in the figure. One can see the good clarity between bright and dark states.

Conclusion

Three new banana-shaped mesogens with azobenzene units containing 2,7-dihydroxynaphthalene as central bent unit are studied and all compounds show B_6 phase. The double bonds can be used for preparation of polymers or silyl functionalized bent-core mesogens, whereas the presence of the azo linkage in these liquid crystal monomers is suitable for photochromism application and *trans-cis-trans* isomerization cycles under UV irradiation. Optical storage device is fabricated by using present molecule, which shows the capability of the discussed materials for device applications. The detailed photochemical *cis-trans* isomerization study of other compounds of this series and all compounds at solid film is now in progress and will be reported in due course.

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