

Synthesis and mesomorphic properties of banana-shaped monomers containing 2,7-naphthalene as central core

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*Two banana-shaped monomers containing 2,7-dihydroxynaphthalene as central unit were synthesized and their mesophase behavior was investigated. The liquid crystals monomers containing azobenzene chromophores were prepared as target molecules, 1,3-naphthalene bis-{4-[(4-allyloxy)phenylazo]benzoate} **4a** and 1,3-naphthalene bis-{4-[3-(4-allyloxy)fluorophenylazo]benzoate} **4b**. The polarizing optical microscopy and DSC measurements reveal that both compounds exhibited nematic mesophases. The presence of allyl bonds to the both wings could be contributed as precursors of polymers for a wide mesophase compounds during photopolymerization under UV irradiation.*

1. Introduction

Thermotropic liquid crystals of banana-shaped molecules have been found a number of phenomena like ferro- and antiferroelectricity and chirality in liquid crystals composed of achiral molecules [1–3]. Although the smectic and B phases exhibited in the banana shaped molecules, a number of banana shaped compounds also show nematic phases [4–8]. Symmetry considerations revealed that the bow shape molecules can give a number of distinct states of nematic ordering, including biaxial phases [9]. A limited number of banana-shaped compounds containing 2,7-dihydroxynaphthalene as the central core have been synthesized as compared to the resorcinol based central core. The first banana-shaped compounds prepared from 2,7-dihydroxynaphthalene by Shen et al. [10], which did not showed mesomorphic properties. At the same time Pelzyl et al. [11] reported banana-shaped compounds with 2,7-dihydroxynaphthalene showed a B1 phase. Several banana-shaped compounds were derived from 2,7-dihydroxynaphthalene central unit with Schiff's base linking groups which exhibited smectic mesophases [12–14]. Amaranatha et al. [15,16] reported a homologous series of such compounds exhibiting nematic and B mesophases. Svoboda et al. [17] also reported some Schiff's base compounds as banana-shaped liquid crystals containing 2,7-dihydroxynaphthalene as central unit with the occurrence of nematic and B mesophases.

Regarding the banana or bent-shaped monomers, a limited number of contributions has been reported and also less investigation of the mesomorphic properties after polymerization with appropriate banana liquid crystals [18–22]. Indeed, 1,3-diene monomers shows various mesophases, which were not stable and suffered degradation under heat or electric field treatment [20]. There are number of bent-core molecules containing an azo linkage reported and they have

not been well investigated. However, a new dimension to the field of photochromism was achieved by the introduction of the –N~N– linkage in such molecules [23]. The occurrence of nematic phase in the banana-shaped compounds consists of naphthalene ring in the core and four aromatic rings linked to the azobenzene of both arms with the terminal chains have polymerizable double bonds were introduced in this work. Thus, due to the presence of the double bonds in the terminal chains of these compounds could be contribute as precursors of polymers for a wide mesophases liquid crystalline materials. There were not too many compounds having the naphthalene central unit prepared and characterized, therefore, we have synthesize a banana-shaped compound containing 2,7-dihydroxynaphthalene as central unit with fluorine and non fluorine containing azobenzene linkage.

2. Experimental

2.1 Materials

Ethyl 4-amino benzoate (Fluka), sodium nitrite (BDH), urea (BDH), phenol (Merck), 2-fluorophenol (Fluka), potassium carbonate (Fluka), allyl bromide ((Fluka), 2,7-dihydroxynaphthalene (Aldrich), 1,3-dicyclohexylcarbodiimide (DCC) (Fluka) and 4-(N,N-dimethylamino)pyridine (DMAP) (Fluka) and silica gel-60 (Merck) were used as received. Acetone and dichloromethane were refluxed over phosphorus pentoxide (Merck) and distilled out before use. Other solvents and chemicals were used without further purification.

2.2.1 Ethyl 4-(4-hydroxyphenylazo)benzoate (1a)

Ethyl 4-amino benzoate (10.0 g, 0.0606 mol) was dissolved in acetone (250 ml). Dilute hydrochloric acid [water (50 ml), conc. hydrochloric acid (22 ml)] was added and the mixture was cooled to 2 °C. Sodium nitrite (5.52 g, 0.080 mol), dissolved in water (20 ml) was added dropwise to the cooled mixture and stirred for 1 h. Exactly, 5 ml of urea (1.16 g, 0.019 mol) solution was added for decomposing the excess of sodium nitrite for 10 min. Then, phenol (5.69 g, 0.0606 mol), dissolved in an acetone/water mixture (300 ml/100 ml) was added to the diazotated mixture and the reaction mixture was maintained at pH 8-9 by adding sodium hydroxide solution, stirring was continued for 2 h. The resulting mixture was made slightly acidic (pH <5) with dilute hydrochloric acid and 400 ml of water for precipitation of the product and the precipitate was collected by filtration. The product was recrystallized twice from methanol. Yield: 11.05 g (67.4%) as red crystals and m.p. 160.6°C. IR (KBr, cm^{-1}): 3323 (νOH), 1724 ($\nu\text{C=O}$, ester), 1604, 1468 ($\nu\text{C=C}$, aromatic), 1245, 1140 ($\nu\text{C-O}$), 828 (νCH , aromatic). ^1H NMR (acetone- d_6) δ : 8.31 (d, 2H, $J = 8.3$ Hz, ArH), 7.96 (dd, 4H, $J = 6.8$ Hz, $J = 7.9$ Hz, ArH), 7.01 (d, 2H, $J = 8.9$ Hz, ArH), 4.02 (t, 2H, $J = 6.9$ Hz, $-\text{CH}_2\text{CH}_3$), 0.88 (3H, $-\text{CH}_2\text{CH}_3$).

2.2.2 4-(4-Hydroxy-3-fluorophenylazo)ethyl benzoate (1b)

The compound **1b** was prepared by the same method used for synthesis of **1a**. Yield: 10.78 g (61.7%) as bright red crystals and m.p. 154.6°C. IR (KBr, cm^{-1}): 3335 (νOH), 1728 ($\nu\text{C=O}$, ester), 1604, 1467 ($\nu\text{C=C}$, aromatic), 1245, 1142 ($\nu\text{C-O}$), 832 (νCH , aromatic). ^1H NMR (acetone- d_6) δ : 8.30 (d, 2H, $J = 8.5$ Hz, ArH), 7.97 (dd, 4H, $J = 6.8$ Hz, $J = 7.8$ Hz, ArH), 7.00 (d, 1H, $J = 8.9$ Hz, ArH), 4.02 (t, 2H, $J = 6.8$ Hz, $-\text{CH}_2\text{CH}_3$), 0.87 (3H, $-\text{CH}_2\text{CH}_3$).

2.3.1 Ethyl 4-[(4-allyloxy)phenylazo]benzoate (2a)

A solution of compound **1a** (1.80 g, 6.66 mmol) in dry acetone (60 ml), allyl bromide (0.926 g, 7.66 mmol), potassium carbonate (1.057 g, 7.66 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 acidified with dilute hydrochloric acid. The precipitate was filtered off and was crystallized from methanol : chloroform (10:2). Yield of **2a**: 1.37g (66.3%) and m.p. 101.8°C. IR (KBr, cm^{-1}): 3078 (vas=CH₂), 2928 (vasCH₂), 2862 (vsCH₂), 1725 (vC=O, ester), 1640 (vC=C, vinyl), 1594, 1496 (vC=C, aromatic), 1248, 1132, 1062 (vC-O), 828 (vCH, aromatic). ¹H NMR (CDCl₃) δ : 8.33 (d, 2H, $J = 6.0$ Hz, ArH), 7.97 (dd, 4H, $J = 5.8$ Hz, $J = 6.8$ Hz, ArH), 7.02 (d, 2H, $J = 6.9$ Hz, Ar-H), 6.03 (m, 1H, CH=), 5.44 (d, 1H, $J = 17.8$ Hz, =CH₂), 5.32 (d, 1H, $J = 10.1$ Hz, =CH₂), 4.62 (d, 2H, $J = 4.1$ Hz, OCH₂-), 4.10 (t, 2H, OCH₂CH₃), 0.88 (t, 3H, -CH₂CH₃).

2.3.2 4-[3-(4-Allyloxy)fluorophenylazo]ethyl benzoate (**2b**)

The compound **2b** was prepared by the same method used for synthesis of **2a**. Yield: 1.55 g (70.8%) and m.p. 94.5°C. IR (KBr, cm^{-1}): 3074 (vas=CH₂), 2925 (vasCH₂), 2860 (vsCH₂), 1724 (vC=O, ester), 1642 (vC=C, vinyl), 1598, 1496 (vC=C, aromatic), 1248, 1132, 1060 (vC-O), 828 (vCH, aromatic). ¹H NMR (CDCl₃) δ : 8.32 (d, 2H, $J = 6.5$ Hz, ArH), 7.98 (dd, 4H, $J = 5.9$ Hz, $J = 6.8$ Hz, ArH), 7.01 (d, 1H, $J = 6.9$ Hz, Ar-H), 6.04 (m, 1H, CH=), 5.44 (d, 1H, $J = 16.8$ Hz, =CH₂), 5.33 (d, 1H, $J = 10.2$ Hz, =CH₂), 4.62 (d, 2H, $J = 4.3$ Hz, OCH₂-), 4.10 (d, 2H, OCH₂CH₃), 0.85 (t, 3H, -CH₂CH₃).

2.4.1 4-[(4-Allyloxy)phenylazo]benzoic acid (**3a**)

The compound **2a** (1.20 g, 3.87 mmol) was dissolved in 120 ml of methanol. A solution of potassium hydroxide (0.651 g, 11.61 mmol) in water (10 ml) was added and the solution was reflux for 4 h. After cooling, the mixture was poured into crushed ice and the precipitate was acidified with dilute hydrochloric acid. The precipitate was filtered off, washed with water and crystallized from ethanol : chloroform (2:1) to give the compound **3a**. Yield: 0.48 g (43.9%) and m.p. 220°C. IR (KBr, cm^{-1}): 3076 (vas=CH₂), 2928 (vasCH₂), 2860 (vsCH₂), 1684 (vC=O, acid), 1640 (vC=C, vinyl), 1594, 1496 (vC=C, aromatic), 1248, 1137, 1068 (vC-O), 828 (vCH, aromatic). ¹H NMR (CDCl₃) δ : 8.32 (d, 2H, $J = 6.1$ Hz, ArH), 7.96 (dd, 4H, $J = 5.5$ Hz, $J = 6.8$ Hz, ArH), 7.01 (d, 2H, $J = 6.9$ Hz, Ar-H), 6.01 (m, 1H, CH=), 5.40 (d, 1H, $J = 17.6$ Hz, =CH₂), 5.30 (d, 1H, $J = 10.2$ Hz, =CH₂), 4.01 (t, 2H, $J = 4.1$ Hz, OCH₂-).

2.4.2 4-[3-(4-Allyloxy)fluorophenylazo]benzoic acid (**3b**)

The compound **2b** was prepared by the same method used for synthesis of **3a**. Yield: 0.47 g (40.4%) and m.p. 204.8°C. IR (KBr, cm^{-1}): 3074 (vas=CH₂), 2925 (vasCH₂), 2860 (vsCH₂), 1684 (vC=O, acid), 1642 (vC=C, vinyl), 1598, 1496 (vC=C, aromatic), 1248, 1137, 1060 (vC-O), 828 (vCH, aromatic). ¹H NMR (CDCl₃) δ : 8.30 (d, 2H, $J = 6.4$ Hz, ArH), 7.97 (dd, 4H, $J = 5.9$ Hz, $J = 6.8$ Hz, ArH), 7.01 (d, 1H, $J = 6.8$ Hz, Ar-H), 6.02 (m, 1H, CH=), 5.41 (d, 1H, $J = 17.2$ Hz, =CH₂), 5.31 (d, 1H, $J = 10.2$ Hz, =CH₂), 4.61 (d, 2H, $J = 4.8$ Hz, OCH₂-).

2.5.1 1,3-Naphthalene bis-{4-[(4-allyloxy)phenylazo]benzoate} (**4a**)

The compound **3a** (0.290 g, 1.02 mmol) and 2,7-dihydroxynaphthalene (0.822 g, 0.514 mmol) was dissolved in 35 ml of dry dichloromethane. Then DCC (0.226 g, 1.10 mmol) and DMAP (0.013 g, 0.11 mmol) were added and the mixture was stirred for 24 h. The precipitate was removed by filtration and the solvent was removed by 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. Solid was recrystallized from methanol : chloroform (2:1) to get the target compound **4a**. Yield: 0.121 g (34.3%). IR (KBr, cm^{-1}): 3078 (vas=CH₂), 2927 (vasCH₂), 2854 (vsCH₂), 1733 (vC=O, ester), 1641 (vC=C, vinyl), 1598, 1492 (vC=C, aromatic), 1239, 1137, 1064 (vC-O), 836

(vCH, aromatic). ^1H NMR (CDCl_3) δ : 8.39 (d, 4H, $J = 8.3$ Hz, $2 \times \text{ArH}$), 8.00 (dd, 8H, $J = 8.2$ Hz, $J = 8.9$ Hz, $2 \times \text{ArH}$), 7.72 (s, 1H, Ar-H), 7.42 (s, 2H, Ar-H), 7.27 (s, 2H, Ar-H), 7.22 (s, 2H, Ar-H), 7.07 (d, 4H, $J = 5.6$ Hz, $2 \times \text{Ar-H}$), 6.07 (m, 2H, CH=), 5.47 (d, 2H, $J = 16.5$ Hz, =CH₂), 5.34 (d, 2H, $J = 9.9$ Hz, =CH₂), 4.39 (d, 4H, $J = 6.8$ Hz, $2 \times \text{OCH}_2$). ^{13}C NMR (CDCl_3) δ : 58.61, 68.80, 70.62, 114.23, 114.82, 119.27, 119.33, 122.54, 124.44, 125.29, 126.38, 129.81, 130.12, 131.08, 131.19, 146.78, 151.34, 155.79, 162.62, 164.44.

2.5 1,3-Naphthalene bis-{4-[3-(4-allyloxy)fluorophenylazo]benzoate} (4b)

The compound **4b** was prepared by the same method used for synthesis of **4a**. Yield: 0.116 g (31.2%). IR (KBr, cm^{-1}): 3075 (vas=CH₂), 2928 (vasCH₂), 2854 (vsCH₂), 1733 (vC=O, ester), 1642 (vC=C, vinyl), 1598, 1496 (vC=C, aromatic), 1249, 1137, 1060 (vC-O), 836 (vCH, aromatic). ^1H NMR (CDCl_3) δ : 8.33 (d, 4H, $J = 8.7$ Hz, $2 \times \text{ArH}$), 7.98 (dd, 8H, $J = 8.1$ Hz, $J = 8.9$ Hz, $2 \times \text{ArH}$), 7.71 (s, 1H, Ar-H), 7.42 (s, 2H, Ar-H), 7.22 (s, 2H, Ar-H), 7.21 (s, 2H, Ar-H), 7.06 (d, 2H, $J = 5.8$ Hz, $2 \times \text{Ar-H}$), 6.06 (m, 2H, CH=), 5.47 (d, 2H, $J = 16.8$ Hz, =CH₂), 5.33 (d, 2H, $J = 9.8$ Hz, =CH₂), 4.38 (d, 4H, $J = 6.7$ Hz, $2 \times \text{OCH}_2$). ^{13}C NMR (CDCl_3) δ : 58.66, 68.80, 70.82, 114.36, 114.95, 119.27, 119.86, 122.72, 124.59, 125.44, 126.18, 130.02, 130.12, 131.24, 131.38, 146.88, 151.66, 155.88, 162.63, 164.74.

3. Measurements

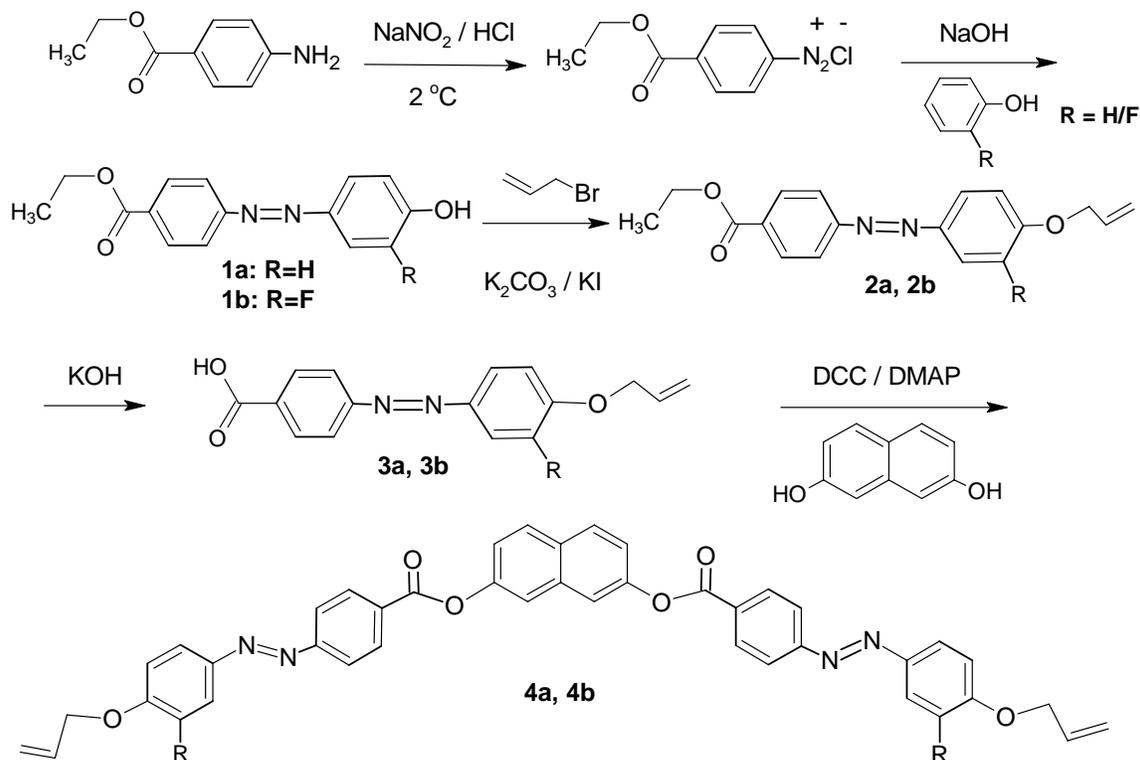
The structures of the intermediates and product were confirmed by spectroscopic methods: FT-IR spectra were recorded with a Thermo Nicolet spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded with a Joel BX50 (600 MHz) spectrometer. The transition temperatures and their enthalpies were measured by differential scanning calorimetry (Perkin DSC 7), and heating and cooling rates were $10\text{ }^\circ\text{C min}^{-1}$. Optical textures were obtained by using Olympus BX50 polarizing optical microscope equipped with a Linkam THMSE 600 heating stage and a VTO 232 control unit.

4. Results and discussion

4.1 Synthesis

The synthetic approach used to prepare the intermediates and target compounds is outlined in scheme 1. The side arms rod-like compound was prepared from ethyl 4-amino benzoate in which the amino group is diazotated by sodium nitrite in the presence of 3 equivalents of hydrochloric acid and the obtained diazonium salt was coupled with phenol to yield ethyl 4-(4-hydroxyphenylazo)benzoate **1a**. Thus compound 4-(4-hydroxy-3-fluorophenylazo)ethyl benzoate **1b** was prepared by same method used for synthesis of **1a** where fluorine was introduced in the phenol i.e. 2-fluorophenol used instead of phenol.

The compound **1a** was alkylated with allyl bromide in the presence of potassium carbonate as base to give ethyl 4-[(4-allyloxy)phenylazo]benzoate **2a**. This compound **2a** was base hydrolyzed to yield 4-[(4-allyloxy)phenylazo]benzoic acid **3a**. The acid compound **3a** was coupling with 2,7-dihydroxynaphthalene by using DCC and DMAP to achieved the target molecule 1,3-naphthalene bis-{4-[(4-allyloxy)phenylazo]benzoate} **4a**. Thus, the fluorine containing intermediate compounds 4-[3-(4-allyloxy)fluorophenylazo]ethyl benzoate **2b**, 4-[3-(4-allyloxy)fluorophenylazo]benzoic acid **3b** and target compound 1,3-naphthalene bis-{4-[3-(4-allyloxy)fluorophenylazo]benzoate} **4b** were prepared by same method used for synthesis of **2a**, **3a** and **4a**, respectively.



Scheme 1: Synthesis of banana-shaped monomers containing 2,7-dihydroxynaphthalene.

4.2 Mesomorphic properties

The phase transition temperatures ($T/^\circ\text{C}$) and as well as the phase transition enthalpy changes ($\Delta H/\text{Jg}^{-1}$) were determined by differential scanning calorimetry (DSC). For compound **4a**, there are two peaks obtained on heating at 170.0 and 227.7 $^\circ\text{C}$ which corresponding to the Cr–N and N–I transitions. On cooling, again there are two peaks, corresponding to I–N and N–Cr transitions were observed and the crystallization peak was appeared at 168.3 $^\circ\text{C}$ as shown in Table 1. Similarly for compound **4b**, two peaks on heating, which corresponding to the Cr–N and N–I transitions and on cooling, again two peaks, corresponding to I–N and N–Cr transitions were observed and the crystallization peak was appeared at 160 $^\circ\text{C}$ (table 1).

Table 1. Phase transition temperature ($T/^\circ\text{C}$) and associated transition enthalpy values ($\Delta H/\text{Jg}^{-1}$) in parentheses given for the second heat and cooling of DSC scans for compounds **4a** and **4b**.

Compounds		Phase transitions
4a	heat	Cr 170.0 (45.0) N 227.7 (32.3) I
	cool	I 218.5 (40.1) N 168.3 (32.3) Cr
4b	heat	Cr 145.8 (5.60) N 204.5 (8.70) I
	cool	I 199.0 (9.70) N 160.0 (15.5) Cr

Abbreviations: Cr = crystal, N = nematic, I = isotropic phase

The mesophase structures were evaluated by means of polarizing optical microscopy. The micrograph of the mesophase of compound **4a** as observed upon cooling is shown in Figure 1. A schlieren texture, as typical for nematic phases, was observed at 192 °C upon cooling from the isotropic phase. This nematic phase is highly fluid. There is no other phase transition on further cooling, except crystallization on exactly at 186 °C, which good agreement with DSC data. This phase is homeotropic alignment which appears optically isotropic. Similarly, a schlieren texture of compound **4b** was observed at 172 °C upon cooling from the isotropic phase. This is also nematic phase and no other phase transition on further cooling, except crystallization.

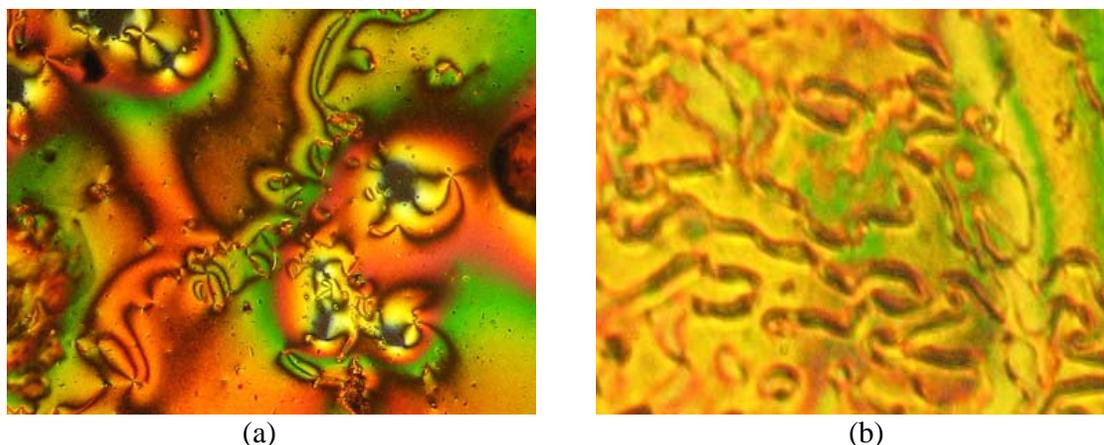


Figure 1. Optical micrographs of (a) compound **4a** at 192 °C and (b) and compound **4b** at 172 °C, both nematic mesophases on cooling from the isotropic phase

We have been compared the transition temperatures and the nature of the mesophases exhibited by 2,7-dihydroxynaphthalene-based compounds of a novel type of banana-shaped containing Schiff's base linking groups [17], to see the relative effect of naphthalene linkages on the mesomorphism. We found that they behave in quite a similar fashion in case of nematic mesomorphism, several compounds exhibited nematic and B2 mesophases. In addition, if we compared to another series of banana-shaped compounds containing fluorine with the same 2,7-dihydroxynaphthalene central unit [16], these compounds showed B1, B6 and nematic mesophases. Although the transition temperatures of the reported compounds [16] shows a little higher at nematic phases in the range of 200°C, but still quite similar transition occurred to our target compounds. The values of transition temperature of fluorine containing compound **4b** were less than non fluorine compound **4a**.

5. Conclusion

A banana-shaped monomer containing 2,7-dihydroxynaphthalene as central unit was synthesized and in addition, another monomer containing fluorine with same central unit used for synthesized. Both compounds exhibited nematic mesophases. The presence of the double bonds to the both wins could be contributed as precursors of polymers for wide mesophase compounds. The presence of the azo linkage in both liquid crystals compounds would be suitable for physical studies for example photoinduced effects and as well as trans-cis-trans isomerizations cycles under UV irradiation.

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