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Synthesis and photoswitching properties of bent-shaped liquid crystals containing azobenzene monomers

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Three novel bent-shaped monomers, namely 1,3-phenylene bis-{4-[4-(n-allyloxyalkyloxy)phenylazo]benzoate} **5a–c**, containing azobenzene as side arms, resorcinol as central units and terminal double bonds as polymerisable functional groups were synthesised and characterised. The mesophase behaviour was investigated by polarising optical microscopy, differential scanning calorimetry and X-ray diffraction measurements and it was found that all three compounds display $SmA_{intercal}$ mesophases. These bent-shaped molecules exhibit strong photoisomerisation behaviour in solutions in which *trans* to *cis* isomerisation takes about 50 seconds whereas the reverse process takes almost 31 hours.

Keywords: azobenzene; bent–shaped monomers; photoswitching; *cis-trans* isomerisation; photonics

1. Introduction

Recently, bent-shaped mesogens or banana liquid crystals (LCs) have attracted considerable research interest in the field of soft condensed matter. The mesomorphic properties of a variety of bent-shaped molecules have been investigated extensively. The polar order of these molecules, owing to their bent shape, displays interesting properties such as ferroelectric or anti-ferroelectric switching (*1–5*). The occurrence of superstructural chirality in the mesophase of bent-core compounds without having any chiral moiety in the molecules is not only of fundamental scientific interest but also of industrial application as this chirality can be switched in external electric fields. In general, the mesophases formed by the banana-shaped compounds are termed as 'Banana' (Bn) phases, designated as B_1– B_8 phases (*6–10*); the B_3 and B_4 phases are crystalline, while the others are mesomorphic (*6–10*). Here, we would like to mention that other nomenclature, such as SmCP (polar tilted smectic) for B_2, Col_r (rectangular columnar) or Col_{ob} (columnar oblique lattice) for B_1 and $SmA_{intercal}$ (intercalated smectic) for B_6, has been used (*6–10*). The most widely studied B_2 phase is identified as a tilted antiferroelectric polar smectic ($SmCP_A$) phase with either synclinic (SmC_sP_A) or anticlinic (SmC_aP_A) structures (*6–10*). In addition to various banana phases, these mesogens also display classical nematic and smectic phases.

In recent years, a field of research that is growing steadily is that of photoinduced phenomenon, in which the incident light brings about the molecular ordering/disordering of the liquid-crystalline system (*11–14*). 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 (*15–17*). The heart of the phenomenon in such systems is the reversible photoinduced shape transformation of the molecules containing the photochromic azo groups (*18*). 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 photochromism and photoisomerisation (*19–21*). Significant attention has been focused in recent years on the preparation of polymerisable bent-core LCs (*22–24*) including the crosslinked LC polymers derived from banana-shaped monomers having acrylate groups (*23*). Main chain LC polymers have been obtained from bent-core liquid crystalline monomers with double bonds at both ends (*24–28*); among them two materials exhibited a monotropic SmCP phase (*26, 28–30*) and others form nematic and smectic C phases. Two series of non-symmetric

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banana-shaped compounds with alkyl as one terminal and alkenyl at the other terminal group have also been reported (*31*). In addition, some compounds having one side olifinic terminal group have been used to prepare oligomeric or polymeric systems (*32, 33*).

Resorcinol is the most widely used central unit for bent-shaped compounds which exhibit B-type phases as well as smectic or nematic phases (*34–46*). The present investigation focuses on the synthesis and photoisomerisation behaviour of three novel bent-shaped monomers derived from resorcinol as the central unit, azobenzene groups in the side arms, and terminal double bonds as polymerisable functional groups.

2. Experimental details

2.1 Materials

Ethyl 4-amino benzoate (Fluka), sodium nitrite (Fluka), phenol (Merck), 1,4-dibromobutane (Fluka), 1,5-dibromopentane (Fluka), 1,6-dibromohexane (Fluka), potassium carbonate (Aldrich), allyl alcohol (Fluka), resorcinol (Fluka), 1,3-dicyclohexylcarbodiimide (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 (Fluka) and distilled out before use. Other solvents and chemicals were used without further purification.

*2.1.1 Ethyl 4-(4-hydroxyphenylazo)benzoate **1***

Compound **1** was prepared according to our earlier paper (*47*). ^{1}H NMR (acetone-d_6) δ: 8.17 (d, 2H, J = 8.2 Hz, ArH), 7.92 (d, 2H, J = 7.5 Hz, ArH), 7.88 (d, 2H, J = 7.5 Hz, ArH), 7.01 (d, 2H, J = 8.2 Hz, ArH), 5.54 (s, 1H, OH), 4.42 (q, 2H, J = 7.2 Hz, -CH_2CH$_3$), 1.44 (t, 3H, -CH$_2$$CH_3$).

*2.1.2 Ethyl 4-[4-(4-bromobutyloxy)phenylazo] benzoate **2a***

Compound **1** (2.52 g, 9.33 mmol) in dry acetone (150 ml), potassium carbonate (8.50 g, 61.6 mmol), a catalytic amount of potassium iodide (50 mg) and a 10-fold excess of 1,4-dibromobutane (20.05 g, 93.38 mmol) was refluxed for 24 h under argon atmosphere. The reaction mixture was filtered hot and the acetone was removed under reduced pressure. About 150 ml of hexane was added to the product to remove unreacted 1,4-dibromobutane and the insoluble product was collected by filtration. The product was recrystallised from ethanol with hot filtration to ensure the removal of the dimeric side-product. Yield of **2a**: 1.97 g (53%) as orange powder and m.p. 133.3°C. IR (KBr, ν_{max}, cm^{-1}): 2930 (CH$_2$), 2858 (CH$_2$), 1724 (C=O, ester), 1596, 1490 (C=C, aromatic), 1242, 1130 (C-O), 830 (CH). ^{1}H NMR (CDCl$_3$) δ: 8.18 (d, 2H, J = 8.3 Hz, ArH), 7.96 (d, 2H, J = 7.4 Hz, ArH), 7.92 (d, 2H, J = 7.3 Hz, ArH), 7.00 (d, 2H, J = 8.9 Hz, ArH), 4.06 (t, 2H, J = 6.8 Hz, OCH$_2$-), 4.01 (d, 2H, -CH_2CH$_3$), 3.47 (t, 2H, -CH$_2$Br), 1.91 (m, 2H, OCH$_2$$CH_2$-), 1.67 (m, 2H, -$CH_2CH_2$O), 1.42 (t, 3H, -CH$_2$$CH_3$). Elemental Analysis Calc. for $C_{19}H_{21}BrN_2O_3$ (405.28): C, 56.31; H, 5.21; N, 6.91%. Found: 56.20; H, 5.12; N, 6.82%.

*2.1.3 Ethyl 4-[4-(5-bromopentyloxy)phenylazo] benzoate **2b***

Compound **2b** was prepared by the same method used for synthesis of **2a**. ^{1}H NMR (CDCl$_3$) δ: 8.17 (d, 2H, J = 9.0 Hz, ArH), 7.96 (d, 2H, J = 7.2 Hz, ArH), 7.93 (d, 2H, J = 7.2 Hz, ArH), 7.00 (d, 2H, J = 8.9 Hz, ArH), 4.05 (t, 2H, J = 6.8 Hz, OCH$_2$-), 4.01 (d, 2H, -CH_2CH$_3$), 3.42 (t, 2H, -CH$_2$Br), 1.91 (m, 2H, OCH$_2$$CH_2$-), 1.63 (m, 2H, -$CH_2CH_2$O), 1.47 (m, 2H, -CH$_2$$CH_2CH_2$), 1.34 (t, 3H, -CH$_2$$CH_3$).

*2.1.4 Ethyl 4-[4-(6-bromohexyloxy)phenylazo] benzoate **2c***

Compound **2c** was prepared by the same method used for synthesis of **2a**. ^{1}H NMR (CDCl$_3$) δ: 8.18 (d, 2H, J = 8.3 Hz, ArH), 7.97 (d, 2H, J = 7.3 Hz, ArH), 7.93 (d, 2H, J = 7.4 Hz, ArH), 7.01 (d, 2H, J = 8.9 Hz, ArH), 4.06 (t, 2H, J = 6.8 Hz, OCH$_2$-), 4.02 (d, 2H, -CH_2CH$_3$), 3.41 (t, 2H, -CH$_2$Br), 1.88 (m, 2H, OCH$_2$$CH_2$-), 1.66 (m, 2H, -$CH_2CH_2$O), 1.50 (m, 4H, -CH$_2$$CH_2$$CH_2CH_2$-), 1.36 (t, 3H, -CH$_2$$CH_3$).

*2.1.5 Ethyl 4-[4-(4-allyloxybutyloxy)phenylazo] benzoate **3a***

A solution of compound **2a** (1.80 g, 4.44 mmol) in dry acetone (80 ml), allyl alcohol (0.321 g, 5.54 mmol), potassium carbonate (0.764 g, 5.54 mmol) and a catalytic amount of potassium iodide (20 mg) was refluxed for 24 h under argon atmosphere. The mixture was poured into ice-cold water and slightly acidified (pH $<$ 5) with dilute hydrochloric acid. The precipitate was filtered off and was crystallised from methanol:chloroform (2:1). Yield of **3a**: 1.37 g (80%) and m.p. 109.4°C. IR (KBr, ν_{max}, cm^{-1}): 3066 (CH$_2$), 2936 (CH$_2$), 2856 (CH$_2$), 1720 (C=O, ester), 1642 (C=C, vinyl), 1588, 1493 (C=C, aromatic), 1248, 1130, 1062 (C-O), 835 (C-H). ^{1}H NMR (CDCl$_3$) δ: 8.17 (d, 2H, J = 8.3 Hz, ArH), 7.97 (d, 2H, J = 7.2 Hz, ArH), 7.93 (d, 2H, J = 7.8 Hz, ArH), 7.01 (d, 2H, J = 8.9 Hz, ArH),),

5.91 (m, 1H, CH=), 5.19 (d, 1H, J = 16.5 Hz, =CH_2), 5.12 (d, 1H, J = 8.9 Hz, =CH_2), 4.07 (t, 2H,, J = 6.9 Hz, OCH_2-), 4.01 (d, 2H, -CH_2CH_3), 3.47 (t, 2H, J = 7.4 Hz, -CH_2O), 3.35 (s, 2H, OCH_2-), 1.90 (m, 2H, OCH_2CH_2-), 1.67 (m, 2H, -CH_2CH_2O), 1.43 (t, 3H, -CH_2CH_3). Elemental Analysis Calc. for $C_{22}H_{26}N_2O_4$ (382.45): C, 69.09; H, 6.84; N, 7.32%. Found: C, 68.94; H, 6.71; N, 7.23%.

*2.1.6 Ethyl 4-[4-(5-allyloxypentyloxy)phenylazo] benzoate **3b***

Compound **3b** was prepared by the same method used for synthesis of **3a**. ^{1}H NMR ($CDCl_3$) δ: 8.18 (d, 2H, J = 8.9 Hz, ArH), 7.97 (d, 2H, J = 7.2 Hz, ArH), 7.94 (d, 2H, J = 7.2 Hz, ArH), 6.99 (d, 2H, J = 8.8 Hz, ArH), 5.84 (m, 1H, CH=), 5.06 (d, 1H, J = 16.2 Hz, =CH_2), 4.99 (d, 1H, J = 9.0 =CH_2), 4.04 (t, 2H, J = 6.8 Hz, OCH_2-), 4.01 (d, 2H, -CH_2CH_3), 3.42 (t, 2H, J = 6.5 Hz, -CH_2O), 3.36 (s, 2H, OCH_2-), 1.91 (m, 2H, OCH_2CH_2-), 1.62 (m, 2H, -CH_2CH_2O), 1.48 (m, 2H, -$CH_2CH_2CH_2$-), 1.33 (t, 3H, -CH_2CH_3).

*2.1.7 Ethyl 4-[4-(6-allyloxyhexyloxy)phenylazo] benzoate **3c***

Compound **3c** was prepared by the same method used for synthesis of **3a**. ^{1}H NMR ($CDCl_3$) δ: 8.17(d, 2H, J = 8.3 Hz, ArH), 7.96 (d, 2H, J = 7.7 Hz, ArH), 7.92 (d, 2H, J = 7.9 Hz, ArH), 7.00 (d, 2H, J = 8.9 Hz, ArH), 5.83 (m, 1H, CH=), 5.06 (d, 1H, J = 15.9 Hz, =CH_2), 4.99 (d, 1H, J = 9.0 Hz, =CH_2), 4.05 (m, 2H, J = 6.8 Hz, OCH_2-), 4.01 (d, 2H, –CH_2CH_3), 3.41 (t, 2H, J = 6.7 Hz, -CH_2O), 3.36 (s, 2H, OCH_2–), 1.87 (m, 2H, OCH_2CH_2–), 1.65 (m, 2H, –CH_2CH_2O), 1.51 (m, 4H, –$CH_2CH_2CH_2CH_2$–), 1.40 (t, 3H, –CH_2CH_3).

*2.1.8 4-[4-(4-Allyloxybutyloxy)phenylazo] benzoic acid **4a***

Compound **3a** (1.20 g, 3.14 mmol) was dissolved in 150ml of methanol. A solution of potassium hydroxide (0.528 g, 9.42 mmol) in water (20 ml) was added, reflux for 4 h. After cooling, the mixture was poured into ice-cold water and the precipitate was acidified with dilute hydrochloric acid. The precipitate was filtered off, washed with water and crystallised from ethanol:chloroform (2:1) to give the compound **4a**. Yield 0.520 g (46%). IR (KBr, ν_{max}, cm^{-1}): 3067 (=CH_2), 2935 (CH_2), 2858 (CH_2), 1684 (C=O, acid), 1642 (C=C, vinyl), 1582, 1492 (C=C, aromatic), 1250, 1137, 1068 (C-O), 838 (C-H). ^{1}H NMR ($CDCl_3$) δ: 8.18 (d, 2H, J = 8.3 Hz, ArH), 7.96 (d, 2H, J = 7.4 Hz, ArH), 7.93 (d, 2H, J = 7.8 Hz, ArH), 7.01 (d, 2H, J = 8.9 Hz, ArH), 5.90 (m, 1H, CH=), 5.18 (d, 1H, J = 16.6 Hz, =CH_2), 5.12 (d, 1H, J = 8.8 Hz, =CH_2), 4.06 (t, 2H, J = 6.8 Hz, OCH_2-), 3.46 (t, 2H, J = 7.5 Hz,-CH_2O), 3.34 (s, 2H, OCH_2-), 1.91 (m, 2H, OCH_2CH_2-), 1.69 (m, 2H, -CH_2CH_2O). Elemental Analysis Calc. for $C_{20}H_{22}N_2O_4$ (354.39): C, 67.77; H, 6.25; N, 7.90%. Found: C, 67.61; H, 6.12; N, 7.78.

*2.1.9 4-[4-(5-Allyloxypentyloxy)phenylazo] benzoic acid **4b***

Compound **4b**: ^{1}H NMR ($CDCl_3$) δ: 8.17 (d, 2H, J = 9.0 Hz, ArH), 7.96 (d, 2H, J = 7.2 Hz, ArH), 7.93 (d, 4H, J = 7.6 Hz, ArH), 6.99 (d, 2H, J = 8.9 Hz, Ar-H), 5.83 (m, 1H, CH=), 5.05 (d, 1H, J = 17.1 Hz, =CH_2), 4.98 (d, 1H, J = 9.0 Hz, =CH_2), 4.04 (t, 2H, J = 6.9 Hz, OCH_2-), 3.40 (t, 2H, J = 6.8 Hz, -CH_2O), 3.37 (s, 2H, OCH_2-), 1.90 (m, 2H, OCH_2CH_2-), 1.60 (m, 2H, CH_2CH_2O), 1.44 (m, 2H, -$CH_2CH_2CH_2$-).

*2.1.10 4-[4-(6-Allyloxyhexyloxy)phenylazo] benzoic acid **4c***

Compound **4c**: ^{1}H NMR ($CDCl_3$) δ: 8.18 (d, 2H, J = 8.3 Hz, ArH), 7.97 (d, 2H, J = 7.8 Hz, ArH), 7.93 (d, 2H, J = 7.9 Hz, ArH), 7.00 (d, 2H, J = 8.9 Hz, ArH), 5.82 (m, 1H, CH=), 5.06 (d, 1H, J = 15.6 Hz, =CH_2), 4.98 (d, 1H, J = 9.1 Hz, =CH_2), 4.03 (t, 2H, J = 6.9 Hz, OCH_2-), 3.41 (t, 2H, J = 6.8 Hz, -CH_2O), 3.38 (s, 2H, OCH_2-), 1.86 (m, 2H, OCH_2CH_2-), 1.66 (m, 2H, -CH_2CH_2O), 1.52–1.42 (m, 4H, - $CH_2CH_2CH_2CH_2$-).

*2.1.11 1,3-Phenylene bis-{4-[4-(4-allyloxybutyloxy) phenylazo]benzoate} **5a***

Compound **4a** (0.50 g, 1.41 mmol) was dissolved in 80 ml of dry dichloromethane. DMAP (0.017 g, 0.14 mmol) were added and the mixture was stirred for 30 min. A solution of resorcinol (0.077 g, 0.70 mmol) in dry dichloromethane (10 ml) was added to the mixture and DCC (0.291 g, 1.41 mmol) in 10 ml of dry dichloromethane was added slowly. The mixture was stirred for 24 h. The precipitate was removed by filtration and the solvent was removed by rotary evaporator. The product was dissolved in dichloromethane and water. The organic phase was washed with dilute acetic acid, sodium carbonate solution and water successively and the solvent was removed by rotary evaporator. The compound was purified by column chromatography using chloroform:methanol (10:1) as eluent. The product was recrystallised from methanol:chloroform (2:1) to get the target compound **5a**. Yield: 0.180 g (33%). IR (KBr, ν_{max}, cm^{-1}): 3070 (=CH_2), 2935 (CH_2), 2862 (CH_2), 1737 (C=O, ester), 1642 (C=C, vinyl), 1598, 1500 (C=C, aromatic), 1252, 1125, 1068 (C–O), 836 (C-H).

^{1}H NMR ($CDCl_3$) δ: 8.32 (d, 4H, J = 8.3 Hz, 2 × ArH), 7.97 (d, 4H, J = 7.8 Hz, 2 × ArH), 7.94 (d, 4H, J = 7.8 Hz, 2 × ArH), 7.50 (t, 1H, J = 8.2 Hz, ArH), 7.23 (s, 1H, ArH), 7.21 (d, 2H, ArH), 7.01 (d, 4H, J = 8.9 Hz, 2 × Ar-H), 5.91 (m, 2H, CH=), 5.19 (d, 2H, J = 16.8 Hz, =CH_2), 5.12 (d, 2H, J = 8.9 Hz, =CH_2), 4.08 (t, 4H, J = 6.8 Hz, 2 × OCH_2-), 3.46 (t, 4H, J = 6.9 Hz, 2 × -CH_2O), 3.34 (s, 4H, 2 × OCH_2-), 1.90 (m, 4H, 2 × OCH_2CH_2-), 1.68 (m, 4H, 2 × -CH_2CH_2O). ^{13}C NMR ($CDCl_3$) δ: 25.78, 29.01, 58.46, 68.20, 70.62, 114.13, 114.71, 119.17, 119.31, 122.44, 125.19, 129.80, 130.02, 131.01, 131.14, 146.78, 151.34, 155.78, 162.32, 164.24. Elemental Analysis Calc. for $C_{46}H_{46}N_4O_8$ (782.87): C, 70.57; H, 5.91; N, 7.15%. Found: C, 70.41; H, 5.80; N, 7.02%.

2.1.12 1,3-Phenylene bis-{4-[4-(5-allyloxypentyloxy) phenylazo]benzoate} ***5b***

Compound **5b** was prepared by the same method used for synthesis of **5a**. ^{1}H NMR ($CDCl_3$) δ: 8.31 (d, 4H, J = 8.9 Hz, 2 × ArH), 7.97 (d, 4H, J = 7.5 Hz, 2 × ArH), 7.94 (d, 4H, J = 7.5 Hz, 2 × ArH), 7.51 (t, 1H, J = 8.3 Hz, ArH), 7.22 (s, 1H, ArH), 7.20 (d, 2H,, J = 8.2 Hz, ArH), 7.01 (d, 4H, J = 8.9 Hz, 2 × Ar-H), 5.84 (m, 2H, CH=), 5.05 (d, 2H, J = 17.2 Hz, =CH_2), 4.99 (d, 2H, J = 10.3 Hz, =CH_2), 4.05 (t, 4H, J = 6.8 Hz, 2 × OCH_2-), 3.38 (t, 4H, J = 6.2 Hz, 2 × -CH_2O), 3.33 (s, 4H, 2 × OCH_2-), 1.83 (m, 4H, 2 × OCH_2CH_2-), 1.61 (m, 4H, 2 × -CH_2CH_2O), 1.43 (m, 4H, 2 × -$CH_2CH_2CH_2$-). ^{13}C NMR ($CDCl_3$) δ: 25.98, 29.21, 29.67. 58.66, 68.40, 70.82, 114.34, 114.91, 119.37, 119.52, 122.64, 124.55, 125.40, 130.00, 130.22, 131.34, 146.98, 151.55, 155.99, 162.53, 164.84.

2.1.13 1,3-Phenylene bis-{4-[4-(6-allyloxyhexyloxy) phenylazo]benzoate} ***5c***

Compound **5c** was prepared by the same method used for synthesis of **5a**. ^{1}H NMR ($CDCl_3$) δ: 8.31 (d, 4H, J = 8.3 Hz, 2 × ArH), 7.97 (d, 4H, J = 7.8 Hz, 2 × ArH), 7.94 (d, 4H, J = 7.9 Hz, 2 × ArH), 7.50 (t, 1H, J = 8.2 Hz, ArH), 7.23 (s, 1H, ArH), 7.21 (d, 2H, J = 8.2 Hz, ArH), 7.01 (d, 4H, J = 9.0 Hz, 2 × Ar-H), 5.82 (m, 2H, CH=), 5.06 (d, 2H, J = 15.9 Hz, =CH_2), 4.99 (d, 2H, J = 8.9 Hz, =CH_2), 4.05 (t, 4H, J = 6.8 Hz, 2 × OCH_2-), 3.38 (t, 4H, J = 6.9 Hz, 2 × -CH_2O), 3.33 (s, 4H, 2 × OCH_2-), 1.83 (m, 4H, 2 × OCH_2CH_2-), 1.61 (m, 4H, 2 × -CH_2CH_2O), 1.54–1.41 (m, 8H, 2 × -$CH_2CH_2CH_2CH_2$-). ^{13}C NMR ($CDCl_3$) δ: 25.78, 25.83, 29.01, 29.67, 58.66, 68.40, 70.82, 114.34, 114.91, 119.17, 119.37, 122.64, 125.40, 129.80, 130.00, 131.22, 131.34, 146.98, 151.55, 155.99, 162.53, 164.44.

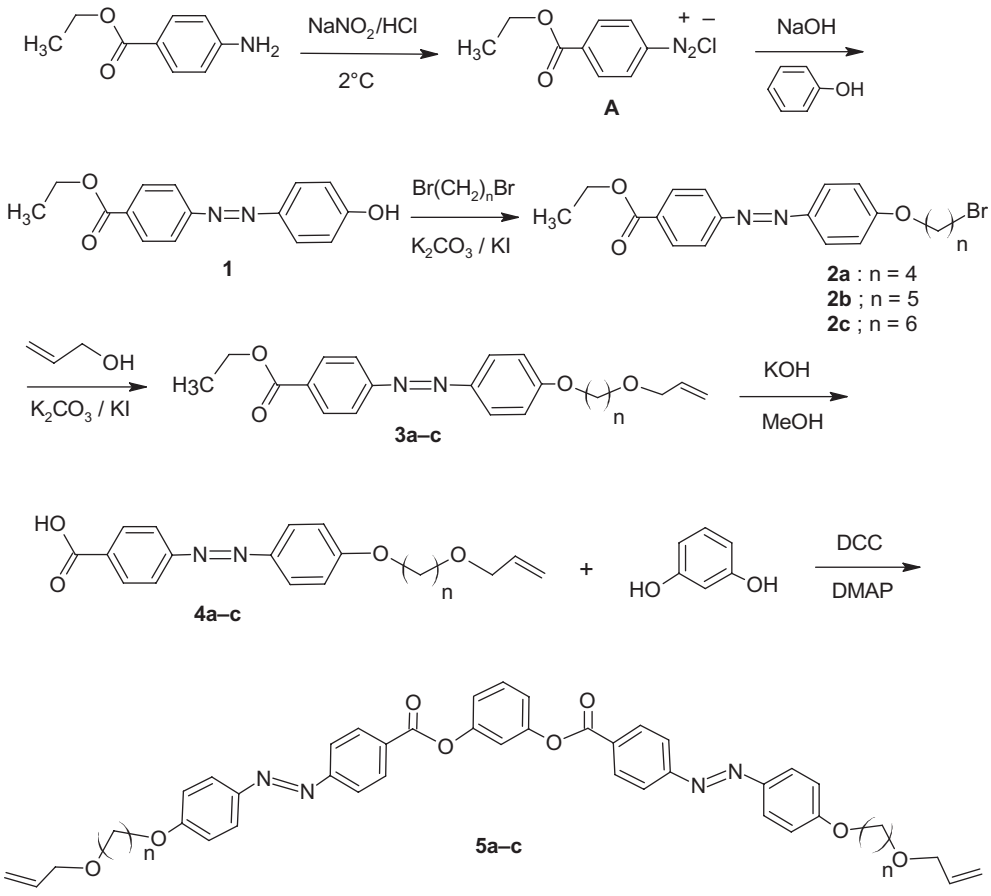
3. Characterisation

The structures of the intermediates and final products were confirmed by spectroscopic methods. Infrared spectra were recorded with a Thermo Nicolet Nexus 670 FTIR spectrometer. ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were recorded with a Jeol (ECA 600) spectrometer. Compositions of the compounds were determined by CHN elemental analyzer (Leco & Co). The transition temperatures and their enthalpies were measured by differential scanning calorimetry (DSC) (Perkin DSC 7), and heating and cooling rates were at 10°C min^{-1}, and the melting point of the intermediate compounds were determined by DSC. Optical textures were determined by using a Mettler FP 82 hot stage and control unit in conjunction with a Nikon Optiphot 2 polarising optical microscope. X-ray diffraction measurements were carried out using Cu-Kα radiation (λ = 1.54Å) using a 40kV voltage, 30mA current from an anode generator (XPERT-PRO) equipped with a graphite monochromator. Absorption spectra were recorded using a Shimazdu 3101 PC UV-Vis spectrometer. All of the solutions were prepared and measured under air in the dark at room at temperature (21 ± 1°C) using 1cm 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 and 436 nm respective, using a 200W 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 for irradiation at 365 nm and 254 nm and Code-No. 805 (both Schott, Jena, Germany) for irradiation at 436 nm were used.

4. Results and discussion

4.1 Synthesis

The intermediates and target compounds **5a–c** were prepared as depicted in Scheme 1. The side arm rod-like compounds were prepared from ethyl 4-amino benzoate in which the amino group is diazotated by sodium nitrite in the presence of 3 equivalents of diluted hydrochloric acid and the obtained diazonium salt (**A**) was coupled with phenol to yield ethyl 4-(4-hydroxyphenylazo)benzoate **1**. The flexible spacer was introduced by alkylation of **1** with 10-fold excess of dibromoalkane in the presence of potassium



Scheme 1. Synthesis of bent-shaped monomers 1,3-phenylene bis-{4-[4-(n-allyloxyalkyloxy)phenylazo]benzoate} **5a-c**.

carbonate as base to give ethyl 4-[4-(n-bromoalkyloxy)phenylazo]benzoate **2a–c**.

For introducing the double bonds at the terminals, compounds **2a–c** were used for further alkylation with allyl alcohol using potassium carbonate as base to yield ethyl 4-[4-(n-allyloxyalkyloxy)phenylazo]benzoate **3a–c**. These **3a–c** compounds were base-hydrolysed to give the compounds 4-[4-(n-allyloxyalkyloxy)phenylazo]benzoic acids **4a–c**. The acids **4a–c** were coupled with resorcinol by using DCC and DMAP to achieve the target molecules 1,3-phenylene bis-{4-[4-(n-allyloxyalkyloxy)phenylazo]benzoate} **5a–c**.

4.2 Mesomorphic properties

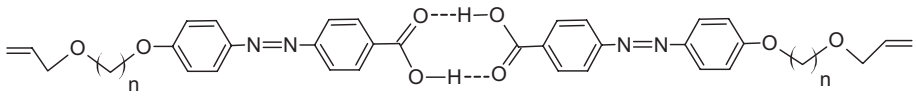
4.2.1 Differential scanning calorimetry studies

The phase transition temperatures as well as the phase transition enthalpy changes were determined by DSC and the results of the second heating and cooling scans are summarised in Table 1.

Table 1. Phase transition temperature (T, °C) and associated transition enthalpy values (ΔH, J g^{-1}) in parentheses given for compounds **4a-c** and **5a-c**.

Compound	Second heating	Second cooling
4a	Cr 169.8 (25.1) N 194.1 (10.5) I	I 181.4 (11.3) N 128.2 (22.3) Cr
4b	Cr_1 149.7 (14.7) Cr_2 196.7 (29.7) N 239.2 (13.9) I	I 234.6 (13.7) N 191.7 (28.1) Cr_2 96.5 (11.6) Cr_1
4c	Cr_1 137.2 (25.1) Cr_2 198.7 (70.1) N 241.6 (11.1) I	I 239.9 (15.8) N 192.1 (55.3) Cr_2 98.4 (19.0) Cr_1
5a	Cr 148.9 (13.4) $SmA_{intercal}$ 170.6 (10.5) I	I 166.9 (11.8) $SmA_{intercal}$ 130.3 (19.5) Cr
5b	Cr 142.7 (38.5) $SmA_{intercal}$ 166.7 (12.2) I	I 162.1 (16.5) $SmA_{intercal}$ 126.7 (38.2) Cr
5c	Cr 154.7 (16.7) $SmA_{intercal}$ 169.1 (20.9) I	I 165.4 (21.7) $SmA_{intercal}$ 131.1 (25.7) Cr

Abbreviations: Cr_1 and Cr_2 = crystalline phase; $SmA_{intercal}$ = smectic phase, I = isotropic phase.



Structure 1.

It is interesting to note that the intermediate compounds 4-[4-(n-allyloxyalkyloxy)phenylazo]benzoic acids **4a–c** show nematic phases. It should be noted that compounds **3a–c**, ethyl ester of acid compounds **4a–c**, are not mesomosphic. Therefore, it is clear that the liquid crystallinity in **4a–c** was induced due to hydrogen-bonded dimer formation (Structure 1). This phenomenon is well documented in literature (*48–56*). A number of LC systems containing hydrogen bonds that function between identical molecules have been reported (*48–50*). Much attention has been paid to hydrogen-bonded supramolecular LCs, including LC dimers based on the hydrogen bonding interactions (*51–53*) and several supramolecular LC trimers based on the hydrogen bonding interactions (*54*, *55*). Recently, LC trimers based on the hydrogen bonding dimerisation of 4-{n-[4-(4-m-alkoxyphenylazo)phenoxy]alkoxy}benzoic acids were synthesised and characterised by Bai *et al.* (*56*). All of the carboxylic acid groups are associated to form the H-bonded cyclic dimers either in crystalline and liquid crystalline phases. Most of the trimers exhibited enantiotropic liquid crystalline behaviour and the mesophases changed from nematic to smectic phase, with the increase of length of the spacer and the terminal substituents (*56*).

There are two peaks observed in heating and cooling cycles of compound **4a** (Table 1). The first one at 169.8 corresponds to Cr–N transition and the other at 194.1 corresponds to N–I transition. Compounds **4b** and **4c** (Table 1) display a crystal-to-crystal transition prior to mesophase formation. On heating, phase transitions of **4b** and **4c** were observed Cr_1 149.7 (14.7) Cr_2 196.7 (29.7) N 239.2 (13.9) I and Cr_1 137.2 (25.1) Cr_2 198.7 (70.1) N 241.6 (11.1) I, respectively. Textural identification shows that compound **4a–c** show nematic phase at relatively higher temperature.

All of the bent-shaped compounds **5a–c** display enantiotropic $SmA_{intercal}$ mesophases. On heating there are two peaks observed for compound **5a** at 148.9 (ΔH = 13.4 J g^{-1}) and 170.5°C (ΔH = 10.5 J g^{-1}) which corresponding to the Cr–$SmA_{intercal}$ and $SmA_{intercal}$–I transitions. On cooling the I–$SmA_{intercal}$ transition occurs at 166.9 (ΔH = 11.8 J g^{-1}) while the $SmA_{intercal}$–Cr transition appears at 130.3°C (ΔH = 19.5 J g^{-1} (Figure 1). Similarly, the second compound **5b** displayed two peaks on heating at 142.7 (ΔH = 38.5 J g^{-1}) and 166.7°C (ΔH = 12.2 J g^{-1}),

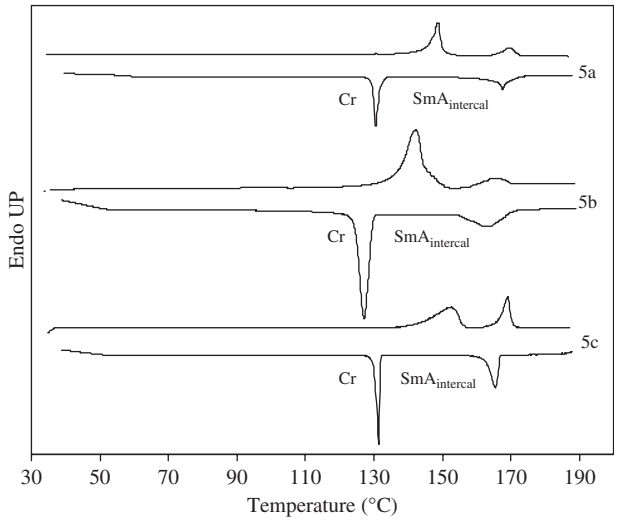


Figure 1. DSC heating and cooling traces of compounds **5a-c** at 10°C min^{-1}.

which were attributed to the Cr–$SmA_{intercal}$ and $SmA_{intercal}$–I transitions. On cooling, again two peaks zat 162.1 (ΔH = 16.5 J g^{-1}) and 126.7°C (ΔH = 38.2 J g^{-1}) corresponding to I–$SmA_{intercal}$ and $SmzA_{intercal}$–Cr transitions were observed in DSC (Figure 1). In the case of **5c,** the DSC heating run displays these transitions at 154.7 (ΔH = 16.7 J g^{-1}) and 169.1°C (ΔH = 20.9 J g^{-1}), which were attributed to the Cr–$SmA_{intercal}$ and $SmA_{intercal}$–I transitions. On cooling, again two peaks at 165.4 (ΔH = 21.7 J g^{-1}) and 131.1°C (ΔH = 25.7 J g^{-1}) corresponding to I–$SmA_{intercal}$ and $SmA_{intercal}$–Cr transitions were observed (Figure 1).

4.2.2 Polarising optical microscopy studies

Under the polarising microscope, a focal conic texture as typical for $SmA_{intercal}$ phase was observed upon cooling of compound **5a** from the isotropic phase. Optical texture was observed for compound **5a** at 154°C (Figure 2(a)). A fan-like texture as typical for $SmA_{intercal}$ phase was observed for compounds **5b** and **5c**. The textures observed at 150°C and 153°C for compound **5b** and **5c,** respectively, are reproduced in Figure 2(b) and (c). No other phase transition, except crystallisation, was realised on further cooling up to room temperature. All the transition temperatures observed under polarising optical microscopy (POM) agreed with DSC data.

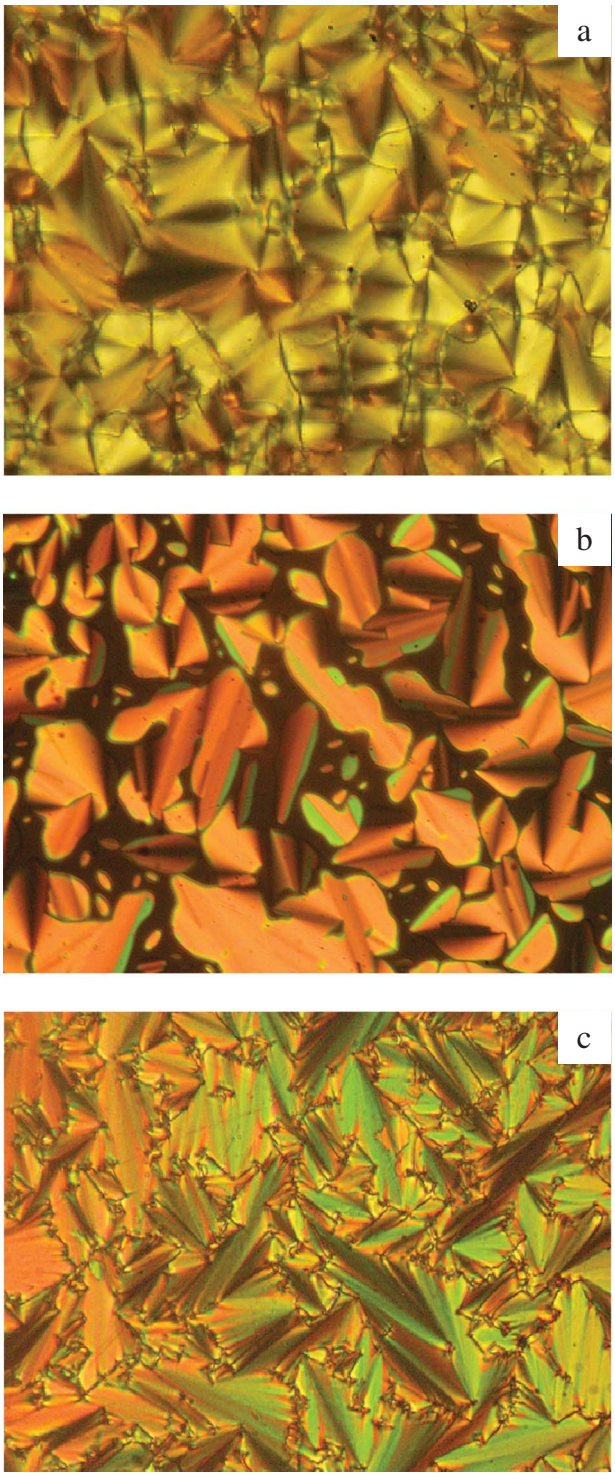


Figure 2. Optical micrographs of (a) compound **5a** at 154 °C, (b) compound **5b** at 152°C and (c) compound **5c** at 150°C on cooling the isotropic phase.

4.2.3 X-ray diffraction studies

The intensity versus θ plot was derived from the diffraction pattern of compound **5a** as shown in Figure 3. X-ray diffraction was carried out in the mesophase obtained on cooling the isotropic phase. The diffraction pattern exhibited a sharp reflection in the small angle region, corresponding to d = 22.25 Å (150°C) and a diffuse scattering in the wide angle region at $d \approx 4.46$ Å. The minimum conformation of compounds **5a, 5b** and **5c** are the bent shape with an end-to-end distance of 45.1, 46.1 and 48.3 Å, respectively (Figure 4). This smallest-angle peak corresponds to d = 22.25 Å, which is one half of the molecular length of **5a**. In the wide-angle range, we have seen only a diffuse peak ($d \approx 4.46$ Å), which means fluid in a plane structure. Therefore, we assume that compound **5a** exhibited a smectic A intercalated phase which is denoted as the $SmA_{intercal}$ phase.

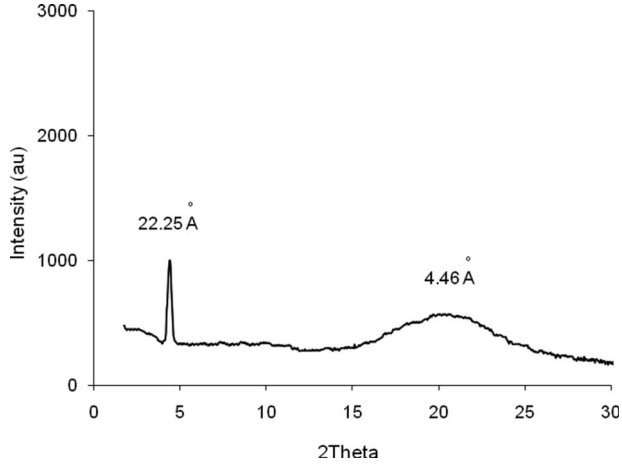


Figure 3. Intensity-theta graph derived from the X-ray diffraction pattern of compound **5a** at 150°C.

X-ray diffraction studies also confirmed the phase assignment of compound **5b**. X-ray diffraction measurements were carried out using Cu-Kα radiation (λ = 1.54 Å) generated from a 4 kW rotating anode generator (Rigaku Ultrax-18) equipped with a graphite crystal monochromator. Sample was placed in Hampton research capillaries (0.5 mm diameter) from 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 on a two-dimensional image plate (Marresearch). Though a magnetic field

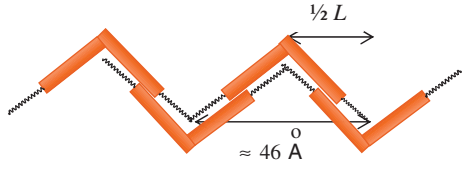


Figure 4. A schematic diagram of $SmA_{intercal}$ structure of compound **5a-c**.

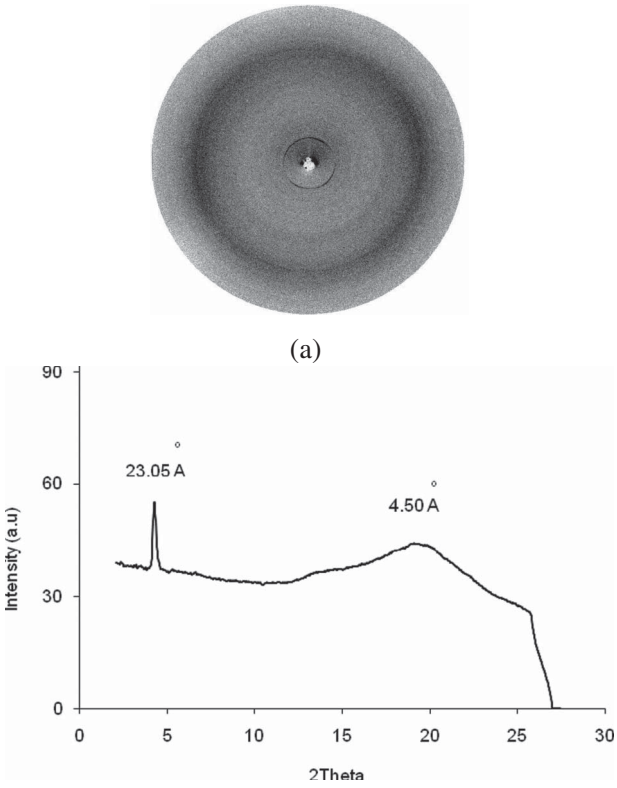


Figure 5. (a) X-ray diffraction pattern of the compound **5b** at 155°C ($SmA_{intercal}$) and (b) the intensity-theta graph derived from the X-ray diffraction pattern.

of about 5k Gauss was used to align the samples, the diffraction patterns indicate that the sample was not aligned perfectly and, therefore, should be considered as unaligned sample. Figure 5(a) shows the X-ray diffraction pattern and Figure 5(b) shows the intensity versus θ plot derived from the diffraction pattern of the compound **5b** at 155°C. In the smectic A intercalated phase, the arc spots in the small angle region are smeared to form a nearly closed ring (Figure 5(a)). The diffraction pattern of the SmA intercalated phase exhibited a sharp reflection in the small angle region, corresponding to d = 23.05 Å (155°C) and a diffuse scattering in the wide angle region at $d \approx 4.50$ Å (Figure 5(b)).

Although our synthesised bent-shaped compounds are not suitable for comparison with other reported compounds due to structural differences, we have however tried to compare the transition temperatures and the nature of the mesophases exhibited by resorcinol-based compounds containing acrylic monomers in absence of azobenzene units. The ester-type banana monomers, 1,3-phenylene bis[4'-(alkenyloxy)biphenylcarboxylate] with different substituents on the central phenyl ring (H, CH_3, Cl or NO_2) and alkenyl tails in the side arms were reported by Fodor-Csorba *et al.* (*28*). The phase transition temperatures and sequences of the monomers greatly depended on their chemical structure. No mesophase was formed by either the unsubstituted or 2-methyl-substituted derivatives. Each of the chloro-substituted analogues showed a nematic phase, while 2-nitro-substituent showed a B7 phase at relatively low temperature. All the compounds were stable, and no degradation or polymerisation was observed under applied electric fields or heat treatments (*28*). A series of V-shaped molecules namely 1,2-phenylene bis[4-(4-alkyloxyphenylazo)benzoates] showed smectic, nematic, and crystal E phases (*19, 20*), and later, bent-shaped azo compounds with variable terminal groups were also reported by Prasad *et al.* (*19, 20*). These compounds exhibited Col_r and SmC_AP_A phases, which showed antiferroelectric switching characteristics with fairly low transition temperatures.

4.3 Photochromism property

The preliminary studies of the photochemical properties were carried out on **5a–c** compounds in the chloroform solution of concentration, $c = 1.5 \times 10^{-5}$ mol l^{-1}. The UV–vis absorption spectra of all the bent-shaped compounds displayed primarily three absorptions with maximum absorbance at about 258, 365 and 450 nm (Figure 6). The absorption spectra are probably identical for three compounds due to same molecular structure, with variation in only one methelene group. Therefore, we have introduced only compound, **5b**, for photoisomerisation study.

The occurrence of photoisomerisation can be determined with the help of UV-Vis absorption

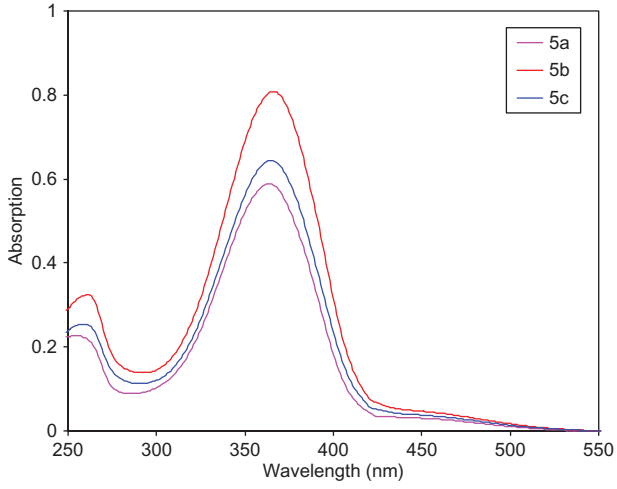


Figure 6. (Colour online). UV/Vis absorption spectra of **5a-c** in chloroform, $c = 1.5 \times 10^{-5}$ mol l^{-1}.

spectra of the sample in the absence and upon illumination with UV. Photoactive compound **5b** dissolved in chloroform, c = 2.5×10^{-5} mol l^{-1} shows three absorptions at 259.5, 364.5 (ε = 31.720l mol^{-1} cm^{-1}) and 446 nm. The peak at 259.5 nm does not participate in the photodriven mechanism and per se is not photoactive, so discussion of this peak is not of interest here. In the absence of UV irradiation (0 sec), two absorption maxima corresponding to photoisomerisation are observed. One maxima is seen which corresponds to π–π* transition of the E (*trans*) form at ~365 nm, and the other maxima is at ~450 nm, usually associated with the n–π* transition of Z (*cis*) isomers of the photoactive molecules. Irradiation of the solution with 365 nm UV light induces E-Z photo-isomerisation and after 50 s of exposure photosaturation is achieved (Figure 7). Also note that there exist two isobestic points at 320 and 425 nm.

As noted earlier, return to the *trans* form can take place either by shining white light of wavelength 400–500 nm, or by keeping the solution in the dark. Figure 8 shows the irradiation of the same solution with light of wavelength $\lambda_{exc.}$ = 436. Once the photostationary state is achieved by UV light, white light is then used. As we increase the time of exposure of 436 nm light, the *cis-trans* process begins, and after around 50 s almost all of the *cis* form is converted back to the *trans* form. Thus this molecule exhibits very strong photoisomerisation phenomena with UV as well as with white light.

Figure 9 shows the thermal back relaxation of **5b** in chloroform. The sample was irradiated at 365 nm for 55 s until the photostationary state (which is *cis* form) was reached. After irradiation the sample was kept in the dark and the absorption spectrum was measured at subsequent time intervals. This recovery takes almost 1890 min, or 31 h, to reach *trans* form from the photo-excited *cis* form.

A linear correlation of ln ($E_\infty - E_t$) as a function of time indicates a reaction of first order (Figure 10). After 1890 min (31 h and 30 min) the thermal back reaction was complete (initial state was reached) and the conversion of *cis* → *trans* was 96%.

Therefore, these bent shaped photoactive molecules show clear photoisomerisation behaviour in solution. A long thermal back reaction is a crucial parameter for

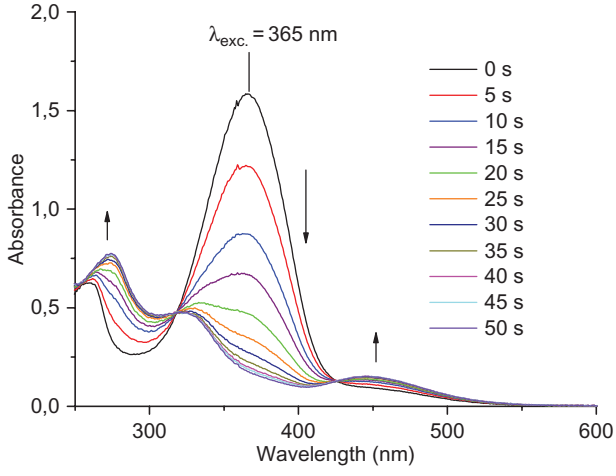


Figure 7. (Colour online). UV/Vis absorption spectra of **5b** in chloroform with different exposure time: '0 sec' corresponds to before irradiation and later plots correspond to different time intervals upon administering UV radiation of 365 nm.

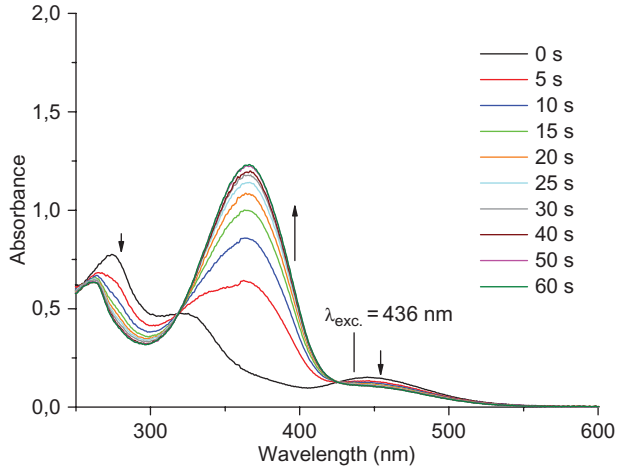


Figure 8. (Colour online). UV/Vis absorption spectra of **5b** in chloroform with different exposure time, '0 sec' corresponds to before irradiation of white light but photosaturated state, and later plots correspond to different time intervals upon administering white light of wavelength 436 nm.

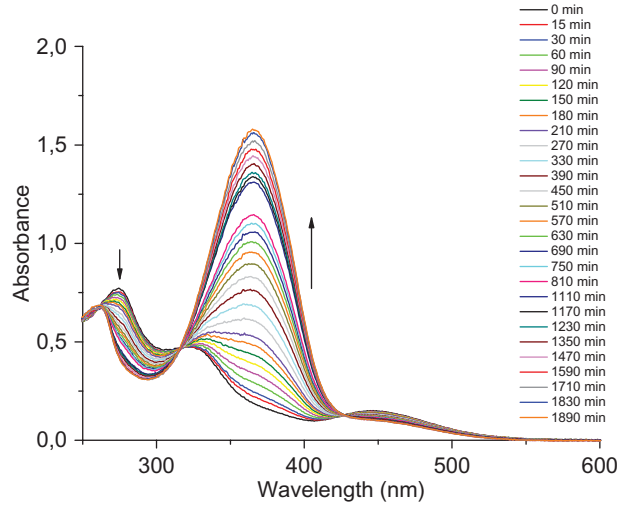


Figure 9. (Colour online). UV/Vis absorption spectra of **5b** in chloroform, showing thermal back relaxation *cis* →trans (at λ = 365 nm). Time 0 min corresponds to photostationary state and later plots correspond to different time intervals when kept in the dark.

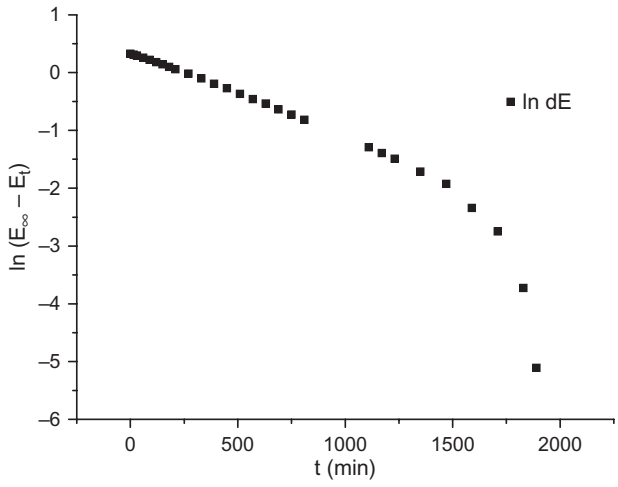


Figure 10 Thermal back reaction of **5b** in chloroform, plot of ln (E_∞ - E_t) as a function of time at λ = 365 nm. Initially all molecules are in *cis* form and after 31 hours, all molecules have converted to *trans* form.

the creation of storage devices, which last longer if one is able to achieve the same kind of thermal back relaxation in solid samples. Investigation on solid samples is under progress. We have estimated the complete reaction time of *trans-cis-trans* isomerisation from Figures 7-10, including back relaxation time, from the first order plot. Indeed, our compound shows very clear and smooth spectral changes, which may be attributed to the purity of our bent-shaped compound.

5. Conclusions

Three bent-shaped monomers containing azobenzene chromophores and derived from resorcinol as central units, namely 1,3-phenylene bis-{4-[4-(n-allyloxyalkyloxy)phenylazo]benzoate} **5a–c** were synthesised. The POM and X-ray diffraction studies confirm the formation of $SmA_{intercal}$ phases in these bent-shaped molecules. Experimental study suggests that these bent-shaped azo molecules exhibit strong photoisomerisation properties. The photochemical *cis-trans* isomerisations study of solid samples is now in progress and will be reported in due course.

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