# Accepted Manuscript

Synthesis, characterization, crystal structure and liquid crystal studies of some symmetric naphthalene derivative molecules



H.T. Srinivasa, B.S. Palakshamurthy, H.C. Devarajegowda, S. Hariprasad

PII: S0022-2860(18)30855-X

DOI: 10.1016/j.molstruc.2018.07.036

Reference: MOLSTR 25441

To appear in: Journal of Molecular Structure

Received Date: 20 April 2018

Accepted Date: 10 July 2018

Please cite this article as: H.T. Srinivasa, B.S. Palakshamurthy, H.C. Devarajegowda, S. Hariprasad, Synthesis, characterization, crystal structure and liquid crystal studies of some symmetric naphthalene derivative molecules, *Journal of Molecular Structure* (2018), doi: 10.1016/j. molstruc.2018.07.036

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

**Graphical abstract** 



# Synthesis, characterization, crystal structure and liquid crystal studies of some symmetric naphthalene derivative molecules

H. T. Srinivasa<sup>1</sup>, B. S. Palakshamurthy<sup>2</sup>, H. C. Devarajegowda<sup>3</sup> and S. Hariprasad<sup>4\*</sup>

<sup>1</sup>Raman Research Institute, Soft Condensed Matter Group, Sadashivanagar, Bengaluru-560 080

<sup>2</sup> Department of PG Studies and Research in Physics, University College of Science,

Tumkur University, Tumakuru-572 103

<sup>3</sup>Department of Physics, Yuvaraja's College, Mysore University, Mysuru-570005

<sup>4</sup>Department of Chemistry, Central College Campus, Bangalore University, Palace Road,

Bengaluru-560 001, KARNATAKA, INDIA

\*Corresponding author E-mail: hariprasad@bub.ernet.in

**Abstract:** The synthesis of a series of symmetrical liquid crystals having naphthalene as the central rigid core and attached to long chain flexible 4'-alkoxybenzoate moiety at positions 2,6 - of the aromatic **ring** are reported. The mesophase behavior of the molecules was investigated using differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction studies. The studies reveal that the synthesized compounds exhibit stable enantiotropic mesophase of Smectic A (SmA) and Nematic (N) phase. The mesophase appearance is independent of the length of the alkyl chain. The molecular structure was determined by single crystal X-ray diffraction technique. The derivative with *n*-heptyloxy-flexible chain crystallizes under triclinic,  $P_i$  space group with unit cell dimension a = 5.569(3) Å, b = 10.540(5) Å, c = 15.254(9) Å,  $a = 73.434(18)^\circ$ ,  $\beta = 80.807(19)^\circ$  and  $\gamma = 82.02(2)^\circ$ , V = 843.1(8) Å<sup>3</sup>. The dihedral angle between the naphthalene ring system and the benzoate moiety is  $63.63(2)^\circ$ .

Key words: Liquid crystal, naphthalene, smectic, nematic, schleiren texture, symmetric.

#### 1. Introduction

Conventional rod-like liquid crystals are composed of a central rigid core with one/two flexible hydrocarbon tails at terminal ends. Over the last three decades, a variety of such motifs have been studied which highlights their significance [1-4]. Many conventional liquid crystal materials have been synthesized which exhibit a variety of mesophases [5]. In order to determine the correlation between molecular structure and physical properties, various molecular designs have been utilized to achieve target molecules with expected and desired properties [6-8]. From these studies, it is generally acknowledged that a simple change in the length of the achiral aliphatic terminal chains can significantly affect the mesomorphic properties of liquid crystals [9, 10].

Naphthalene is a molecule with central rigid core. Due to its aromaticity, it is planar. Its derivatives have been extensively investigated for their fascinating liquid crystal properties such as electromagnetic and photophysical properties. Their unusual characteristics have been applied to use in LCD devices.

In this regard, we expected that their further study and development would attract the interest of the vast scientific community by-and-large [11-13]. Recent studies by other scientists too have focused on naphthalene cores with various differing functionalities. A variety of derivatives have been examined for their liquid crystalline mesophases by taking into consideration the geometric shapes of the molecular structures. The studies have inferred that the acute angle at central naphthalene core does not favor mesomorphism. However, it is also found that moderate and strain free molecular structures do favor the LC property [14, 15].

The modification of naphthalene core with straight molecular shapes by slightly differing the positions of the alkyl chains have resulted in the strong formation of smectic phase [16, 17]. Other examples for this observation include single benzene ring compounds with a semi-fluorinated chain, which unexpectedly exhibited stable smectic phase [18, 19].

In practice, with naphthalene core, only small alkyl chain derivatives can be used to get low temperature nematic phase which is useful for the liquid crystal applications [20, 21]. There also exists a report on naphthalene molecules showing an intense bluish purple luminescence in the crystal state as a photophysical property [22]. Thermotropic polyesters based on 2,6-disubstituted naphthalene are also reported to possess unique thermotropic properties and find applicability as high strength plastics and fiber material [23].

We were also of the opinion and reasoned that some insight into their solid-state structures may widen their applicability further since the thermotropic polyesters are utilized as solids. In this regard, it may be noted that the 2,6-disubstituted naphthalene units give structures parallel to a polymer backbone. Thus, it was of interest to study the effects of incorporation of a 2,6-disubstituted naphthalene unit on mesomorphic properties and solid-state structures [24].

To our knowledge, the liquid crystal and single crystal formation in symmetric naphthalene rod-like molecules has been not explored [25]. We presumed that naphthalene core will promote the single crystal characters, which is the main aim of our present studies under liquid- and single- crystal studies.

In this article, we report the preparation and investigation of the mesophasic properties of a series of homologous rod-like molecules: the 2,6-bis-(4'-alkoxybenzoate)naphthalene derivatives which possess the 2,6-etheric-naphthalene core, in conjunction with straight alkyl chains attached to the external side of the naphthalene core.

#### 2. Experimental

All chemicals used were of analytical grade. Purity of the compounds were checked by TLC silica gel 60 F<sub>254</sub> using pure dichloromethane as mobile phase and purified by column chromatography on silica gel (230-400) mesh with dichloromethane as eluent. Re-crystallisation of the solids was performed using appropriate protic alcoholic solvents like ethanol. The structures of newly synthesized compounds were determined using infrared spectroscopy (Shimadzu FTIR-8400 spectrophotometer), <sup>1</sup>H NMR, <sup>13</sup>C NMR, (Bruker Biospin 500 spectrometer), elemental analysis (Carlo-Erba1106 analyser). UV-Vis absorption spectra were recorded using Perkin Elmer  $\lambda$  35 double-beam spectrophotometer. The transition temperature and the associated enthalpy value for all compounds were determined using differential scanning calorimetry (DSC): Perkin-Elmer, Model Pyris 1. The textures of mesophase were observed using a polarising optical microscope (POM): Olympus BX50 equipped with a heating hot stage: Mettler FP82HT and a central processor Mettler FP90. The thermogravimetric analysis (TGA) was measured under nitrogen atmosphere at a heating rate of 20 °C/min using a Perkin Elmer TGA-4000 thermal analyzer. X-Ray diffraction (XRD) patterns were obtained at liquid crystalline state using a DY 1042-Empyrean X-ray diffractometer with a pixel 3D detector and Cu-K $\alpha$  radiation.

Single crystal of compound **5b** of the size  $0.28 \times 0.2 \times 0.16 \text{ mm}^3$ , was selected under a polarizing microscope and affixed to Hampton Research Cryoloops using paratone-N oil for single crystal data collection. The X-ray diffraction data sets were collected on a Bruker SMART APEX II CCD diffractometer using Mo K $\alpha$  radiation. The crystal-to-detector distance was fixed at 40 mm for all the crystals. The scan width per frame was  $\Delta \omega = 0.5^{\circ}$ . The cell

refinement and data reduction were carried out using the SAINT [26]. The crystal structure was solved by direct methods using SHELXS97 [27] and refined in the spherical-atom approximation (based on  $F^2$ ) by using SHELXL97 [28] included in the WinGX package suite [29]. The *ORTEP* and packing diagrams (Figures 7 and 8) were generated using the *MERCURY* package [30]. The experimental and all crystallographic information are listed in Table 2.

# 2.1 General synthetic procedure for the preparation of 2,6-bis-(4'alkoxybenzoate)naphthalene derivatives:

То suspension of 2,6-dihydroxynaphthalene (4)(0.1)6.2 mmol). g, dicyclohexylcarbodiimide (DCC) (0.146 g, 7.0 mmol) and dimethylaminopyridine (DMAP) (0.04 g) catalyst in dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL), the 4-alkoxybenzoic acids **3a-i** (12.42 mmol) were added individually. The reaction mixture was stirred for 1 h at room temperature and progress of the reaction was monitored by thin layer chromatography using dichloromethane as mobile phase. After completion of the reaction, as indicated by the disappearance of the reactant spots, the reaction mass was diluted with water and extracted with  $CH_2Cl_2$  (25 mL × 2). The organic layer was washed with water and dried over anhydrous sodium sulphate. The crude product thus obtained was concentrated on a rotary evaporator and purified by column chromatography using silica gel as stationary phase and pure CH<sub>2</sub>Cl<sub>2</sub> as mobile phase. The eluted product was concentrated under vacuum to isolate off-white solids. Further re-crystallization from ethanol gave the pure products 5a-i with isolated yields in the range 85-90%.

## 2.2 Spectroscopic data:

2,6-Bis-(4'-n-hexyloxybenzoate)naphthalene 5a.

IR (KBr): v = 2924, 2854, 1720, 1604, 1464, 1259, 1066 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 8.20$  (m, 4H, Ar-H), 7.88 (m, 2H, Ar-H), 7.70 (s, 2H), 7.38 (m, 2H), 6.99 (m, 4H), 4.06 (t, J = 6.5 Hz, 4H), 1.92-1.80 (m, 4H), 1.56-1.35 (m, 12H), 0.93 (t, J = 6.65 Hz, 6H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 165.1, 163.5, 148.4, 132.2, 131.7, 129, 122.2, 121.6, 118.8, 114.4, 68.4, 31.8, 29.2, 29.0, 25.8, 22.7, 14.2 ppm. Elemental analysis calculated for C<sub>36</sub>H<sub>40</sub>O<sub>6</sub>; C, 76.03; H, 7.09; found C, 76.10; H, 7.17%.

**2,6-Bis-(4'-***n***-heptyloxybenzoate)naphthalene 5b.** IR (KBr): *ν* = 2924, 2852, 1722, 1602, 1458, 1257, 937 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.23 (m, 4H, Ar-H), 7.90 (m, 2H, Ar-H), 7.74 (s, 2H), 7.42 (m, 2H), 7.0 (m, 4H), 4.09 (t, *J* = 6.5 Hz, 4H), 1.88-1.84 (m, 4H), 1.59-1.36 (m, 16H), 0.95 (t, *J* = 6.65 Hz, 6H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 165.1, 163.6, 148.6, 132.3, 131.8, 129, 122.2, 121.5, 118.7, 114.3, 68.3, 31.8, 29.1, 29.0, 25.9, 22.6, 14.1 ppm. Elemental analysis calculated for C<sub>38</sub>H<sub>44</sub>O<sub>6</sub>; C, 76.48; H, 7.43; found C, 76.53; H, 7.49%.

**2,6-Bis-(4'-***n***-octyloxybenzoate)naphthalene 5c.** IR (KBr): v = 2922, 2854, 1724, 1604, 1456, 1257, 844 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 8.22$  (m, 4H, Ar-H), 7.87 (m, 2H, Ar-H), 7.69 (s, 2H), 7.36 (m, 2H), 6.97 (m, 4H), 4.02 (t, J = 6.5 Hz, 4H), 1.91-1.80 (m, 4H), 1.54-1.34 (m, 20H), 0.92 (t, J = 6.65 Hz, 6H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 165.2, 163.7, 148.5, 132.4, 131.9, 129, 122.3, 121.4, 118.8, 114.4, 68.4, 31.9, 29.2, 29.1, 26, 22.5, 14.2 ppm. Elemental analysis calculated for C<sub>40</sub>H<sub>48</sub>O<sub>6</sub>; C, 76.89; H, 7.74; found C, 76. 97; H, 7.83%.

**2,6-Bis-(4'-***n***-nonyloxybenzoate)naphthalene 5d.** IR (KBr): *ν* = 2924, 2852, 1730, 1602, 1456, 1377, 1257, 1064, 844 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): *δ* = 8.20 (m, 4H, Ar-H), 7.88 (m, 2H,

Ar-H), 7.70 (s, 2H), 7.38 (m, 2H), 6.99 (m, 4H), 4.06 (t, J = 6.5 Hz, 4H), 1.92-1.80 (m, 4H), 1.56-1.35 (m, 24H), 0.93 (t, J = 6.65 Hz, 6H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 165.1, 163.5, 148.5, 132.2, 131.7, 129, 122.1, 121.4, 118.6, 114.2, 68.2, 31.7, 29.1, 29.0, 25.8, 22.7, 14.2 ppm. Elemental analysis calculated for C<sub>42</sub>H<sub>52</sub>O<sub>6</sub>; C, 77.27; H, 8.03; found C, 77.33; H, 8.10%.

**2,6-Bis-(4'-***n***-decyloxybenzoate)naphthalene 5e.** IR (KBr): v = 2924, 2853, 1723, 1605, 1454, 1256, 845 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 8.22$  (m, 4H, Ar-H), 7.86 (m, 2H, Ar-H), 7.72 (s, 2H), 7.39 (m, 2H), 7.00 (m, 4H), 4.05 (t, J = 6.5 Hz, 4H), 1.93-1.81 (m, 4H), 1.57-1.36 (m, 28H), 0.94 (t, J = 6.65 Hz, 6H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 165.3, 163.5, 148.7, 132.2, 131.7, 129, 122.3, 121.6, 118.8, 114.4, 68.4, 31.9, 29.2, 29.0, 26, 22.5, 14.2 ppm. Elemental analysis calculated for C<sub>44</sub>H<sub>56</sub>O<sub>6</sub>; C, 77.61; H, 8.29; found C, 77.67; H, 8.35%.

**2,6-Bis-(4'-***n***-dodecyloxybenzoate)naphthalene 5f.** IR (KBr): v = 2924, 2855, 1729, 1605, 1458, 1259, 1056, 840 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 8.23$  (m, 4H, Ar-H), 7.90 (m, 2H, Ar-H), 7.72 (s, 2H), 7.40 (m, 2H), 7.01 (m, 4H), 4.08 (t, J = 6.5 Hz, 4H), 1.93-1.80 (m, 4H), 1.57-1.36 (m, 36H), 0.96 (t, J = 6.65 Hz, 6H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 165.2, 163.7, 148.7, 132.4, 131.9, 129, 122.3, 121.6, 118.8, 114.4, 68.4, 31.9, 29.2, 29.0, 25.9, 22.7, 14.1 ppm. Elemental analysis calculated for C<sub>48</sub>H<sub>64</sub>O<sub>6</sub>; C, 78.22; H, 8.75; found C, 78.29; H, 8.83%.

**2,6-Bis-(4'-***n***-tetradecyloxybenzoate)naphthalene 5g.** IR (KBr): v = 2924, 2858, 1726, 1606, 1458, 1256, 1060, 786 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 8.20$  (m, 4H, Ar-H), 7.88 (m, 2H, Ar-H), 7.71 (s, 2H), 7.38 (m, 2H), 6.98 (m, 4H), 4.06 (t, J = 6.5 Hz, 4H), 1.93-1.80 (m, 4H), 1.54-1.35 (m, 44H), 0.93 (t, J = 6.65 Hz, 6H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 165.1, 163.5,

148.6, 132.3, 131.7, 129, 122.2, 121.7, 118.7, 114.5, 68.3, 31.9, 29.1, 29.0, 25.9, 22.7, 14.1 ppm. Elemental analysis calculated for C<sub>52</sub>H<sub>72</sub>O<sub>6</sub>; C, 78.75; H, 9.15; found C, 78.85; H, 9.24 %.

**2,6-Bis-(4'-***n***-hexadecyloxybenzoate)naphthalene 5h.** IR (KBr): v = 2928, 2850, 1730, 1608, 1454, 1253, 842 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 8.21$  (m, 4H, Ar-H), 7.88 (m, 2H, Ar-H), 7.70 (s, 2H), 7.38 (m, 2H), 6.99 (m, 4H), 4.06 (t, J = 6.5 Hz, 4H), 1.92-1.80 (m, 4H), 1.56-1.35 (m, 52H), 0.93 (t, J = 6.65 Hz, 6H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 165.2, 163.7, 148.6, 132.4, 131.8, 129, 122.3, 121.6, 118.7, 114.6, 68.3, 31.9, 29.1, 29.1, 25.9, 22.8, 14.2 ppm. Elemental analysis calculated for C<sub>56</sub>H<sub>80</sub>O<sub>6</sub>; C, 79.20; H, 9.50; found C, 79.27; H, 9.59 %.

**2,6-Bis-(4'-***n***-octadecyloxybenzoate)naphthalene 5i.** IR (KBr): v = 2920, 2852, 1720, 1602, 1454, 1257, 1165, 937 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 8.23$  (m, 4H, Ar-H), 7.89 (m, 2H, Ar-H), 7.71 (s, 2H), 7.39 (m, 2H), 7.0 (m, 4H), 4.06 (t, J = 6.5 Hz, 4H), 1.94-1.82 (m, 4H), 1.56-1.37 (m, 60H), 0.95 (t, J = 6.65 Hz, 6H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 165.1, 163.8, 148.8, 132.4, 131.7, 129, 122.5, 121.7, 118.6, 114.5, 68.5, 31.6, 29.3, 29.1, 25.9, 22.5, 14.2 ppm. Elemental analysis calculated for C<sub>60</sub>H<sub>88</sub>O<sub>6</sub>; C, 79.60; H, 9.80; found C, 79.67; H, 9.88 %.

## 3. Results and discussion

Low and high molecular mass mesogens of naphthalene derivatives which exhibit attractive thermosetting and photophysical properties have been reported in literature [10-22]. Due to these interesting properties of the naphthalene core unit, the present work is mainly focused on the synthesis of a library of naphthalene derivatives which may exhibit liquid crystal and single crystal properties. We now report the synthesis of the naphthalene derivatives **5a-i**, and their liquid crystalline property studies.

All 4-alkoxybenzoic acids **3a-i** were prepared according to reported literature procedures [**31**, **32**]. The esterification of 2,6-dihydroxynaphthalene with the 4-alkoxybenzoic acids **3a-i** using DCC as coupling reagent gave the products **5a-i**. The general broad outline for the preparation of nine products of 2,6-bis-(4'-alkoxybenzoate)naphthalene derivatives **5a-i** is highlighted in Scheme 1.



Scheme 1. Synthetic scheme for the series of compounds of 5a-i

The chemical structures of new compounds **5a-i** were characterized by IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR spectral studies and elemental analysis techniques. The general observations for the spectral data are highlighted below for some individual compounds:

In the IR spectrum of compound **5a**, the alkyl (C-H) stretching frequency was observed at 2924 cm<sup>-1</sup>, where as the carboxyl group (C=O) stretching frequency showed a strong absorption band at 1720 cm<sup>-1</sup>. The ether (C-O) stretching frequency exhibited a strong absorption band at 1259 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum of compound **5b** exhibited multiplet peaks in the region  $\delta$  =

8.23-7.0 for fourteen aromatic (Ar-H) protons. This range was found to be standard throughout for the aromatic proton signals for the entire series of compounds. A triplet was observed at  $\delta$  = 4.09 due to the etheric methylene protons (-OCH<sub>2</sub>-) of alkoxy chain. The terminal methyl (-CH<sub>3</sub>) group protons of alkyl chain were found to resonate as a triplet at  $\delta$  = 0.95 cm<sup>-1</sup>. The <sup>13</sup>C NMR spectral data of compound **5c** shows singlets for the carboxylic carbon (C=O) of the ester functionality and the aryloxy- carbon at  $\delta$  = 165.2 and 163.7 cm<sup>-1</sup> respectively, where as the etheric methylene (C-O) signal peak appeared at  $\delta$  = 68.3 cm<sup>-1</sup>. These values confirmed the molecular structures of target compounds.

Thermotropic and LC texture behaviour of synthesized compounds were studied and confirmed by the combination of DSC, POM and X-ray diffraction measurements at mesophase stages, respectively. The DSC curves were obtained during two successive heating-cooling scans at a heating/cooling rate of 5 °C min<sup>-1</sup>. As can be seen from the curves, all compounds exhibit enantiotropic liquid crystal properties. The spectral results are presented in experimental section while transition temperatures along with associated enthalpies and mesophase types are presented in Table 1.

Sl No	n	Heating Scan	Cooling Scan		
5a	6	Cr <sub>1</sub> 133.02 (15.54) Cr <sub>2</sub> 145.34 (62.70) N	Iso 262.01 (3.72) N 120.74		
		263.37 (3.76) Iso	(59.06) Cr		
5b	7	Cr <sub>1</sub> 154.61 (85.73) N 248.46 (3.10) Iso	Iso 247.19 (2.90) N 120.20		
		()	(76.21) Cr		
5c	8	Cr 137.93 (13.29) SmA 142.84 (2.38) N	Iso 228.97 (2.66) N 141.94 (2.34)		
		229.99 (2.44) Iso	SmA 100.95 (53.58) Cr		
5d	9	Cr 143.89 (70.55) SmA 160.24 (3.71) N	Iso 227.46 (1.86) N 159.0 (3.55)		
		228.15 (2.31) Iso	SmA 114.82 (67.79) Cr		
5e	10	Cr 135.84 (67.12) SmA 170.84 (4.17) N	Iso 220.66 (2.36) N 169.93 (4.00)		

Table 1. Transition temperatures and mesophase types of compounds 5a-i

		221.27 (2.44) Iso	SmA 112.83 (63.84) Cr		
5f	12	Cr 127.10 (67.86) SmA 181.33 (5.39) N	Iso 206.35 (1.98) N 180.65 (5.11)		
		206.96 (2.10) Iso	SmA 108.50 (44.18) Cr		
5g	14	Cr <sub>1</sub> 104.28 (18.46) Cr <sub>2</sub> 125.01 (67.49) SmA	Iso 194.62 (2.10) N 182.80 (5.70)		
		184.40 (5.82) N 195.72 (2.32) Iso	SmA 105.0 (65.77) Cr		
5h	16	Cr <sub>1</sub> 117.15 (22.32) Cr <sub>2</sub> 126.03 (75.52) SmA	Iso 186.54 (1.95) N 183.12 (9.01)		
		183.83 (9.23) N 187.0 (2.08) Iso	SmA 106.28 (73.40) Cr		
5i	18	Cr 125.98 (73.77) SmA 180.54 (13.55) Iso	Iso 179.46 (13.64) SmA 108.55		
			(74.59) Cr		

Cr = Crystal; SmA = Smectic A phase; N = Nematic phase; n = number of carbon atoms in the terminal alkyl chain

## 3.1 Liquid crystal property

All the compounds **5a-i** was found to possess rich mesomorphism, as smeetic and nematic liquid crystalline phases over a wide temperature range. Compound **5a** showed enantiotropic phase sequences of Cr-Cr-N-I transitions which were confirmed by DSC and POM textural observation. On cooling, the isotropic-nematic transition appeared and it crystallized at 120.74 °C (Table 1). The compound **5b** also showed similar transitions with similar mesophase behavior as that of **5a**. DSC thermogram of compound **5b** is given in Figure 1, where heating and cooling transitions can be clearly seen. Compound **5c** exhibited enantiotropic phase sequences of Cr-Cr-SmA-N-I transitions. On cooling, the isotropic-nematic-smeetic transitions appeared and crystallized at 100.95 °C. An additional smeetic A phase was introduced in the compound **5c** as shown in Figure 2 (a). A typical mosaic texture for nematic phase Fig 2 (b) of compound **5c** was also observed. The compounds **5d-h** showed resemblance of **5c** transition peaks on heating and cooling cycles, which are attributed to the Cr-

smectic-N-Iso. On cooling, similar reverse peaks corresponding to and I-N-smectic-Cr transitions were observed. The POM observations revealed that the other type of texture for nematic phase is Schlieren texture. Figure 2 (c) texture was also observed for compound **5h**. Compound **5i** on heating melted at about 125.98 °C to the SmA mesophase ( $\Delta H = 73.77$  kJ mol<sup>-1</sup>) and finally cleared (isotropic) at 180.54 °C ( $\Delta H = 13.55$ kJ mol<sup>-1</sup>). On cooling, it showed a transition in DSC centered at around 179.46 °C ( $\Delta H = 13.64$ kJ mol<sup>-1</sup>) followed by crystallization at 108.55 °C ( $\Delta H = 74.59$  kJ mol<sup>-1</sup>). Under POM, it exhibited a well-defined smectic batonnets texture for smectic A mesophase as shown in Figure 2 (d). Compound **5i** exhibited only smectic A phase, which is good agreement with the theory of the homologous series of liquid crystals. Thus, the mesomorphic range of the smectic phase is shorter than that of the nematic phase.

From these observations, we conclude that the series **5a-i** under present discussion here is predominantly smectogenic and partly nematogenic. The statement that liquid crystallinity involving the naphthyl- unit with lower chain length substitutions yields nematic phase is reiterated. Moderate chain length gives both nematic and smectic phase; and higher chain length affords predominantly only smectogenic character in the homologues and is found in the present investigation.

Further, the crystallizing tendency arising in lower members is probably due to their relatively high level of forces of attraction. The lack of flexibility also causes for nematic mesophase formation in the lower members **5a** and **5b** of the series.





The thermal behavior of all compounds **5a-i** is in accordance with literature. Hence, increasing the terminal chain length (**5a** vs. **5i**), as expected, decreases the transition temperature (Table 1). In addition, the odd-even effect on the melting temperature was seen to compound **5a-d**, where compounds **5a-d** has a higher isotropic transition temperature compared to **5e-i**. The enthalpy changes determined by DSC are in agreement with the values usually observed for typical crystalline-nematic, nematic-isotropic, crystalline-smectic, smectic-nematic, nematic-isotropic, smectic-isotropic and smectic-crystalline transitions which confirm the presence of a smectic and a nematic mesophases. The solid-liquid crystal or liquid crystal-solid transitions involve much more energy than the liquid crystal-isotropic liquid or liquid crystal-liquid crystal transitions [33-35]. It is also found that increasing terminal chain length decreases the transition temperature as expected. A number of reports are found in literature to support such studies in calamatic liquid crystalline materials [36, 37].



**Fig. 2** Polarizing optical microscope images. (a) Focal-conic texture of SmA phase of **5c**, (b) Mosaic texture of nematic phase for **5c**, (c) Schlieren nematic texture of **5h**, (d) Batonnets texture of SmA phase for **5h**.

A plot of heating cycle transition temperatures as a function of the number of carbon atoms in the terminal *n*-alkoxy chain is shown in Figure 3. The plot shows fairly dropping smooth curves in relation to both melting and isotropic transition temperatures of compounds **5a-i**. This study shows that lower homologous members' exhibit only nematic phase, middle homologous members show both SmA and N phases and finally higher homologues members' exhibit only SmA phase.



**Fig. 3** Plot of heating cycle melting and clearing points (T/°C) with number of carbon atoms in the terminal alkyl chains for the homologues series **5a-i**.

The UV-Visible absorption spectra were recorded over the range of wavelengths ( $\lambda = 200-500$  nm) in dichloromethane solution at concentrations of 1mg/mL for compounds **5a**, **5e** and **5h**. The respective UV-visible absorption spectra are shown in Figure 4. In the absorption spectra of **5a**, **5e** and **5f**, a strong absorption band at  $\lambda = 270$  nm is attributed to the E band of aromatics for the  $\pi$ - $\pi$ \* electronic transitions. The low-intensity n- $\pi$ \* transitions observed at  $\lambda = 370-380$  nm are due to the non-bonding *n*-electrons of the ester oxygens. All ultra violet spectra were found to be similar in shape because of their structural similarities [38]. Interestingly, all of the compounds were found to be luminescent with very weak blue light emission in solid state in the visible light region. This observed blue light emission may be attributed to extended conjugation in association with the mesogenic core.



Figure 4. UV/visible absorption spectra of 5a, 5e and 5h in dichloromethane.

Thermogravimetric analysis was performed for the compound **5b**, **5f** and **5i** under a nitrogen atmosphere at a heating rate of 20 °C min<sup>-1</sup>. The thermogravimetric traces are shown in Figure 5. The temperatures correspond to 100 % weight loss which occurs between 350 °C-500 °C. The compounds are stable up to 350 °C and start degrading thereafter in nitrogen. The degradation occurs in a single step between 350 °C-500 °C. The data revealed that in general all the compounds in a homologues series are stable up to 325 °C.



Figure 5. Thermogravimetric analysis traces of 5b, 5f and 5i.

The representative liquid crystal state X-ray analysis carried out to confirm the mesophases obtained for the compound **5e** are shown in Figure 6. In the X-ray pattern of non-oriented sample of **5e** at 190 °C for nematic phase, only one reflection at wide angle region with *d*-space value 4.60 Å indicates the nematic phase. Two reflections were found at 130 °C for SmA phase, the *d*-space value 29.33 Å in the small angle region and *d*-space value 4.53 Å in wide angle region confirming the SmA phase. The typical X-ray patterns established the presence of both nematic and smectic mesophase. Further, in this regard, the practically obtained *d*-spacing value (29.33 Å) is smaller than theoretically obtained *d*-spacing value (42.97 Å) of compound **5e**. These values give the insight that the molecules are inter-digitized and showing layered SmA mesophase.



Figure 6. X-ray diffraction studies of 5e at nematic phase and Smectic phase.

The rigidity of the central naphthalene with benzene core connected via ester bond accomplished the growth of single crystal. Interestingly, we found that lower member with heptyloxy- chain length has a perfect crystal structure at room temperature and hence it helped us to study the crystal structure as a representative compound **5b**. The single crystal study parameters are tabulated in Table 2. The atoms were joined together by using reflections obtained from single crystal X-ray studies and which provides ORTEP diagram (Figure 7) of actual structure of the chemical structure. The H atoms of **5b** was positioned with idealized geometry using a riding model with C—H = 0.93-0.97 Å. All H-atoms were refined with isotropic displacement parameters (set to 1.2-1.5 times of the U<sub>eq</sub> of the parent atom).

## 3.2 Single crystal X-ray diffraction studies

Details	Compound ( <b>5b</b> )
Empirical formula	$C_{19}H_{22}O_3 (C_{38}H_{44}O_6)$
Formula weight	298.37
Temperature/K	300.15
Wavelength/ Å	0.71073
Crystal system, Space group	Triclinic, $P_{\tilde{1}}$
a/Å	5.569(3)
b/Å	10.540(5)
c/Å	15.254(9)
a/°	73.434(18)
β/°	80.807(19)
γ/°	82.02(2)
Volume/Å <sup>3</sup> , Z	843.1(8), 2
Calculated density	1.175
Absorption coefficient/mm <sup>-1</sup>	0.078
F(000), F'(000)	320.0, 320.26
Crystal size/mm <sup>3</sup>	0.28  imes 0.2  imes 0.16
Theta range for data collection/°	2.8 to 50
Limiting indices	$-6 \le h \le 6, -12 \le k \le 12, -18 \le l \le 1$
Reflection collected/unique	16846 / 2963 [R(int) = 0.0691]
Data/restraints/parameters	2963/54/234
Goodness-of-fit on F <sup>2</sup>	1.062
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0612, wR_2 = 0.1750$
Final R indexes [all data]	$R_1 = 0.0931$ , $wR_2 = 0.2022$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.32/-0.23
Measurement	Bruker SMART APEX II diffractometer
Program system	SAINT
Structure determination	Direct method (SHELX97, SHELXS97)
CCDC	985487

 Table 2. Crystallographic data, experimental details of the compound (5b)





Figure 7. ORTEP diagram obtained by single crystal X-ray diffraction for 5b.

**Figure 8.** The crystal packing of the compound **5b**. Cg1 is the centroid of the ring C7/C8/C9/ C10/C11/C12.

The molecular structure of the compound **5b** shows that the asymmetric unit contains half of the molecule, the planes of the naphthalene ring C1/C2/C3/C4/C5/C1A/C2A/C3A/C4A/C5AC6 and C7/C8/C9/C10/C11/C12 and C7A/C8A/C9A/C10A/C11A/C12A benzene rings form a dihedral angle of 63.62(2)° and 63.60 (5)° respectively, and there is no significant difference in the dihedral angles. The crystal structure is stabilized by C4—H4. . . Cg1 interaction, where Cg1 is the centroid of C7/C8/C9/C10/C11/C12 benzene ring shown in Figure 8. Further, the hydrogen bond was established and the data obtained tabulated in Table 3 with centroid and carbon numbers which are involved in hydrogen bond formation.

**Table 3.** Hydrogen-bond exhibited by compound **5b**, in (Å, °); where Cg1 is the centroid for the ring C7/C8/C9/ C10/C11 /C12

D-HA	D-H	H <i>A</i>	DA	<i>D</i> -H <i>A</i>
$C4-H4Cg1^{ii}$	0.93	2.80	3.5227	135

Symmetry code (ii): −*x*+1, −*y*+1, −*z*.

## 4. Conclusions

In the present study, a library of nine compounds as a homologous series of new symmetric naphthalene derivatives have been prepared and characterized to determine their liquid crystal properties. All the molecular structures were confirmed by different spectroscopic techniques and elemental analysis. The POM and DSC analysis reveals the presence of smectic and nematic phase. The thermal behavior of all the compounds and their mesophase thermal stabilities are comparable with each other and it is in good agreement with the practical values. The ORTEP diagram generated by single crystal structure analysis also supports and confirms the molecular structure with necessary chemical compositions.

## Acknowledgement

The authors are thankful to SIF for NMR spectral analysis, Indian Institute of Science, Bengaluru. BSPM thank the VGST (Grant No: VGST/CISEE/GRD319) Karnataka. Thanks to K. N. Vasudha for DSC and X-ray analysis.

## **Additional Information**

Crystallographic data for **5b** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the

data can be obtained free of charge on quoting the depository numbers CCDC-985487. (Fax: +44-1223-336-033; E-Mail: deposit-@ccdc.cam.ac.uk).

## References

- W. Drzewinski, Esters of (R)-2-(6-hydroxynaphthalene-2-yl)octane, Liq. Cryst. 40 (2013) 1060-1066.
- [2] M. L. Rahman, H. T. Srinivasa, M. Y. Mashitah, H. C. Kwong, C. K. Quah,
   6-Cyanonaphthalen-2-yl 4-hexylbenzoate, Acta Cryst. E70 (2014) o620.
- [3] M. K. Usha, H. V. Deepak, H. T. Srinivasa, M. B. Nanda Prakash, R. Somashekar, D. Revannasiddaiah, Synthesis and x-ray studies of liquid crystalline 2-cyanonaphthalen-6yl 4-(3,7-dimethyloctyloxy)benzoate, The third national conference on applied physics and materials science (APMS-2015), 150-152, [ISBN 978-93-82570-64-6].
- [4] V. Novotna, J. Z urek, V. Kozmik, J. Svoboda, M. Glogarova, J. Kroupa, D. Pociecha, Novel hockey-stick mesogens with the nematic, synclinic and anticlinic smectic C phase sequence, Liq. Cryst. 35 (2008) 1023-1036.
- [5] S. L. Wu, T. C. Lin, Ferroelectric liquid crystals derived from
   (S)-2-(6-methoxy-2-naphthyl)propionic acid with non-fluorinated or semi-fluorinated alkanes at a chiral terminal chain, Liq. Cryst. 32 (2005) 797-804.
- [6] C. Rodridgo, A. A. Vieira, F. Ely, H. Gallardo, Synthesis and characterization of luminescent hockey stick-shaped liquid crystalline compounds, Liq. Cryst. 33 (2006) 381-390.
- [7] A. A. Vieira, R. Cristiano, A. J. Bortoluzzi, H. Gallardo, Luminescent 2,1,3benzothiadiazole-based liquid crystalline compounds, J. Mol. Str. 875 (2008) 364-371.
- [8] V. Kozmik, P. Polasek, A. Seidler, M. Kohout, J. Svoboda, V. Novotna, M. Glogarova,
   D. Pociecha, The effect of a thiophene ring in the outer position on mesomorphic properties of the bent-shaped liquid crystals, J. Mater. Chem. 20 (2010) 7430-7435.
- [9] W. L. Tasi, S. W. Yeh, M. J. Hsie, H. C. Lee, C. M. Fu, Effect of the naphthalene moiety on

the mesogenic properties of ferroelectric liquid crystals containing diastereomeric propionic acids, Liq. Cryst. 29 (2002) 251-253.

- [10] H.-G. Moon, M. -S. Jung, J. -H. Chang, New liquid crystals and liquid crystalline thermosets based on wholly aromatic rigid-rod mesogens. Macromol. Res. 19 (2011) 2-7.
- [11] M. Hird, Fluorinated liquid crystals-properties and applications, Chem. Soc. Rev. 36 (2007) 2070-2095.
- [12] D. Pauluth, K. Tarumi, Advanced liquid crystals for television, J. Mater. Chem. 14 (2004) 1219-1227.
- [13] S. Senthil, V.R. Kamalraj, S.L. Wu, Synthesis and characterization of ferroelectric liquid crystal dimers containing thioester and carboxylate linking groups in the inner side of the molecule, J. Mol. Stru. 886 (2008) 175–182.
- [14] Y. Gonzalez, M. B. Ros, J. L. Serrano, Naphthalene system as origin of unconventionally shaped ferroelectric liquid crystals, Chem. Mater. 6 (1994) 1516-1525.
- [15] V. Kozmík, E. Rodinova, T. Prausova, J. Svoboda, V. Novotna, E. Gorecka, D. Pociechac, Mesogens with central naphthalene core substituted at various positions, Liq. Cryst. 44 (2017) 746-756.
- [16] W. L. Chia, C. W. Lin, Synthesis and thermotropic studies of a novel series of nematogenic liquid crystals 2-(6-alkoxynaphthalen-2-yl)-5-cyanopyridines, Liq. Cryst. 40 (2013) 922-931.
- [17] W. L. Chia, C. L. Li, C. H. Lin, Synthesis and mesomorphic studies on the series of 2-(4alkoxyphenyl)-5-phenylpyridines and 2-(6-alkoxynaphthalen-2-yl)-5-phenylpyridines, Liq. Cryst. 37 (2010) 23-30.
- [18] H. F. Hsu, W. C. Lin, Y. H. Lai, S. Y. Lin, Effects of reducing structural symmetry on mesophase behaviour: the synthesis and characterization of the 2-alkoxy-6-[4-(4alkoxyphenyl)buta-1,3-diynyl]naphthalenes, Liq. Cryst. 30 (2003) 939-944.

- [19] J. Lydon, Liq. Cryst. Chromonic liquid crystalline phases, 38 (2011) 1663-1681.
- [20] P. Luciana, C. Giuseppe, A. Antonio, Synthesis and characteristics of naphthalene derivatives: liquid crystal mesophase range, Annali di Chimica. 63 (1973) 195-199.
- [21] B. K. Chen, S. Y. Tsay, J. Y. Chen, Synthesis and properties of liquid crystalline polymers with low T<sub>m</sub> and broad mesophase temperature range, Polymer. 46 (2005) 8624-8633.
- [22] Q. Chen, M. Hird, Synthesis, mesomorphic behaviour and optical anisotropy of some novel liquid crystals with lateral and terminal fluoro substituents and a 2,6-disubstituted naphthalene core, Liq. Cryst. 42 (2015), 877-886.
- [23] S. P. Jonjzs, C. C. Faint, D. D. Edie, structural development in mesophase pitch based carbon fibers produced from naphthalene. Carbon 35 (1997) 1533-1543.
- [24] B. K. Sadashiva, V. Prasad, Mesomorphic properties of 1-(4'-dodecylbiphenyl-4-yl)-3-(2 or 3alkoxyphenyl)propane-1,3-diones: the influence of alkoxy-substituent position, J. Chem, Soc., Perkin Trans. 2 (1996) 755-759.
- [25] V. R. Patel, M. L. Chauhan, A. V. Doshi, Synthesis and study of a novel azoester mesogenic homologous series: 4-[4'-n-alkoxy benzoyloxy]-naphthylazo-4"-acetyl benzenes, Mol. Cryst. Liq. Cryst. 569 (2012) 57-63.
- [26] Bruker, APEX2, SAINT and SADABS. Bruker AXS Inc. 2013, Madison, Wisconsin, USA.
- [27] G. M. Sheldrick, A short history of SHELX, Acta Cryst. Sect. A. 64 (2008) 112-122.
- [28] G. M. Sheldrick, T. R. Schneider, Methods enzymol, 277 (1997) 319-343.
- [29] L. J. Farrugia, *WinGX* (Version 1.80.03). WinGX suite for small-molecule single-crystal crystallography, J. Appl. Crystallogr. 32 (1999) 837-838.

- [30] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, Mercury CSD 2.0 new features for the visualization and investigation of crystal structures, J. Appl. Cryst. 41 (2008) 466-470.
- [31] J. J. Han, X. Y. Chang, Y. M. Wang, M. L. Pang, J. B. Meng, Synthesis, crystal structures, mesomorphic and photo-luminescent properties of 1,3,4-thia(oxa)diazole-based compounds with a terminal methoxy or methylthio group, J. Mol. Str. 937 (2009) 122-130.
- [32] H. T. Srinivasa, M. A. Venkatesha, M. B. Madhusudana Reddy, Effect of lateral substituent and chain length on mesomorphic properties of novel alkoxy benzyloxy benzoates of cyanophenyl rod-shaped compounds, J. Therm. Anal. Calorim. 119 (2015) 1887-1893.
- [33] S. Radhika, H.T. Srinivasa, B.K. Sadashiva, Anticlinic smectic C phase in new and novel five-ring hockey stick-shaped compounds, Liq. Cryst. 38 (2011) 785-792.
- [34] H. T. Srinivasa, New symmetric azobenzene molecules of varied central cores: Synthesis and characterisation for liquid crystalline properties, Liq. Cryst. 44 (2017) 1384-1393.
- [35] S. K. Lee, M. Tokita, Y. Shimbo, K. -T. Kang, H. Takezoe, J. Watanabe, Ferroelectric and antiferroelectric behavior in chiral bent-shaped molecules with an asymmetric central naphthalene core, Bull. Korean Chem. Soc. 28 (2007) 2241.
- [36] M. AbdulKarim-Talaq, R. Y. Alwari, H. T. Srinivasa, S. M. H. Al-Majidi, O. I.
   Alajrawy. Preparation, spectral and thermal properties of new isoflavone derivatives: mesomorphic properties and DFT studies, Liq. Cryst. (2018) DOI: 10.1080/02678292.2018.1475685
- [37] S. -L. Wu, K. -J. Wang, M. -C. Yu. Structural effects on the mesomorphic properties of chiral liquid crystal materials derived from optically active (R)-3-alkylmercapto-2methylpropionic acids, Ferroelectrics, 2002, 276, 93-100.

[38] P. L. Praveen, D. P. Ojha. Photosensitivity, substituent and solvent-induced shifts in UVvisible absorption bands of naphthyl-ester liquid crystals: a comparative theoretical approach. Liq. Cryst. 41 (2014) 872-882.

- > We have synthesized symmetric naphthalene centered molecules
- > All the molecules were characterized by UV, IR, NMR analysis
- Liquid crystal property was evaluated by DSC and POM techniques
- Single crystal structure was confirmed by X-ray analysis