

# Bent Shaped 1,3,4-Oxadiazole/Thiadiazole heterocyclic rings containing liquid crystals

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**Abstract.** Two series of bent shaped 1,3,4-oxadiazole/thiadiazole heterocyclic ring containing liquid crystalline (LC) compounds were synthesized and characterized by FT-IR,  $^1\text{H}$ ,  $^{13}\text{C}$ -NMR and ESI-Mass spectroscopic techniques. Liquid crystal properties were investigated by polarized optical microscopy and differential scanning calorimetry. All the compounds exhibited mesophases such as nematic, smectic A and smectic C phases. The liquid crystalline effects were ascertained by changing the central atom in the heterocyclic ring and by increasing the length of the terminal alkyloxy chains which bring considerable improvements on the mesomorphic properties. The absorption and emission spectral studies of all the compounds were investigated and confirmed.

**Keywords.** Schiff's base; 1,3,4-oxadiazoles; 1,3,4-thiadiazoles; liquid crystals

## 1. Introduction

Liquid crystalline compounds containing heterocyclic ring have been synthesized by many research groups because of their versatility and wide range of applications like optical, electrical and biological fields.<sup>1–3</sup> Particularly, the compounds containing 1,3,4-oxadiazole/thiadiazole moiety have been extensively investigated because their high quantum yield of luminescence, thermal stability and electron-transport properties.<sup>2</sup> 1,3,4-oxadiazole/thiadiazole containing Schiff's base as core is a new type of liquid crystalline compound with bent shape which makes this compound as a convenient model for the study of molecular design dependence on liquid crystal properties.<sup>3</sup> Among the heterocyclic mesogens, much attention has been paid to 2,5-disubstituted 1,3,4-oxadiazole/thiadiazole owing to their rich mesophases and good thermal stability attributes.<sup>4</sup> Furthermore, this type of liquid crystals emit strong fluorescence and are potentially useful as functional materials.<sup>5,6</sup> On the other hand, bridging ester and imine groups<sup>7–9</sup> as functional central moiety enhances the mesomorphic property. Incorporation of five-membered thiadiazole ring into the principal structure of calamitic mesogen was studied by Parra *et al.*<sup>10</sup> In contrast, Dimitrowa *et al.* have synthesized compounds of 1,3,4-oxadiazole derivatives with oxadiazole ring in the central position and revealed that replacement of sulphur by oxygen atom causes complete loss of liquid crystalline properties.<sup>11</sup>

Compared to 1,3,4-oxadiazole unit, the analogous 1,3,4-thiadiazole moiety is often used to construct rod-like mesogens which are regarded to be more beneficial in forming stable thermotropic nematic and smectic phases than 1,3,4-oxadiazole.<sup>12</sup> Recently, effect of short end groups, length of alkoxy chains and mesogenic cores on mesomorphic properties of 1,3,4-oxadiazole/thiadiazole compounds have been investigated.<sup>13–15</sup> Till now, quite a lot of mesogenic 1,3,4-oxadiazoles with various molecular shapes such as rod-shaped,<sup>16–18</sup> disk-like<sup>19</sup> and star-shaped mesogens<sup>20,21</sup> have been studied.

On the other hand, the corresponding 1,3,4-thiadiazole are barely reported in the literature, although 1,3,4-thiadiazole is regarded as being more favourable to form mesophases in a wide mesomorphic temperature range.<sup>22,23</sup> The formation of 1,3,4-thiadiazole ring is usually carried out by sulphuration of the N, N'-diacylhydrazines using reagents such as  $\text{P}_4\text{S}_{10}$ <sup>24</sup> and Lawesson's reagent<sup>25</sup> in anhydrous hydrocarbon solvent at elevated temperatures.

The present work deals with studies on two series of bent shaped azomethine containing low molar mass organic compounds containing 1,3,4-oxadiazole/thiadiazole derivatives. Two combinations of N, N'-((1,3,4-oxadiazole-2,5-diyl)bis(4,1-phenylene))bis(1-(4-(alkyloxy)phenyl)methanimine) and their corresponding 1,3,4-thiadiazole analogues have been characterized using spectral and analytical methods. The relationship between their molecular structures and liquid crystal properties are discussed. Liquid crystalline properties measured by Differential Scanning Calorimetry (DSC)

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and Hot stage Optical Polarized Microscopy (HOPM) are correlated to the length of alkoxy groups.

## 2. Experimental

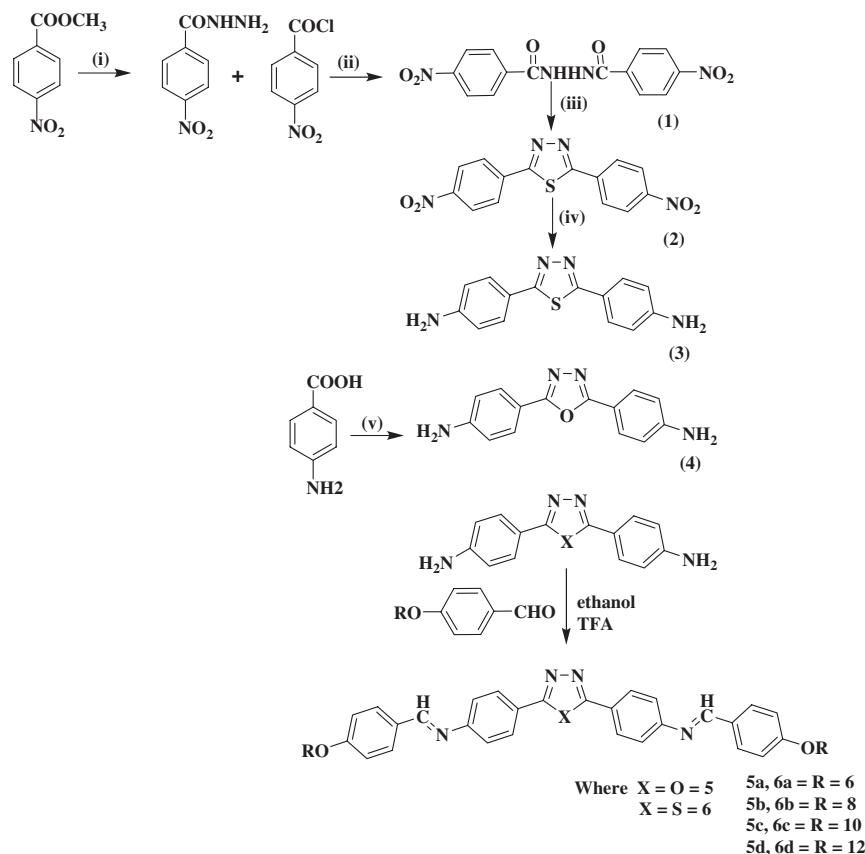
### 2.1 Materials and Methods

All reagents and starting materials were purchased from Aldrich and Merck (India) and used without further purification unless otherwise noted. 4-Nitrobenzoyl chloride, 4-aminobenzoic acid, methyl 4-nitrobenzoate, pyridine, stannous chloride, N-methyl-2-pyrrolidone (NMP) were kept under dry atmosphere of nitrogen. Lawesson's reagent and hydrazine hydrate were used as received. Solvents such as dry toluene, tetrahydrofuran, ethanol and dichloromethane were purified by the reported procedure.<sup>26</sup> Elemental analysis of the compounds was determined by Heraeus CHN analyzer. The FT-IR spectra of the compounds were obtained from Perkin Elmer FT-IR spectrometer using KBr pellets. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker 400 MHz spectrometer in CDCl<sub>3</sub> and THF-d<sub>8</sub> with TMS as

an internal standard. ESI Mass spectra were recorded on Q-ToF Mass spectrometer. DSC measurement was carried out at a heating rate of 5°C min<sup>-1</sup>, and samples taken in an aluminium pan with a pierced lid under dry nitrogen atmosphere with an empty pan as reference on a TA instrument (model Q10). The liquid crystal textures of the compounds were observed using Euromex HOPM equipped with a Linkem HFS91 heating stage and a TP-93 temperature programmer. Samples were placed in between two thin glass cover slips and melted with heating and cooling at the rate of 1°C min<sup>-1</sup>. The photographs were taken using Canon 1000 D camera. The absorbance spectra of the compounds were measured using Shimadzu UV-1650 spectrophotometer using chloroform as solvent. Fluorescence measurements in a quartz cell (1 cm × 1 cm) were taken using an LS-45 fluorescence spectrometer (Perkin Elmer).

### 2.2 Synthesis

Synthesis of two series of compounds **5a-5d** and **6a-6d** is outlined in scheme 1. 2,5-bis-(4-aminophenyl)-1,3,



Reagents and conditions (i) Hydrazine hydrate, Ethanol, (ii) NMP, Pyridine, rt  
(iii) Lawesson's reagent, toluene, reflux 24h (iv) SnCl<sub>2</sub>, ethanol, reflux 24h (v) N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O / PPA

**Scheme 1.** Synthesis of compounds **5a-5d** and **6a-6d**.

4-oxadiazole (**4**) was synthesized by following the reported procedure.<sup>27</sup> The target compounds **5a-5d** were synthesized by utilizing Schiff's-base reaction by taking 2,5-bis-(4-aminophenyl)-1,3,4-oxadiazole and *n*-(alkyloxy)benzaldehyde.<sup>28</sup> 4,4'-(1,3,4-thiadiazole-2,5-diyl)dianiline (**3**) was synthesized by starting with 4-nitromethylbenzoate followed by condensation of hydrazine hydrate, which yielded 4-nitrobenzohydrazide.<sup>29</sup> 4-nitrobenzohydrazide was allowed to react with 4-nitrobenzoylchloride, affording the corresponding diacylhydrazines (**1**). Then, it was allowed to react with Lawesson's reagent, which led to the formation of 2,5-bis(4-nitrophenyl)-1,3,4-thiadiazole (**2**). Reduction of nitro group in the compounds with stannous chloride gave 4,4'-(1,3,4-thiadiazole-2,5-diyl)dianiline (**3**).

**2.2a Synthesis of 2, 5-bis(4-nitrophenyl)-1,3,4-thiadiazole (2):** The 4-nitrobenzoylchloride (7.8 g, 4.2 mmol) was added to a solution containing 4-nitrobenzohydrazide (7.6 g, 4.2 mmol) and 30 mmol of pyridine in 50 mL of NMP. The reaction mixture was stirred for 24 h at room temperature and then poured into water. The solid product was filtered off and crystallized from ethanol. Subsequently, the solution of corresponding 4-nitro-N'-(4-nitrobenzoyl)benzohydrazide (6.54 g, 1.9 mmol) (**1**) in Lawesson's reagent (8.8 g, 2.1 mmol) and dry toluene (50 mL) were refluxed for 24 h and then cooled to room temperature. Toluene was removed under reduced pressure and the residue was poured into ethanol. The precipitated product was filtered and recrystallized from ethanol with 69% yield. M.p. 245-247°C. FT-IR (KBr,  $\text{cm}^{-1}$ ): 1596 (C=N), 1560 (C=C), 1429 (1,3,4-thiadiazole), 1254  $\text{cm}^{-1}$  ( $\text{NO}_2$ ).  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ ):  $\delta$  8.09 (d, 4H,  $J = 6.8$  Hz), 8.29 (d, 4H,  $J = 7.1$  Hz).  $^{13}\text{C}$  NMR (100 MHz, THF- $d_8$ ):  $\delta$  124, 128, 138, 147 (aromatic), 173 (1,3,4-thiadiazole). Elemental Analysis: Calculated for  $\text{C}_{14}\text{H}_8\text{N}_4\text{O}_4\text{S}$  C 51.02 N 17.06 H 2.45%; found C 51.07 N 17.01 H 2.49%.

**2.2b Synthesis of 4, 4'-(1,3,4-thiadiazole-2, 5-diyl)dianiline (3):** A mixture of corresponding nitro-thiadiazole (**2**) (1 g, 0.3 mmol), stannous chloride (6.83 g, 3 mmol) and absolute ethanol (60 mL) were refluxed for 24 h. The resulting solution was brought to room temperature and neutralized with 10% aqueous sodium hydroxide to get pH 7. The precipitate formed was filtered and dried in a vacuum oven for 12 h. The dried solid was allowed to stir with chloroform for 2 h and insoluble solid filtered off. The solid obtained after evaporation of chloroform was recrystallized from ethanol to yield 69%. M.p. 204-206°C. FT-IR (KBr,

$\text{cm}^{-1}$ ): 1604 (CH=N), 1516 (C=C), 1455 (1,3,4-thiadiazole), 3463 ( $\text{NH}_2$ ).  $^1\text{H}$  NMR (THF- $d_8$ ):  $\delta$  7.31-7.29 (d, Ar-H, 4H,  $J = 6.7$  Hz), 6.76-6.74 (d, Ar-H, 4H,  $J = 5.91$  Hz), 4.70 (s, Ar-NH, 4H).  $^{13}\text{C}$  NMR (100 MHz, THF- $d_8$ ):  $\delta$  93.5, 94.7, 118.5, 80.9 (aromatic), 128 (1,3,4-thiadiazole). ESI-MS:  $m/z$ , 269.06. Elemental Analysis: Calculated for  $\text{C}_{14}\text{H}_{12}\text{N}_4\text{S}$  C 62.66 N 20.87 H 4.50%; found C 61.98 N 21.02 H 4.10%.

### 2.3 Synthesis of compounds 5a-5d and 6a-6d

**2.3a *N,N'*-((1,3,4-oxadiazole-2,5-diyl)bis(4,1-phenylene))bis(1-(4-(hexyloxy)phenyl) methanimine) (5a):** 4,4'-(1,3,4-oxadiazole-2,5-diyl)dianiline (**4**) (0.1 gm, 0.39 mmol) and 4-(alkyloxy)benzaldehyde (0.16 gm, 0.79 mmol) were mixed with ethanol (20 mL) and one drop of TFA was added and refluxed for 24 h. The solid obtained after evaporation of chloroform was recrystallized from ethanol. Similar procedure was adapted to synthesize other alkyl compounds (**5b-5d**; scheme 1) with yield: **5a** 61%, **5b** 56%, **5c** 65% and **5d** 58%.

(**5a**): FT-IR (KBr,  $\text{cm}^{-1}$ ): 1596 (C=N), 1601 (CH=N), 1422(1,3,4-oxadiazole), 2954 ( $-\text{C}_{\text{sp}}^3-\text{H}$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.94 (s, Ar-CH=N-, 2H), 7.80 – 6.94 (m, 16H), 4.01 (t, 4H,  $J = 6.4$  Hz), 1.81 (q,  $J = 6.4$  Hz, 4H), 1.39 – 1.27 (m, 12H), 0.82 (t, 6H,  $J = 6.1$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 14.1, 22.5, 25.4, 29.3, 31.9 (aliphatic), 68.3 (methoxy), 114.0, 121.3, 127.6, 128.4, 129.8, 131.7, 149.5 (aromatic), 160.3 (CH=N), 161.4, 164.5 (1,3,4-oxadiazole). Elemental Analysis: Calculated for  $\text{C}_{40}\text{H}_{44}\text{N}_4\text{O}_3$  C 76.38 N 8.91 H 7.05%; found C 76.21 N 8.78 H 7.0%.

**2.3b *N,N'*-((1,3,4-oxadiazole-2,5-diyl)bis(4,1-phenylene))bis(1-(4-(octyloxy)phenyl) methanimine) (5b)** FT-IR (KBr,  $\text{cm}^{-1}$ ): 1594 (C=N), 1607 (CH=N), 1426 (1,3,4-oxadiazole), 2952 ( $-\text{C}_{\text{sp}}^3-\text{H}$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.95 (s, Ar-CH=N-, 2H), 7.82 – 6.94 (m, 16H), 4.05 (t, 4H,  $J = 6.3$  Hz), 1.80 (q,  $J = 6.3$  Hz, 4H), 1.40 – 1.24 (m, 20H), 0.83 (t, 6H,  $J = 5.8$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 14.0, 22.5, 25.3, 29.0, 31.8 (aliphatic), 68.2 (methoxy), 114.0, 121.5, 127.5, 128.4, 129.4, 131.8, 149.2 (aromatic), 160.0 (CH=N), 161.3, 164.0 (1,3,4-oxadiazole). Elemental Analysis: Calculated for  $\text{C}_{44}\text{H}_{52}\text{N}_4\text{O}_3$  C 77.15 N 8.18 H 7.65%; found C 77.10 N 8.12 H 7.58%.

**2.3c *N,N'*-((1,3,4-oxadiazole-2,5-diyl)bis(4,1-phenylene))bis(1-(4-(decyloxy)phenyl) methanimine) (5c):** FT-IR (KBr,  $\text{cm}^{-1}$ ): 1590 (C=N), 1604 (CH=N), 1429 (1,3,4-oxadiazole), 2952 ( $-\text{C}_{\text{sp}}^3-\text{H}$ ).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.96 (s, Ar-CH=N-, 2H), 7.83

– 6.95 (m, 16H), 4.04 (t, 4H,  $J = 6.5$  Hz), 1.80 (q,  $J = 6.5$  Hz, 4H), 1.42 – 1.23 (m, 28H), 0.85 (t, 6H,  $J = 5.9$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 14.2, 22.5, 25.6, 29.3, 31.9 (aliphatic), 68.6 (methoxy), 114.1, 121.4, 127.5, 128.3, 129.6, 131.8, 149.2 (aromatic), 160.2 (CH=N), 161.3, 164.1 (1,3,4-oxadiazole). Elemental Analysis: Calculated for  $\text{C}_{48}\text{H}_{60}\text{N}_4\text{O}_3$  C 77.80 N 8.15 H 7.56%; found C 77.76 N 8.10 H 7.52%.

2.3d *N,N'*-((1,3,4-oxadiazole-2,5-diyl)bis(4,1-phenylene))bis(1-(4-(dodecyloxy)phenyl) methanimine) (**5d**): FT-IR (KBr,  $\text{cm}^{-1}$ ): 1591 (C=N), 1610 (CH=N), 1420 (1,3,4-oxadiazole), 2952 ( $-\text{C}_{\text{sp}^3}\text{-H}$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.97 (s, Ar-CH=N-, 2H), 7.84 – 6.97 (m, 16H), 4.06 (t, 4H,  $J = 6.6$  Hz), 1.83 (q,  $J = 6.4$  Hz, 4H), 1.41 – 1.26 (m, 36H), 0.85 (t, 6H,  $J = 5.9$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 14.1, 22.6, 25.4, 29.0, 31.9 (aliphatic), 68.4 (methoxy), 114.1, 121.5, 127.8, 128.4, 129.7, 131.9, 149.3 (aromatic), 160.2 (CH=N), 161.2, 164.2 (1,3,4-oxadiazole). Elemental Analysis: Calculated for  $\text{C}_{52}\text{H}_{68}\text{N}_4\text{O}_3$  C 78.34 N 8.59 H 7.02%; found C 78.03 N 8.52 H 7.0%.

2.3e *N,N'*-((1,3,4-thiadiazole-2,5-diyl)bis(4,1-phenylene))bis(1-(4-(hexyloxy)phenyl) methanimine) (**6a**): The similar procedure was adapted to synthesis of 1,3,4-thiadiazole compounds (**6a-6d**; scheme 1) with yield: **6a** 51%, **6b** 56%, **6c** 49% and **6d** 53%.

**6a**: FT-IR (KBr,  $\text{cm}^{-1}$ ): 1591 (C=N), 1607 (CH=N), 1428 (1,3,4-thiadiazole), 2936 ( $-\text{C}_{\text{sp}^3}\text{-H}$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.67 (s, Ar-CH=N-, 2H), 7.74 – 6.94 (m, 16H), 4.05 (t, 4H,  $J = 6.4$  Hz), 1.82 (q,  $J = 6.1$  Hz, 4H), 1.40 – 1.25 (m, 12H), 0.84 (t, 6H,  $J = 5.8$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 14.2, 22.6, 25.3, 29.0, 31.8 (aliphatic), 68.4 (methoxy), 114.2, 121.5, 127.7, 128.4, 129.6, 131.8, 149.2 (aromatic), 160.1 (CH=N), 161.3, 164.1 (1,3,4-thiadiazole). Elemental Analysis: Calculated for  $\text{C}_{40}\text{H}_{44}\text{N}_4\text{O}_2\text{S}$  C 74.50 N 8.68 H 6.87%; found C 74.28 N 8.56 H 6.74%.

2.3f *N,N'*-((1,3,4-thiadiazole-2,5-diyl)bis(4,1-phenylene))bis(1-(4-(octyloxy)phenyl) methanimine) (**6b**): FT-IR (KBr,  $\text{cm}^{-1}$ ): 1595 (C=N), 1602 (CH=N), 1423 (1,3,4-thiadiazole), 2932 ( $-\text{C}_{\text{sp}^3}\text{-H}$ ).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.64 (s, Ar-CH=N-, 2H), 7.72 – 6.96 (m, 16H), 4.05 (t, 4H,  $J = 6.2$  Hz), 1.82 (q,  $J = 6.2$  Hz, 4H), 1.42 – 1.25 (m, 20H), 0.85 (t, 6H,  $J = 5.9$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 14.1, 22.3, 25.4, 29.2, 31.9 (aliphatic), 68.5 (methoxy), 114.1, 121.4, 127.8, 128.3, 129.6, 131.7, 149.4 (aromatic), 160.3 (CH=N), 161.4, 164.3 (1,3,4-thiadiazole). Elemental Analysis:

Calculated for  $\text{C}_{48}\text{H}_{52}\text{N}_4\text{O}_2\text{S}$  C 76.96 N 7.48 H 6.99%; found C 76.88 N 7.33 H 6.85%.

2.3g *N,N'*-((1,3,4-thiadiazole-2,5-diyl)bis(4,1-phenylene))bis(1-(4-(decyloxy)phenyl) methanimine) (**6c**): FT-IR (KBr,  $\text{cm}^{-1}$ ): 1596 (C=N), 1606 (CH=N), 1418 (1,3,4-thiadiazole), 2941 ( $-\text{C}_{\text{sp}^3}\text{-H}$ ).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.65 (s, Ar-CH=N-, 2H), 7.73 – 6.54 (m, 16H), 4.04 (t, 4H,  $J = 6.5$  Hz), 1.82 (q,  $J = 6.0$  Hz, 4H), 1.42 – 1.22 (m, 28H), 0.84 (t, 6H,  $J = 5.7$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 14.0, 22.5, 25.4, 29.2, 31.9 (aliphatic), 68.6 (methoxy), 114.2, 121.6, 127.7, 128.4, 129.5, 131.8, 149.4 (aromatic), 160.1 (CH=N), 161.3, 164.4 (1,3,4-thiadiazole). Elemental Analysis: Calculated for  $\text{C}_{48}\text{H}_{60}\text{N}_4\text{O}_2\text{S}$  C 76.14 N 7.40 H 7.98%; found C 76.10 N 7.34 H 7.88 %.

2.3h *N,N'*-((1,3,4-thiadiazole-2,5-diyl)bis(4,1-phenylene))bis(1-(4-(dodecyloxy)phenyl) methanimine) (**6d**): FT-IR (KBr,  $\text{cm}^{-1}$ ): 1591 (C=N), 1606 (CH=N), 1423 (1,3,4-thiadiazole), 2935 ( $-\text{C}_{\text{sp}^3}\text{-H}$ ).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.66 (s, Ar-CH=N, 2H), 7.72–6.89 (m, 16H), 4.03 (t, 4H,  $J = 6.3$  Hz), 1.83 (q,  $J = 6.3$  Hz, 4H), 1.42–1.24 (m, 36H), 0.83 (t, 6H,  $J = 5.8$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 14.0, 22.5, 25.4, 29.3, 31.9 (aliphatic), 68.7 (methoxy), 114.3, 121.4, 127.9, 128.5, 129.6, 131.7, 149.5 (aromatic), 160.4 (CH=N), 161.2, 164.3 (1,3,4-thiadiazole). Elemental Analysis: Calculated for  $\text{C}_{52}\text{H}_{68}\text{N}_4\text{O}_2\text{S}$  C 79.01 N 6.88 H 8.42%; found C 79.0 N 6.79 H 8.37%.

### 3. Results and Discussion

#### 3.1 Mesophase characterization and thermal properties

The liquid crystal properties of the compounds **5a-5d** and **6a-6d** were studied using DSC. Further, liquid crystal textures were confirmed using HOPM. The compounds **5a-5d** and **6a-6d** were found to exhibit mesomorphism and their transition temperatures associated enthalpy values are summarized in table 1. The phase transition temperatures observed by polarising optical microscopy were in good agreement with the corresponding DSC thermograms. Microphotographs of observed textures of **5a-5d** are tabulated in figure 1. Among them,  $R = 4$  was reported earlier by Luminita Marin et al., and it was repeated for comparison needed for the present study.<sup>28</sup> The synthesized compounds in series I, **5a-5d** with varying terminal alkyl chain length ( $R = 6, 8, 10$  and 12) did not render liquid crystalline phase, while increase in terminal alkyl chain

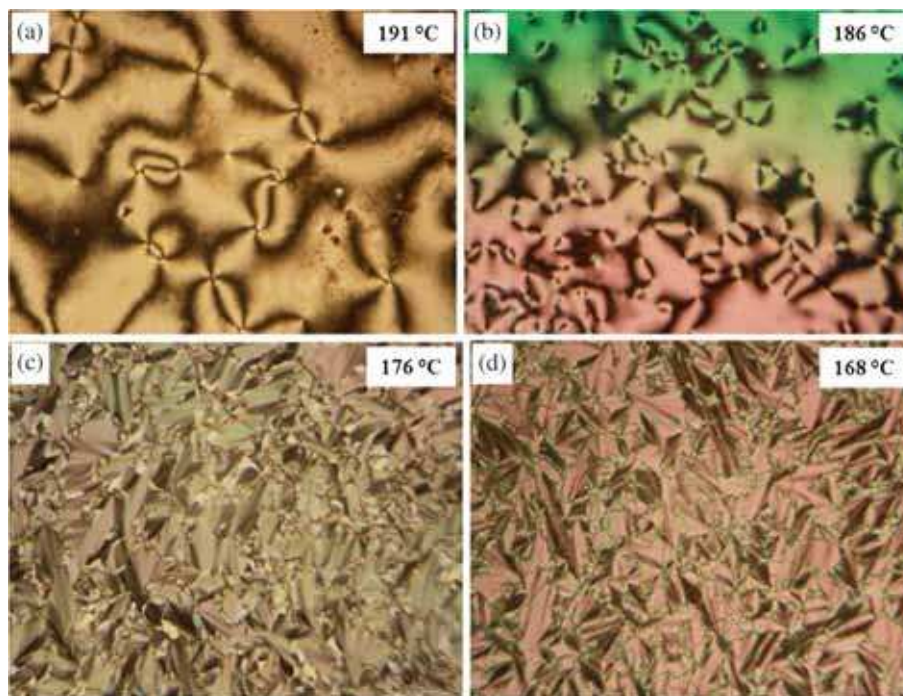
**Table 1.** Phase transition temperatures (°C) and enthalpies (kJ mol<sup>-1</sup>, in parentheses) of **5a-5d** and **6a-6d** compounds.

Compound	Phase transitions	
	Heating	Cooling
<b>5a</b>	Cr 136 (14.9) Cr <sub>1</sub> 158 (20.9) N 213 (12.7) I	I 210 (11.5) N 138 (22.0) Cr
<b>5b</b>	Cr 128 (14.5) Cr <sub>1</sub> 154 (21.7) N 208 (13.4) I	I 205 (12.4) N 130 (22.2) Cr
<b>5c</b>	Cr 127 (14.3) SmA 167 (21.9) N 198 (14.1) I	I 195 (13.2) N 188 (1.0) SmA 126 (22.6) Cr
<b>5d</b>	Cr 126 (14.0) SmC 172 (22.4) N 196 (14.7) I	I 190 (13.7) N 178 (1.6) SmC 136 (23.2) Cr
<b>6a</b>	Cr 98 (12.8) Cr <sub>1</sub> 210 (21.3) N 310 (9.6) I	I 307 (0.9) N 140 (15.1) Cr
<b>6b</b>	Cr 104 (11.2) N 295 (9.7) I	I 293 (0.6) N 135 (14.5) Cr
<b>6c</b>	Cr 110 (10.3) SmA 288 (9.8) I	I 286 (0.5) SmA 131 (15.5) Cr
<b>6d</b>	Cr 114 (6.4) SmC 258 (0.9) N 279 (10.6) I	I 277 (0.4) N 269 (1.9) SmC 127 (16.7) Cr

<sup>a</sup>Cr= crystal phase; N = Nematic phase; SmA = Smectic A phase; SmC= Smectic C phase; I = isotropic liquid.

length (compounds **5a**, **5b**) with shorter alkyloxy chain length (R = 6 and 8) exhibited enantiotropic nematic phase, assigned from the typical schlieren or thread-like textures<sup>30</sup> as indicated in figure 1(a, b) for **5a**. The corresponding DSC data for compound **5b** are included in figure S6 in Supplementary Information. While increasing alkyloxy chain length (R = 10 and 12), compounds **5c** exhibits nematic and SmA, and compound **5d** demonstrated nematic and SmC textures as shown in figure 1(c, d). The compounds **5a-5d** exhibited enantiotropic behaviour of nematic and smectic phases in both heating and cooling cycles.

The representative DSC thermograms of compound **5d** are shown in figure 2. DSC thermogram of compound **5d** displayed three endothermic peaks at 124, 160 and 192°C which are assigned to transition from crystal to SmC, SmC to nematic and nematic to isotropic liquid, respectively. Whereas in the cooling cycle, two exothermic peaks were observed corresponding to transformation from isotropic liquid to nematic, nematic to SmC, SmC to crystalline phase. The transition temperatures of compounds **5a-5c** and their associated enthalpy changes are summarised in table 1. It can be seen that the isotropic transition temperature decreases



**Figure 1.** Microphotographs of compounds liquid crystal phase upon isotropic from cooling: (a) nematic texture observed for **5a**; (b) schlieren nematic texture observed for **5b**; (c) Smectic A phase observed for **5c**; (d) Smectic C phase observed for **5d**.

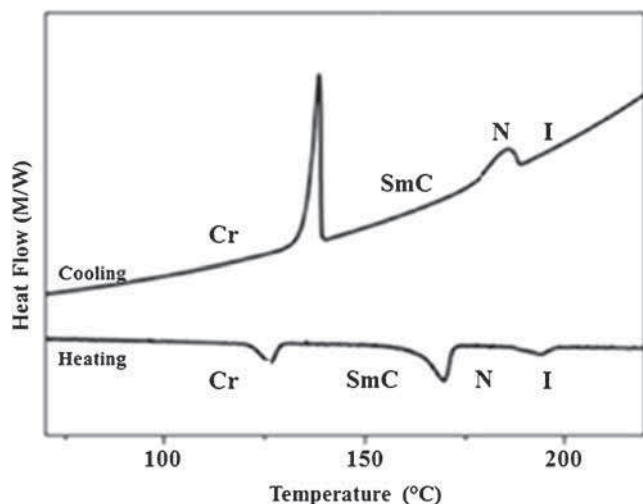


Figure 2. DSC thermogram of compound **5d**.

with increasing length of alkyl chain from 6 to 12. Thus, the mesophase is stabilized by extending the length of terminal alkyl chain. The nature of mesophases is influenced by change in length of alkyloxy chain and also by mesomorphic temperature.<sup>31</sup> An enhanced induced dipole-dipole interaction between terminal chains, leading to formation of more ordered smectic mesophase in rod-like mesogens is attributed to increase in terminal chain length.

The second series of 1,3,4-thiadiazole compounds **6a-6d** exhibit mesomorphism. The compounds **6a** and **6b** exhibit low order nematic phase, whereas when increasing the alkyl chain length in compound **6c** exhibits SmA texture and compound **6d** exhibits SmC texture. For R = 12 (**6d**), three endothermic peaks were observed in thermograms at 114, 258 and 279°C, which

are assigned to transitions from crystal to Smectic-C, Smectic-C to nematic and nematic to isotropic liquid, respectively. There are three exothermic peaks observed in cooling cycle, corresponding to transformation from isotropic state to nematic, nematic to Smectic-C and Smectic-C to crystalline state as indicated in table 1. The transition temperature of compounds **6a-6d** and their corresponding enthalpy changes are summarised in table 1. Mesomorphic behaviour was found to be dependent on the number of alkyl chains as well as central core. The 1,3,4-thiadiazole compound has a bent angle of 167–169° accounting for a lower dipole moment as compared to 1,3,4-oxadiazole whose bent angle is 134–136° and having a larger dipole moment. Hence, 1,3,4-thiadiazole compounds displayed higher mesomorphic temperature at about 310°C and 1,3,4-oxadiazole at 213°C.

### 3.2 Photophysical Properties

Representative absorption and fluorescence spectra of 1,3,4-oxadiazole (**5a**) and 1,3,4-thiadiazole (**6a**) compounds in chloroform ( $5 \times 10^{-6}$ M) are depicted in figure 3. The compound **5a** exhibits absorption maximum at 320 nm whereas, the corresponding 1,3,4-thiadiazole derivative **6a** indicates maximum at 335 nm. For the whole series, there is not much change in the absorption maximum due to variation of the terminal length of alkyl chain in the compounds at similar concentrations. The absorption at 293 and 287 nm were attributed to  $\pi$ - $\pi^*$  and, 320 and 335 nm are due to  $n$ - $\pi^*$  transitions involving the azomethine-phenyl-oxadiazole and thiadiazole segment, respectively.<sup>31</sup>

The compounds **5a** and **6a** excited at 320 and 335 nm, respectively, exhibit fluorescence maxima at 375 and

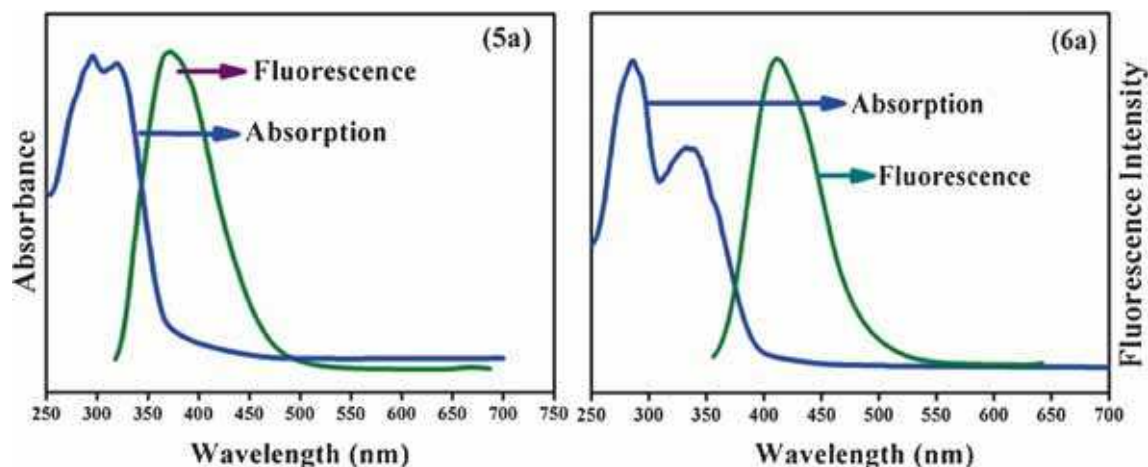


Figure 3. UV-absorption and emission spectra of compound **5a** and **6a**.

410 nm, respectively.<sup>32,33</sup> The observed larger red shift in the absorption and emission of thiadiazole compounds is ascribed to the higher polarizability and also attributed to the basic nature of sulphur atom in the thiadiazole moiety compared to the oxadiazole compounds.<sup>34</sup> In the entire series of compounds, **5a-5d** and **6a-6d**, with increasing length of alkoxy chain, there is no change in wavelength of absorption and emission bands as the increase in the alkoxy terminal chain does not influence on photophysical properties.

#### 4. Conclusions

Two series of bent shaped heterocyclic mesomorphic compounds containing 1,3,4-oxadiazole/thiadiazole with different lengths of terminal alkyloxy chain were synthesized and characterized. All the compounds were found to exhibit mesomorphism. The 1,3,4-oxadiazole compounds form more stable mesomorphic state. On the other hand, thiadiazole compounds display wide mesomorphic transition temperature. Their respective alkyloxy chains exhibit smectic C liquid crystalline phases. Hence, we can conclude that various changes in mesomorphic liquid crystal textures are effected by altering the heterocyclic core and by changing the length of terminal alkyloxy chain. These compounds also exhibit fluorescence.

#### Supplementary Information

Spectral and DSC data are given (figures S1–S5 and S6) which are available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

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