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Liquid crystalline banana-shaped monomers derived from 2,7-naphthalene: synthesis and properties

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Three banana-shaped monomers, i.e. 2,7-naphthalene bis[4-(4-allyloxyphenylazo)-benzoate], 2,7-naphthalene bis [4-(4-allyloxy-3-fluorophenylazo)benzoate] and 2,7-naphthalene bis{4-[4-(10-undecenyloxy)phenylazo]benzoate}, containing azobenzene as side arms, 2,7-dihydroxynaphthalene as central units and terminal double bonds as polymerisable functional groups, were synthesised and their mesophase behaviour investigated. Polarizing optical microscopy and DSC measurements reveal that all compounds exhibit nematic mesophases. The absorption spectrum of the trans-azobenzene groups displays a high-intensity π–π^* transition at about 365 nm and a low-intensity n–π^* transition at around 450 nm for all compounds. Hence, photochromism can be achieved by the introduction of the azo linkage to banana-shaped liquid crystals molecules.

Keywords: naphthalene; bent-shaped monomer; azobenzene; *cis-trans* isomer; photochromism

1. Introduction

A number of phenomena, such as ferro- and antiferroelectricity and chirality, have been found in the thermotropic liquid crystalline phases of bent-core (banana-shaped) molecules (*1–4*). Although the majority of bent-core molecules displays polar smectic (SmC_P and SmA_P) phases and modulated smectic phases (columnar phases, B1-type phases), a number of banana-shaped compounds are also known to exhibit nematic phases (*5–10*). Symmetry considerations have revealed that bow-shaped molecules can exhibit a number of distinct states of nematic ordering, including biaxial nematic phases (*11*). Compared to the numerous bent-core compounds with a resorcinol unit as central core only a limited number of compounds containing 2,7-dihydroxynaphthalene as the central core have been synthesised. The first bent-core compounds based on 2,7-dihydroxynaphthalene were synthesised by Shen *et al.* (*5*), but these compound were high-melting solids without mesomorphic properties. Simultaneously, Pelzl *et al.* (*12*) reported ester-type bent-core molecules derived from 2,7-dihydroxynaphthalene having B1-type columnar phases. Several banana-shaped compounds derived from the 2,7-dihydroxynaphthalene central core with Schiff base units exhibit polar smectic (SmC_{PA}) mesophases (*13–15*). Reddy and Sadashiva (*16, 17*) reported homologous series of compounds derived from 2,7-dihydroxynaphthalene and the majority of these compounds exhibit different types of columnar phases (Col_r, Col_{ob}) as well as polar smectic phases, and some of the compounds also have nematic phases. The nematic phases are formed by the lower homologues, and in several cases columnar phases were observed below these nematic phases. Svoboda *et al.* (*18*) reported 2,7-dihydroxynaphthalene-based bent-core molecules with Schiff base units, which exhibit different types of mesophases, among them polar smectic and B4-type phases.

A number of bent-core molecules containing an azo linkage have been reported (*19*). The –N=N– linkage in such molecules introduces the possibility of photochromism and photoisomerisation (*19*). In addition, polymerisation of appropriate bent-core liquid crystals has received significant attention in recent years (*20–22*). Bent-core liquid crystalline monomers with double bonds at both ends have been reported and used for polymerisation to give main-chain liquid crystal polymers (*22–26*), among which two materials that exhibited a monotropic SmC_P phase (*24, 26, 27*) and others that form nematic and smectic C phases. Polyacrylates derived from monomeric banana liquid crystals were also reported to give crosslinked liquid crystal polymers (*23*). Achten *et al.* (*28*) reported two series of non-symmetric banana-shaped compounds, combining alkyl and alkenyl terminal groups. Such vinyl-terminated compounds were used for incorporation as side chains in oligomeric or polymeric systems (*29*) and for the synthesis of polysiloxane-based liquid crystals with a bent-core mesogenic unit (*27*).

In this study, banana-shaped compounds that consist of a naphthalene ring in the core and two

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azobenzene based aromatic wing groups were combined with terminal chains having double bonds. In addition, we have studied the influence of fluorine substitution (*30*) at the periphery.

2. Experimental

Materials

Sodium nitrite (BDH), ethyl 4-aminobenzoate (Fluka), urea (BDH), phenol (Merck), 2-fluorophenol (Fluka), potassium carbonate (Fluka), allyl bromide ((Fluka), 11-bromo-1-undecene (Aldrich), 2,7-dihydroxynaphthalene (Aldrich), 1,3-dicyclohexylcarbodiimide (DCC, Fluka) and 4-(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-hydroxyphenylazo)benzoate (**1a**).*

Compound **1a** was prepared following the reported procedure (*31*) from ethyl 4-aminobenzoate (10.0 g, 0.061 mol), conc. hydrochloric acid (22 ml), sodium nitrite (5.52 g, 0.080 mol) and phenol (5.69 g, 0.061 mol) in an acetone/water mixture. Yield: 10.1 g (62%) as red crystals; m.p. 160°C. IR (KBr, ν_{max}, cm^{-1}): 3321 (OH), 1728 (C=O, ester), 1602, 1484 (C=C, aromatic), 1248, 1140 (C–O), 829 (C–H). ^{1}H NMR (acetone-d_6): δ 8.18 (d, 2H, J=8.2 Hz), 7.92 (d, 2H, J=6.9 Hz), 7.89 (d, 2H, J=7.9 Hz), 7.01 (d, 2H, J=8.8 Hz), 5.54 (s, 1H, OH), 4.41 (q, 2H, J=6.8 Hz, –CH_2CH$_3$), 1.44 (3H, –CH$_2$$CH_3$). ^{13}C NMR (CDCl$_3$): δ 14.41, 61.40, 116.01, 122.43, 125.50, 130.64, 131.61, 147.16, 155.36, 159.18, 166.39. Elemental analysis: calculated for $C_{15}H_{14}N_2O_3$ (270.2832), C 66.69, H 5.22, N 10.36%; found, C 66.56, H 5.26, N 10.27%.

*Ethyl 4-(4-hydroxy-3-fluorophenylazo)benzoate (**1b**).*

Prepared as described for **1a** from 2-fluorophenol. Yield: 10.8 g (61 %), bright red crystals, m.p. 155°C. IR (KBr, ν_{max}, cm^{-1}): 3335 (OH), 1728 (νC=O, ester), 1604, 1467 (C=C, aromatic), 1245, 1142 (C–O), 832 (C–H). ^{1}H NMR (acetone-d_6) δ 8.18 (d, 2H, J=8.2 Hz), 7.93 (d, 2H, J=6.8 Hz), 7.91 (d, 2H, J=7.8 Hz), 7.00 (t, 1H, J=8.9 Hz), 4.38 (q, 2H, J=6.8 Hz, –CH_2CH$_3$), 1.42 (3H, –CH$_2$$CH_3$). ^{13}C NMR (CDCl$_3$): δ 14.41, 62.05, 117.01, 122.43, 124.50, 130.64, 131.06, 147.15, 155.48, 159.89, 165.86. Elemental analysis: calculated for $C_{15}H_{13}FN_2O_3$ (288.2737), C 62.49, H 4.54, N 9.71%; found, C 62.46, H 4.38, N 9.66%.

*Ethyl 4-(4-allyloxyphenylazo)benzoate (**2a**).*

Compound **1a** (2.0 g, 7.4 mmol) was dissolved 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) 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<5). The precipitate was filtered off and was crystallised from methanol/chloroform (10:2). Yield of **2a**: 1.44 g (63 %), m.p. 101°C. IR (KBr, ν_{max}, cm^{-1}): 3077 (=CH$_2$), 2925 (CH$_2$), 2860 (CH$_2$), 1728 (C=O, ester), 1642 (C=C, vinyl), 1599, 1497 (C=C, aromatic), 1242, 1139, 1060 (C–O), 824 (C–H). ^{1}H NMR (CDCl$_3$): δ 8.18 (d, 2H, J=8.2 Hz), 7.93 (d, 2H, J=6.8 Hz), 7.91 (d, 2H, J=6.8 Hz), 7.01 (d, 2H, J=6.8 Hz), 6.04 (m, 1H, CH=), 5.46 (d, 1H, J=16.8 Hz, =CH$_2$), 5.34 (d, 1H, J=10.2 Hz, =CH$_2$), 4.60 (d, 2H, J=4.8 Hz, OCH$_2$–), 4.38 (q, 2H, OCH_2CH$_3$), 1.42 (t, 3H, –CH$_2$$CH_3$). ^{13}C NMR (CDCl$_3$): δ 14.43, 61.24, 69.15, 115.13, 118.24, 122.41, 125.22, 130.62, 131.66, 132.70, 147.15, 155.39, 161.71, 166.23. Elemental analysis: calculated for $C_{18}H_{18}N_2O_3$ (310.3471), C 69.66, H 5.84, N 9.02%; found, C 69.58, H 5.76, N 9.11%.

*Ethyl 4-(4-allyloxy-3-fluorophenylazo)benzoate (**2b**).*

Compound **2b** was prepared by the same method as used for synthesis of **2a** from compound **1b**. Yield: 1.55 g (71 %), m.p. 95°C. IR (KBr, ν_{max}, cm^{-1}): 3074 (=CH$_2$), 2925 (CH$_2$), 2860 (CH$_2$), 1724 (C=O, ester), 1642 (C=C, vinyl), 1598, 1496 (C=C, aromatic), 1248, 1132, 1060 (C–O), 828 (C–H). ^{1}H NMR (CDCl$_3$): δ 8.17 (d, 2H, J=8.2 Hz), 7.94 (d, 2H, J=6.9 Hz), 7.91 (d, 2H, J=6.8 Hz), 7.01 (t, 1H, J=8.9 Hz), 6.04 (m, 1H, CH=), 5.44 (d, 1H, J=16.8 Hz, =CH$_2$), 5.33 (d, 1H, J=10.2 Hz, =CH$_2$), 4.62 (d, 2H, J=4.3 Hz, OCH$_2$–), 4.36 (q, 2H, OCH_2CH$_3$), 1.42 (t, 3H, –CH$_2$$CH_3$). ^{13}C NMR (CDCl$_3$): δ 14.43, 62.27, 69.15, 115.13, 118.24, 122.41, 125.22, 130.62, 131.65, 132.70, 147.15, 155.39, 161.71, 165.93. Elemental analysis: calculated for $C_{18}H_{17}FN_2O_3$ (328.3375), C 65.84, H 5.21, N 8.53%; found, C 65.68, H 5.28, N 8.42%.

*Ethyl 4-[4-(10-undecenyloxy)phenylazo]benzoate (**2c**).*

Compound **2c** was prepared by the same method used for synthesis of **2a** with 11-bromo-1-undecene as alkylation reagent. Yield: 2.11 g (68 %), m.p. 87°C. IR (KBr, ν_{max}, cm^{-1}): 3070 ($=CH_2$), 2923 (CH_2), 2858 (CH_2), 1712 (νC=O, ester), 1651 (C=C, vinyl), 1606, 1504 (C=C, aromatic), 1260, 1140, 1015 (C–O), 832 (C–H). ^1H NMR ($CDCl_3$): δ 8.18 (d, 2H, J=8.2 *Hz*), 7.93 (d, 2H, J=6.9 Hz), 7.90 (d, 2H, J=7.9 Hz), 7.02 (d, 2H, J=8.8 Hz), 6.03 (m, 1H, CH=), 5.42 (d, 1H, J=16.8 Hz, $=CH_2$), 5.09 (d, 1H, J=9.6 *Hz*, $=CH_2$), 4.39 (t, 2H, J=6.7 *Hz*, OCH_2–), 4.08 (q, 2H, O$CH_2$$CH_3$), 2.18 (m, 4H, –$CH_2$–), 1.85 (m, 4H, –$CH_2$–), 1.47 (m, 4H, –$CH_2$–), 1.36 (m, 4H, –$CH_2$–), 1.43 (t, 3H, –$CH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 14.43, 20.44, 25.56 26.68, 29.68, 29.88, 30.15, 30.31, 32.99, 62.22, 69.18, 116.23, 118.24, 122.88, 125.32, 130.68, 131.67, 132.79, 147.25, 155.38, 161.77, 165.23. Elemental analysis: calculated for $C_{26}H_{34}N_2O_3$ (422.5597), C 73.90, H 8.10, N 6.62%; found, C 73.85, H 8.18, N 6.52%.

*4-(4-Allyloxyphenylazo)benzoic acid (**3a**).*

Compound **2a** (1.30 g, 4.19 mmol) was dissolved in 140 ml of methanol. 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. 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 crystallised from ethanol/chloroform (2:1) to give compound **3a**. Yield: 0.45 g (38 %), m.p. 221°C. IR (KBr, ν_{max}, cm^{-1}): 3072 ($=CH_2$), 2922 (CH_2), 2864 (CH_2), 1684 (C=O, acid), 1644 (C=C, vinyl), 1597, 1496 (C=C, aromatic), 1249, 1136, 1064 (C–O), 829 (C–H). ^1H NMR ($CDCl_3$): δ 8.18 (d, 2H, J=8.2 Hz), 7.94 (d, 2H, J=7.1 Hz), 7.93 (d, 2H, J=6.7 Hz), 7.05 (d, 2H, J=8.9 Hz), 6.04 (m, 1H, CH=), 5.45 (d, 1H, J=16.6 Hz, $=CH_2$), 5.31 (d, 1H, J=10.2 Hz, $=CH_2$), 4.60 (d, 2H, J=4.1 *Hz*, OCH_2–). ^{13}C NMR ($CDCl_3$): δ 69.13, 115.18, 118.25, 122.41, 125.24, 130.64, 131.66, 132.73, 147.23, 155.38, 161.69, 166.98. Elemental analysis: calculated for $C_{16}H_{14}N_2O_3$ (282.2939), C 68.07, H 4.99, N 9.92%; found, C 68.01, H 4.84, N 9.88%.

*4-(4-Allyloxy-3-fluorophenylazo)benzoic acid (**3b**).*

The hydrolysis of **2b** was carried out according to the method described for **3a**. Yield of **3b**: 0.47 g (40 %), m.p. 205°C. IR (KBr, ν_{max}, cm^{-1}): 3074 ($=CH_2$), 2935 (CH_2), 2866 (CH_2), 1694 (νC=O, acid), 1651 (C=C, vinyl), 1602, 1504 (C=C, aromatic), 1268, 1142, 1015 (C–O), 836 (C–H). ^1H NMR ($CDCl_3$): δ 8.16 (d, 2H, J=8.2 Hz), 7.95 (d, 2H, J=6.9 Hz), 7.93 (d, 2H, J=6.8 Hz), 7.01 (t, 1H, J=8.8 Hz), 6.02 (m, 1H, CH=), 5.41 (d, 1H, J=17.2 *Hz*, $=CH_2$), 5.31 (d, 1H, J=10.2 *Hz*, $=CH_2$), 4.61 (q, 2H, J=4.8 Hz, OCH_2–). ^{13}C NMR ($CDCl_3$); δ 69.18, 115.22, 118.28, 122.53, 125.32, 130.66, 131.59, 132.73, 147.23, 155.28, 161.66, 167.91. Elemental analysis: calculated for $C_{16}H_{13}FN_2O_3$ (300.2844), C 68.99, H 4.36, N 9.32%; found, C 68.88, H 4.44, N 9.24%.

*4-[4-(10-Undecenyloxy)phenylazo]benzoic acid (**3c**).*

The compound was prepared by hydrolysis of **2c** according to the method used for **3a**. Yield of **3c**: 0.37 g (48%), m.p. 187°C. IR (KBr, ν_{max}, cm^{-1}): 3066 ($=CH_2$), 2923 (CH_2), 2850 (CH_2), 1684 (C=O, acid), 1640 (C=C, vinyl), 1594, 1496 (C=C, aromatic), 1268, 1133, 1023 (C–O), 836 (C–H). ^1H NMR ($CDCl_3$): δ 8.16 (d, 2H, J=8.2 Hz), 7.96 (d, 2H, J=6.9 Hz), 7.93 (d, 2H, J=6.8 Hz), 7.01 (d, 2H, J=8.6 Hz), 6.04 (m, 1H, CH=), 5.41 (d, 1H, J=16.8 Hz, $=CH_2$), 5.08 (d, 1H, J=9.6 Hz, $=CH_2$), 4.38 (d, 2H, J=6.7 Hz, OCH_2–), 2.15 (m, 4H, –CH_2–), 1.83 (m, 4H, –CH_2–), 1.48 (m, 4H, –CH_2–), 1.37 (m, 4H, –CH_2–). ^{13}C NMR ($CDCl_3$): δ 20.50, 25.86, 26.12, 29.67. 29.65, 30.34, 30.32, 32.79, 69.88, 115.66, 118.34, 122.78, 125.33, 130.68, 131.69, 132.89, 147.27, 155.48, 161.78, 167.73. Elemental analysis: calculated for $C_{16}H_{14}N_2O_3$ (282.2939), C 73.06, H 7.66, N 7.10%; found, C 72.96, H 7.74, N 7.18%.

*2,7-Naphthalene bis[4-(4-allyloxyphenylazo)benzoate] (**4a**).*

Compound **3a** (0.35 g, 1.24 mmol) was dissolved in 40 ml of dry dichloromethane. DMAP (0.015 g, 0.11 mmol) was added and the mixture was stirred for 30 min. Then 2,7-dihydroxynaphthalene (0.10 g, 0.062 mmol), dissolved in dry dichloromethane (10 ml) and DCC (0.27 g, 1.30 mmol) was added and the mixture was stirred for 24 h. The precipitate was removed by filtration and the solvent was removed at reduced pressure. 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 under reduced pressure. The residual solid was crystallised twice from methanol:chloroform (2:1) to obtain the target compound **4a**. Yield: 0.16 g (37 %). IR (KBr, ν_{max}, cm^{-1}): 3078 ($=CH_2$), 2927 (CH_2), 2854 (CH_2), 1733 (C=O, ester), 1641 (C=C, vinyl), 1598, 1492 (C=C, aromatic), 1239, 1137, 1064 (C–O), 836 (C–H). ^1H NMR ($CDCl_3$): δ δ: 8.39 (d, 4H, J=8.9 Hz), 8.00 (d, 4H, J=8.2 Hz), 7.98 (d, 4H, J=8.9 Hz), 7.97 (d, partially merged with 7.98 d, 2H), 7.72 (d, 2H, J=2.1 Hz) 7.42 (dd, 2H, J=8.8 and 2.1 Hz), 7.07 (d, 4H, J=8.9 Hz), 6.07 (m, 2H, CH=), 5.47 (d, 2H, J=16.5 Hz, $=CH_2$), 5.34 (d, 2H, J=9.9 Hz, $=CH_2$), 4.39 (d, 4H, J=6.8 Hz, OCH_2–). ^{13}C NMR ($CDCl_3$): δ

69.18, 114.34, 115.19, 118.29, 118.69, 119.38, 121.30, 122.68, 124.33, 125.37, 129.55, 130.50, 131.38, 132.60, 134.43, 147.18, 149.41, 155.94, 161.90, 164.86. Elemental analysis: calculated for $C_{42}H_{32}N_4O_6$ (688.7266), C 73.23, H 4.67, N 8.13%; found, C 73.08, H 4.54, N 8.02%.

*2,7-Naphthalene bis[4-(4-allyloxy-3-fluorophenylazo)-benzoate] (**4b**).*

Prepared as reported for **4a** from compound **3b**. Yield: 0.116 g (32%). IR (KBr, ν_{max}, cm^{-1}): 3075 (=CH$_2$), 2928 (CH$_2$), 2854 (CH$_2$), 1733 (νC=O, ester), 1642 (C=C, vinyl), 1598, 1496 (C=C, aromatic), 1249, 1137, 1060 (C–O), 836 (C–H). ^{1}H NMR (CDCl$_3$): δ 8.33 (d, 4H, J=8.7 Hz), 8.0 (d, 4H, J=8.3 Hz) 7.96 (d, 2H, J=8.9 Hz), 7.82 (d, 2H, J=8.9 Hz), 7.75 (dd, 2H, J=2.1, 8.9 Hz), 7.72 (d, 2H, J=2.1 Hz), 7.40 (dd, 2H, J=8.9, 2.9 Hz), 7.10 (t, 2H, J=8.3 Hz), 6.06 (m, 2H, CH=), 5.47 (d, 2H, J=16.8 Hz, =CH$_2$), 5.33 (d, 2H, J=9.8 Hz, =CH$_2$), 4.38 (d, 4H, J=6.7 Hz, OCH$_2$–). ^{13}C NMR (CDCl$_3$): δ 70.02, 114.36, 114.95, 119.27, 119.86, 122.72, 124.59, 125.44, 126.18, 130.02, 130.12, 131.24, 131.38, 147.88, 150.66, 155.88, 161.63, 164.74. Elemental analysis: calculated for $C_{42}H_{30}F_2N_4O_6$ (724.7076), C 69.60, H 4.16, N 7.73%; found, C 69.45, H 4.04, N 7.65%.

*2,7-Naphthalene bis{4-[4-(10-undecenyloxy)phenylazo] benzoate} (**4c**).*

Prepared as reported for **4a** from compound **3c**. Yield: 0.251 g (38%). IR (KBr, ν_{max}, cm^{-1}): 3078 (=CH$_2$), 2923 (CH$_2$), 2846 (CH$_2$), 1733 (C=O, ester), 1631 (C=C, vinyl), 1590, 1480 (C=C, aromatic), 1247, 1133 1023 (C–O), 848 (C–H). ^{1}H NMR (CDCl$_3$): δ 8.17 (d, 4H, J=8.2 Hz), 7.97 (d, 4H, J=6.9 *Hz*), 7.93 (d, 4H, J=6.8 Hz), 7.72 (d, 2H, J=8.8 Hz), 7.46 (d, 2H, J=8.8 Hz), 7.22 (d, 2H, J=5.2 Hz), 7.02 (d, 4H, J=8.6 Hz), 6.02 (m, 2H), 5.42 (d, 2H, J=16.5 *Hz*), 5.01 (d, 2H, J=9.9 Hz), 4.06 (d, 4H, J=6.7 *Hz*, OCH$_2$–), 2.05 (m, 8H, –CH$_2$–), 1.83 (m, 8H, –CH$_2$–), 1.47 (m, 8H, –CH$_2$–), 1.35 (m, 8H, –CH$_2$–). ^{13}C NMR (CDCl$_3$): δ 20.49, 25.46, 26.69, 29.62, 29.85, 30.05, 30.28, 32.92, 69.16, 114.84, 115.54, 119.80, 122.26, 124.39, 125.32, 126.03, 130.63, 130.83, 131.96, 132.30, 147.57, 150.15, 155.61, 161.20, 164.07. Elemental analysis: calculated for $C_{58}H_{64}N_4O_6$ (913.1519), C 76.28, H 7.05, N 6.13%; found, C 76.12, H 7.11, N 6.05%.

Measurements

The structures of the intermediates and product were confirmed by spectroscopic methods. IR 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 analyser (Leco & Co). The transition temperatures and their enthalpies were measured by differential scanning calorimetry (DSC, Perkin DSC 7) with heating and cooling rates were 10°C min^{-1} and melting points of the intermediate compounds were determined by DSC. Optical textures were obtained by using Olympus BX50 polarising optical microscope equipped with a Linkam THMSE 600 heating stage and a VTO 232 control unit. Absorption spectra were recorded using a Perkin Elmer UV/visible spectrometer (Lambda 25).

3. Results and discussion

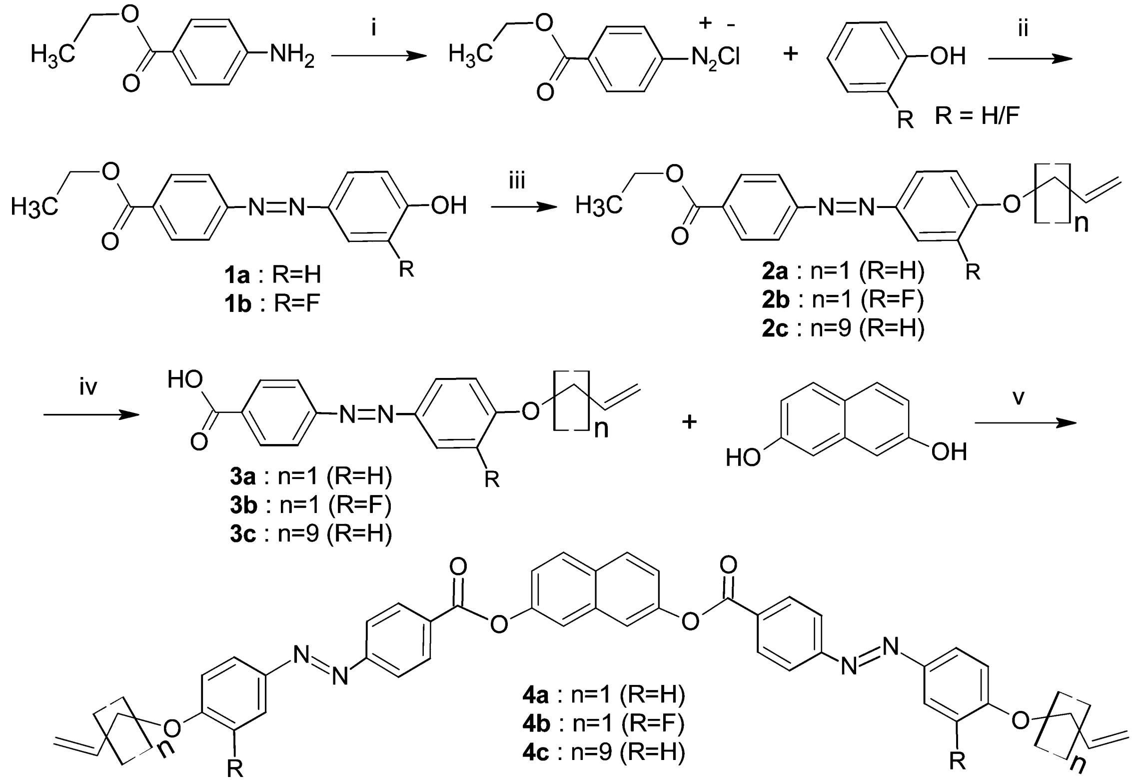
Synthesis

Compounds **4a–4c** were prepared using the procedures shown in Scheme 1. The azobenzene-containing rod-like side arms were prepared from ethyl 4-aminobenzoate. Initially, the diazonuim salt was prepared with sodium nitrite in the presence of three equivalents of aqueous hydrochloric acid, which was coupled with phenol to yield ethyl 4-(4-hydroxyphenylazo) benzoate (**1a**). The fluoro-substituted compound (**1b**) was prepared by the same method using 2-fluorophenol instead of phenol.

Compounds **1a** and **1b** were alkylated with allyl bromide in the presence of potassium carbonate as base to give ethyl 4-(4-allyloxyphenylazo)benzoate (**2a**) and the corresponding fluoro-substituted compound (**2b**), respectively. Then the ester groups of compounds **2a** and **2b** were hydrolyzed under basic conditions to yield the benzoic acids **3a** and **3b**, respectively. In the final step, two equivalents of the acids **3a** or **3b** were esterified with one equivalent of 2,7-dihydroxynaphthalene by using DCC and DMAP to achieved the target molecules **4a** and **4b**. In a similar manner, compound **4c** was prepared by alkylation of **1a** with 11-bromo-1-undecene followed by hydrolysis and esterification with 2,7-dihydroxynaphthalene (see Scheme 1) .

Mesomorphic properties

Using polarising optical microscopy (POM), a schlieren texture typical of nematic phases (see Figure 1) was observed upon cooling compounds **4a–4c** from the isotropic phase. Optical textures observed for compound **4a** at 192°C, compound **4b** at 165°C and compound **4c** at 136°C are shown in Figure 1. There was no other phase transition on



Scheme 1. Synthesis of compounds **4a–4c**. Reagents and conditions: (i) $NaNO_2$, 3 equiv HCl, 2°C; (ii) NaOH, pH 9, 2°C; (iii) K_2CO_3, KI, $BrCH_2CH{=}CH_2$ or $Br(CH_2)_9CH{=}CH_2$, reflux; (iv) KOH, MeOH; (v) DCC, DMAP.

further cooling, except crystallisation. For compound **4c**, the clearing temperature of the nematic phase is much lower than for compounds **4a** and **4b**, due to the long alkyl chains on both sides of the molecule. All the transition temperatures observed by POM were matched with DSC data.

DSC studies confirmed the phase transition temperatures (T/°C) observed by POM and gave the enthalpy changes (ΔH/kJ mol^{-1}) associated with these phase transitions. Compound **4a** exhibits two peaks on heating, at 218.5°C (ΔH=58.7 kJ mol^{-1}) and 227.7°C (ΔH=1.8 kJ mol^{-1}), which correspond to the Cr–N and N–I transitions. On cooling, the I–N transition appears at 220.5°C, with crystallisation at 168.7°C (Table 1).

The corresponding fluoro-substituted compound **4b** displayed two peaks on heating at 176.5°C (ΔH=16.8 kJ mol^{-1}) and 198.2°C (ΔH=1.1 kJ mol^{-1}), which were attributed to the Cr–N and N–I transitions. On cooling, again two peaks at 186.5 and 160.8°C corresponding to I–N and N–Cr transitions were observed. Similarly, compound **4c** with long chains shows Cr–N and N–I transitions at 119.5 and 160.3°C, respectively (Table 1).

As can be seen from Table 1, addition of the F atoms to the periphery of the aromatic core (compound **4a** *vs.* **4b**) decreases the crystal–mesophase transition as well as the mesophase–isotropic transition temperature. Similar effects have been reported in other materials (*17*). Increasing the terminal chain length (compound **4a** *vs.* **4c**), as expected, decreases the transition temperature significantly.

In the following, compounds **4a–4c** will be compared with other bent-core mesogens incorporating 2,7-dihydroxynaphthalene units (Scheme 2) connected with rod-like wings containing Schiff base units [**5** (*18*)] or phenyl benzoate linking groups as well as with fluorine substituted bent-core molecules [**6** (*17*)].

Svoboda *et al.* (*18*) did not find nematic phases for related Schiff base derivatives (**5**) of 2,6-dihydroxynaphthalene, even for the compounds with the shortest chains (n=6, but without terminal double bonds) and also additional substituents at the naphthalene core could not induce a nematic phase. Kozmi *et al.* (*32*) and Reddy *et al.* (*33*) reported bent-shaped mesogens based on substituted naphthalene-2,7-diol having phenylbenzoate wings and a double bond at one or at both end of the terminal chains. These compounds were prepared with relatively long chains (comparable to **4c**), but only smectic phases and no nematic phases were observed for these ester-based bent-core molecules.

Another series of fluorinated banana-shaped compounds with 2,7-dihydroxynaphthalene central

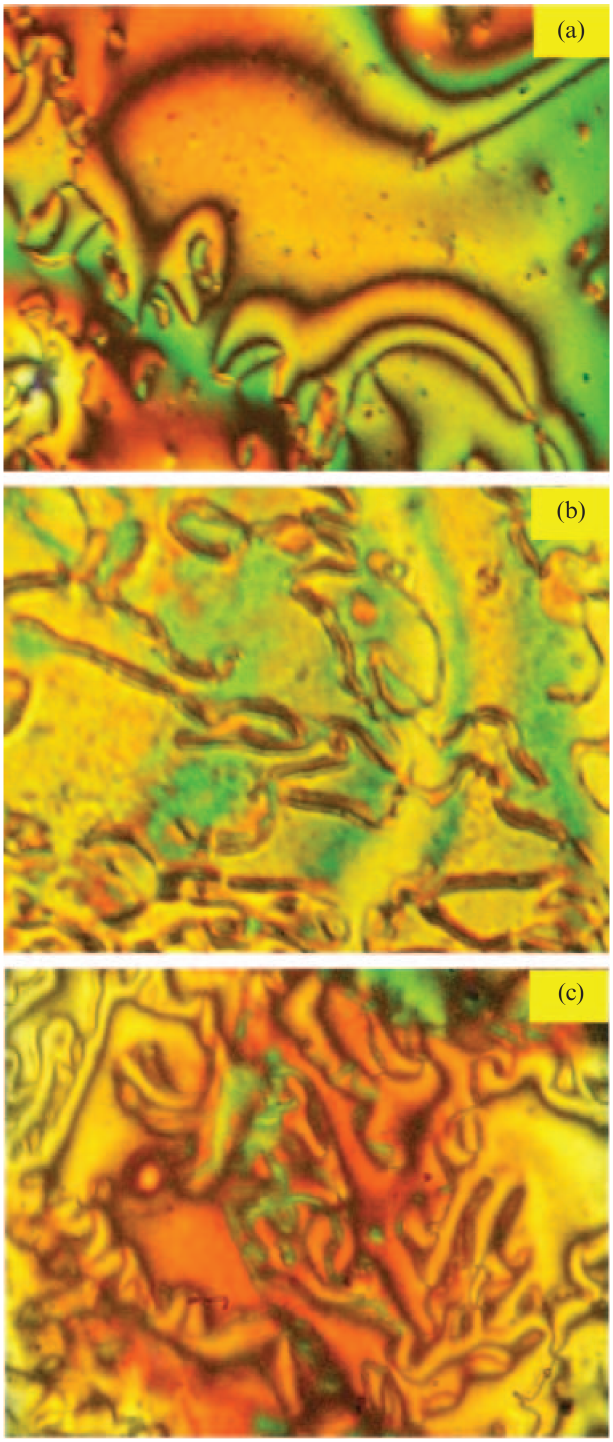


Figure 1. Optical micrographs of (a) compound **4a** at 192°C, (b) compound **4b** at 165°C and (c) compound **4c** at 136°C; all compounds show schlieren textures typical of nematic phases on cooling.

Table 1. Phase transition temperatures (°C) and enthalpies (kJ mol^{-1}, in parentheses) obtained for the second heat and cooling DSC scans for compounds **4a**–**4c**.

Compound	Scan	Phase transitions
4a	heating	Cr 218.5 (58.7) N 227.7 (1.8) I
	cooling	I 220.5 (2.0) N 168.7 (39.0) Cr
4b	heating	Cr 176.5 (16.8) N 198.2 (1.1) I
	cooling	I 186.5 (1.0) N 160.8 (12.5) Cr
4c	heating	Cr 119.5 (58.1) N 160.3 (2.8) I
	cooling	I 148.8 (2.4) N 98.1 (52.4) Cr

Cr=crystal, N=nematic, I=isotropic phase.

unit (**6**) showed SmC$_{PA}$ phases, B1-type rectangular columnar phases (Col$_r$) and B6-type intercalated smectic phases (Sm$_{intercal}$) as well as nematic mesophases (*17*). The phase transitions of the first compound of series **6-I** (*n*=4) showed the phase sequence Cr 197 Col$_r$ 210 N 213 I and the corresponding fluoro-substituted compounds of series 6-II (*n*=3) showed the phase sequence Cr 162 Col$_r$ 176 Sm$_{intercal}$ 191 N 204 I. The compounds of the series containing fluorine have lower transitions temperature compared to non-fluoro compounds (*17*). Hence, the overall mesophase stability of the reported compounds (*17, 18*) is quite similar to our compounds **4a** and **4b** and there is a similar effect of fluorine substitution (though in a different position), leading to lower transition temperatures for the fluorinated compounds. In contrast to compounds of type **6**, in our case no transition to smectic or columnar phases could be observed. In addition, the long chain compound **4c** shows much lower transition temperature compared to the compounds of series **6**. These comparisons indicate the stabilizing effect of azobenzene units on the nematic phases of bent-core mesogens.

Moreover, the azobenzene units introduce functional properties into the bent-core mesogens (*34*), leading to the possibility of photoisomerisation and

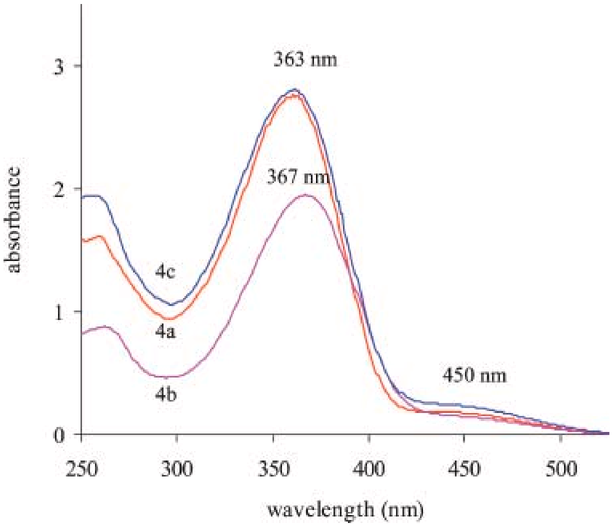
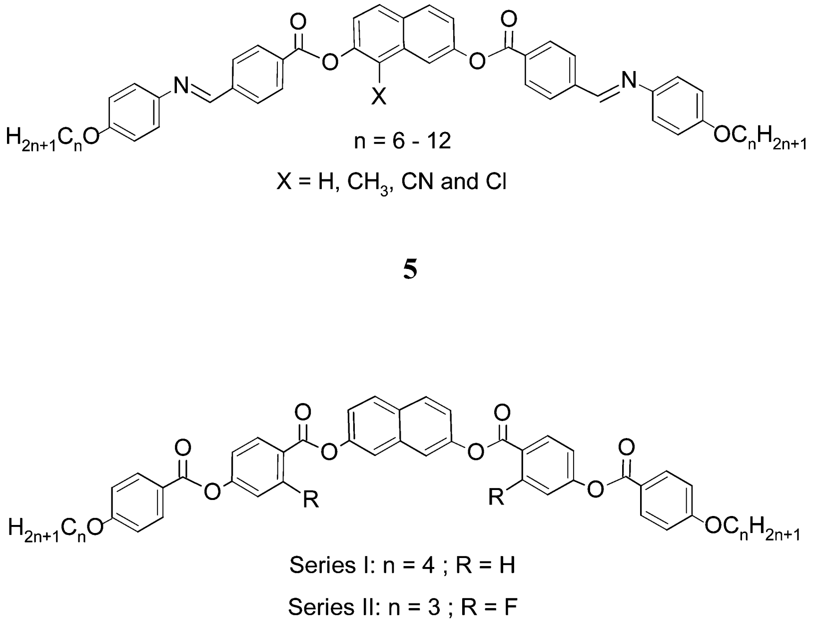


Figure 2. UV/visible absorption spectra of **4a**, **4b** and **4c** in chloroform at a concentration of 5.0×10^{-5} mol l^{-1}.



5

6

Scheme 2. Structures of **5** and **6** compounds.

photochromic behaviour. Therefore, preliminary studies of the photochemical properties were carried out in solution. Solutions with concentrations of $5.0 \times 10^{-5}\,\mathrm{mol\,l^{-1}}$ **4a, 4b** and **4c** were prepared in chloroform for UV/visible absorption studies. The spectrum of **4a** shows three absorptions with maximum absorbance at 260, 363 and 450 nm and **4b** shows three absorptions at 264, 367 and 450 nm (Figure 2). Similarly, **4c** shows also three absorptions with maximum absorbance at 259, 363 and 450 nm (Figure 2). The azo-containing monomers in the *trans* form all show a strong band in the UV region (~365 nm), which is attributed to the π–π^* transition, and a weak band in the visible region (~450 nm) due to the n–π^* transition. The *trans* form is generally more stable than the *cis* form, but each isomer can be converted into the other by light irradiation of the appropriate wavelength. Polarised light can induce the reorientation of azobenzene groups through photochemical *trans–cis–trans* isomerisation (*35*).

4. Conclusion

Three new bent-core mesogens with azobenzene units containing 2,7-dihydroxynaphthalene as central bent unit were synthesised. Two of them have allyl groups at the termini, one is fluorine substituted at the aromatic core (**4b**), and the other one (**4a**) is not. A third compound **4c** has long alkyl chains with double bond at the terminals. All three bent-shaped compounds exhibited nematic mesophases. The double bonds can be used for preparation of polymers or silyl-functionalised bent-core mesogens, whereas the presence of the azo linkage in these liquid crystals monomer is suitable for photochromism studies and *trans–cis–trans* isomerisation cycles under UV irradiation. A photochemical *cis–trans* isomerisation study is now in progress and will be reported in due course.

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