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# Alkyloxy azo-cinnamate ester based thermotropic liquid crystals and their photophysical investigations

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# Alkyloxy azo-cinnamate ester based thermotropic liquid crystals and their photophysical investigations

Chinnaiyan Selvarasu and Palaninathan Kannan

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#### ABSTRACT

Two series of rod shaped Schiff base containing azo-cinnamate thermotropic liquid crystalline compounds were synthesized and characterized. These molecules have four different alkyl spacers (n = 6, 8, 10, and 12) at one end and a dodecyloxy chain at another end (n = 12)which influence their liquid crystalline properties. Liquid crystallinity commence from six methylene spacer onwards in the series exhibiting with Nematic to Smectic-C mesophases. Analytical data confirm the molecular structures of homologues series of compounds. The characteristic texture of liquid crystalline phases obtained using polarizinglight microscope with a heating stage. The structural transformation of these liquid crystals was confirmed by differential scanning calorimetry. All the compounds exhibited various calamitic mesophases with wide mesomorphic temperature ranges. The relationship between structure and mesomorphic properties was discussed in framework of geometrical configuration of central unit, linking part, and length of alkoxy chains. Photosensitive azobenzene group undergoes photoisomerization under UV light and monitored by UV-Visible spectroscopy.

#### **KEYWORDS**

Azo-cinnamate; Nematic; photoisomerization; Smectic-C; thermotropic liquid crystal

### 1. Introduction

Azo compounds are exceedingly colored and studied broadly because of their excellent thermal and optical properties. These compounds are linked with two core groups having stepped core structure and maintaining molecular linearity, allowing mesophase formation and higher thermal stability [1,2]. Azobenzene based liquid crystalline materials are potentially interesting class of compounds due to their distinctive mechanical properties [3, 4]. The reversible cis-trans photoisomerization enables them promising candidate towards variety of applications involving photonic devices, [5] nonlinear optics, [6] optical data storage, [7, 8] photoswitching materials [9], liquid crystal display [10, 11], polarization holography [12], nanogels for drug delivery [13], and optical modulation [14]. Azobenzene functionalized photoresponsive materials have been widely explored, for instance surface photoalignment [15], photoinduced mass transport [16], and phase transition [17]. The liquid crystals obtained from the molecules possessing Schiff base linkages particularly attracted profound attention ascribed to their rich mesomorphism. Moreover, the Schiff base linkages are easily achievable under mild reaction conditions yielding molecules with high thermal stability, high purity and calamitic

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liquid crystalline texture [18, 19]. The mesomorphic nature of azo-cinnamate was found to be strongly depended on the nature of substituent in the terminal alkyl position. The presence of substituent at different alkyl positions on benzene ring (ortho-, meta-, and on attached alkyl chain) have influenced the liquid crystalline structure [20] along with crystal-mesophase and mesophase-isotropic transition temperatures as compared with their unsubstituted counterpart. The liquid crystalline behavior of the material is also governed by chemical nature of rod like mesogen attached to azobenzene. In a significant work, the extent of increasing temperature depends on the size and morphology of lateral substituents present in the molecules. It is proved that using appropriate combinations of these chemical parameters, one can modulate technological importance of liquid crystalline phases [21]. The complete understanding of structure property correlation of azo-cinnamate based esters is still challenging as the delicate modifications in structure of these molecules create an extreme impact on the liquid crystalline behavior [22–24].

The necessity in designing liquid crystalline compounds possessing double bond with an additional functional group in their molecular architecture brings mesomorphic behavior by revelation. The double bond of cinnamic acid has already been the keen area of research in the field of liquid crystals [25]. Thus upon bringing a double bond in skeletal framework enables electro-optical switching to mesomorphic properties [26], such as photoisomerization of molecules in liquid crystalline state [27]. The terminal substituents are of prime importance to obtain liquid crystals since compounds with flexible chain have intrinsic tendency to form a mesophase. A number of homologous series of mesogenic esters with terminal substituents of azobenzene and branched terminal alkyl chain have been reported previously. Recent work on cinnamate ester with terminal substituents of azobenzene by Kannan et al has demonstrated that they are of wide Nematic range, high Nematic-isotropic transition temperature and low melting points. Thus, molecules with azo core attract lot of interest as they form liquid crystalline (Nematic and Smectic) textures depending upon the terminal substituents attached to an azobenzene [28]. In a significant work by Yang et al. have demonstrated that self-assembled azobenzene substituted compounds bearing six or eleven methylene segments exhibited oily, streaky, and cholesteric phases [29]. Furthermore, Sadashiva et al. reported synthesis and mesomorphic property studies on certain esters of trans-4-n-alkoxycinnamic acid and trans-4-n-alkoxy-a-methylcinnamic acid with branchedchain alkyl tails exhibit ferroelectric and antiferroelectric phases [30]. Vora and Rajput [31] reported a binary mixture of cinnamate esters indicates a wide range of Nematic and Smectic mesophases.

In this article, we report the study on mesophase stabilities of Schiff base containing azo and ester linkages in the molecular frameworks. The initially obtained results encouraged us to synthesize compounds of similar family (azo and ester) facilitating further understanding of the effect central linkage and spacer length on mesomorphism. The series of compounds obtained were based on higher spacer length (n = 12) on one end of the cinnamate ester and with tuned azobenzene and ester linkages possessing different terminal chain lengths (n = 6, 8, 10, and 12) on the other end. We have obtained an improved liquid crystalline property, being geometrically closely related to known rod shaped molecules, upon introduction of dodeclyoxycinnamate group, containing azo and ester linkage seemed to be particularly economic and straightforward. The mesomorphic behavior was primarily controlled mainly by length of alkyl chain and character of olefinic group bearing cinnamate group. Structural parameters of different calamitic phases were carefully analyzed and compared. Furthermore, this observation provides an in-sight on significance from the fact that introduction of an azo linkage in homologues series involve a new dimension to this field, known as photochromism. The photophysical behavior (trans-cis isomerization) in azo group functionalized molecules within tetrahydrofuran medium was also explored.

### 2. Experimental section

### 2.1. Materials

4-Hydroxycinnamic acid (Sigma-Aldrich, India), triethylamine, trifluoroacetic acid (TFA), hydrochloric acid, thionyl chloride (Merck, India), 4-hydroxybenzaldehyde, and potassium dichromate were used as received. Solvents such as benzene, ethanol are purified by reported procedure [32].

#### 2.2. Instrumentation

The crude samples were purified by column chromatography using silica gel (400 mesh). Thin layer chromatography (TLC) was performed on aluminum sheets pre-coated with silica gel (Merck, Kiesinger 60 and F254). The infrared spectra of compounds were measured using KBr disk in Perkin Elmer FT-IR spectrometer. <sup>1</sup>H (400 MHz) and <sup>13</sup>C NMR (100 MHz) measurements were performed with Bruker spectrometer using TMS as an internal standard. Compositions of compounds were determined by Heraeus CHN elemental analyzer. The sequence of phases and phase transition temperatures were determined from optical textures and their changes were observed under a polarizing optical microscope (Linkem HFS91). 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 with a Canon 1000D camera. Differential scanning calorimetry (DSC) was carried out for the selected compounds by employing a Perk-Elmer Pyris Diamond calorimeter. Samples of about 2-5 mg, hermitically sealed in aluminum pan, were placed in N2 atmosphere working place. The calorimeter data were calibrated on extrapolated onset temperatures and enthalpy changes of water, indium and zinc. The measurements were performed on heating/cooling run at a rate of 5 °C min<sup>-1</sup>. UV absorption spectra were recorded on a UV-1650PC UV-visible spectrophotometer (Shimadzu). The sample dissolved in tetrahydrofuran was prepared with concentration of  $1 \times 10^{-5}$  M.

# 2.3. Synthesis of 4-formylphenyl (E)-3-(4-(dodecyloxy)phenyl)acrylate (5)

The dodecyloxycinnamoyl chloride (2) prepared by the reported procedure [26] (5 g, 3.37 mmol) was added drop wise to the reaction mixture containing 4-hydroxybenzaldehyde (4.12 gm, 3.37 mmol) and triethylamine (3.35 mmol) dissolved in dry THF and stirred for 24 hr. After completion of reaction, triethylamine hydrochloride was precipitated out and removed by filtration. The crude product was subjected to column chromatography (hexane:ethylacetate (95:5%)) to obtain colorless compound (5) (7.21 g, 78%). M.p: 174 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm:9.90 (s, 1H, CHO), 7.85–6.83 (d, 16H, J = 7.3 Hz, Aromatic-H) 7.43–7.75 (d, J = 13.2 Hz, 1H, olefinic- H), 6.41–6.37 (d, J = 13.4 Hz, 1H, olefinic- H), 3.92–3.89 (t, J = 7.6 Hz, 2H, -OCH<sub>2</sub>-), 1.73–1.18 (m, 20H, -CH<sub>2</sub>-), 0.78 (m, 3H, aliphatic-CH<sub>3</sub>). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 13.10, 21.67, 24.97, 28.11, 28.33, 28.61, 30.90, 67.21, 112.59, 113.97, 121.42, 125.38, 129.17, 130.16, 132.80, 146.31, 154.74, 160.63, 163.95, 189.90.Selected IR bands (cm<sup>-1</sup>):  $\nu$  2856, 2921, 1727, 1608, 1494, 1255, 1023, 1102. Anal.Calcd for C<sub>28</sub>H<sub>36</sub>O<sub>4</sub>C, 77.03%; H, 8.31%. Found: C, 76.67%; H, 7.89%.

# 2.4. General procedure for the preparation of Schiff base compounds (6a-d and 7a-d)

The synthesis of Schiff base compounds was performed by condensation reaction of appropriate aldehyde (5) with (E)-4-((4-(alkyloxy)phenyl)diazenyl)aniline (**3a-d**) or 4-aminophenyl 4-(alkyloxy)benzoate (**4a-d**) taken in 1:1 molar ratio. The reagents were dissolved in ethanol to form a 15%–20% solution and reaction mixture heated and stirred for 6 hr, in an inert atmosphere. After cooling, the crystalline product was separated by filtration and purified by recrystallization. Finally, the compounds dried overnight in vacuum at 60 °C. Pure, Schiff base compounds were obtained as yellowish crystals with yields of 68%–74%. Their structure was confirmed by FT-IR and <sup>1</sup>H-NMR spectroscopy.

# 2.4.1. (E)-4-((E)-((4-((E)-(4-(hexyloxy)phenyl)diazenyl)phenyl)imino)methyl)phenyl 3-(4-(dodecyloxy)phenyl)acrylate

**6a**: Yield: 70%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ/ppm: 8.70 (s, Ar-CH = N-, 1H), 7.92–7.89 (d, J = 7.7 Hz, aromatic-H, 2H), 7.94 (d, J = 7.8 Hz, aromatic-H, 6H), 7.51–7.35 (m, 5H, aromatic-H), 7.19 (d, J = 7.7 Hz, aromatic-H, 2H), 7.15–7.17 (d, J = 7.9 Hz, aromatic-H, 2H), 7.48 (d, J = 12.7 Hz, olefinic-H, 1H), 6.61 (d, J = 11.6 Hz, olefinic-H, 1H), 4.07–3.95 (t, 4H, J = 8.1 Hz, -OCH<sub>2</sub>), 1.86–1.74 (m, 4H, aliphatic-CH<sub>2</sub>), 1.31–1.06 (m, aliphatic-CH<sub>2</sub>, 24H), 0.91–0.86 (t, 6H, J = 6.8 Hz, aliphatic-CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)δ/ppm: 14.1, 22.8, 26.3, 28.7, 29.2, 31.6, 69.6, 115.2, 121.7, 123.2, 124.5, 128.6, 129.2, 131.3, 134.5, 144.7, 147.6, 151.4, 155.2, 159.9, 162.3, 163.0, 168.1. Selected IR bands (cm<sup>-1</sup>): ν 2852, 2913, 1726, 1604, 1472, 1476, 1253, 1024, 1137.Anal.Calcd for C<sub>46</sub>H<sub>57</sub>N<sub>3</sub>O<sub>4</sub>. C, 77.17%; N, 5.87%; H, 8.02%. Found:C, 76.39%; N, 5.27; H, 7.59.

**2.4.2. 6b**: Yield: 69%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 8.71 (s, Ar-CH = N-, 1H), 7.93–7.94 (d, J = 7.5 Hz, aromatic-H, 2H), 7.93 (d, J = 7.7 Hz, aromatic-H, 6H), 7.58–7.25 (m, 5H, aromatic-H), 7.15 (d, J = 7.6 Hz, aromatic-H, 2H), 7.21–7.19 (d, J = 7.29 Hz, aromatic-H, 2H), 7.48 (d, J = 12.3 Hz, olefinic-H, 1H), 6.52 (d, J = 11.9 Hz, olefinic-H, 1H), 4.05–3.96 (t, 4H, J = 8.3 Hz, -OCH<sub>2</sub>), 1.89–1.72 (m, 4H, aliphatic-CH<sub>2</sub>), 1.37–1.03 (m, aliphatic-CH<sub>2</sub>, 28H), 0.96–0.94 (t, 6H, J = 6.8 Hz, aliphatic-CH<sub>3</sub>).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) $\delta$ /ppm: 14.1, 22.8, 26.3, 28.7, 29.1, 31.5, 69.6, 115.4, 121.7, 123.2, 124.4, 128.6, 129.2, 131.3, 134.4, 144.6, 147.6, 151.4, 155.2, 159.8, 162.3, 163.1, 168.0. Selected IR bands (cm<sup>-1</sup>):  $\nu$  2849, 2915, 1729, 1607, 1474, 1502, 1252, 1024, 1139.Anal.Calcd for C<sub>48</sub>H<sub>61</sub>N<sub>3</sub>O<sub>4</sub>. C, 77.49%; N, 5.65%; H, 8.26%. Found: C, 76.83%; N, 5.15%; H, 7.68%.

**2.4.3.** 6c: Yield: 71%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 8.70 (s, Ar-CH = N-, 1H), 7.92 – 7.90 (d, J = 7.5 Hz, aromatic-H, 2H), 7.93 (d, J = 7.3 Hz, aromatic-H, 6H), 7.42–7.31 (m, 5H, aromatic-H), 7.16 (d, J = 7.5 Hz, aromatic-H, 2H), 7.15–7.17 (d, J = 7.5 Hz, aromatic-H, 2H), 7.48 (d, J = 12.2 Hz, olefinic-H, 1H), 6.49 (d, J = 11.8 Hz, olefinic-H, 1H), 4.06–3.97 (t, 4H, J = 8.4 Hz, -OCH<sub>2</sub>), 1.86–1.79 (m, 4H, aliphatic-CH<sub>2</sub>), 1.35–1.09 (m, aliphatic-CH<sub>2</sub>, 32H), 0.98–0.96 (t, 6H, J = 6.8 Hz, aliphatic-CH<sub>3</sub>).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) $\delta$ /ppm:14.02, 22.8, 26.4, 28.6, 29.1, 31.6, 69.5, 115.4, 121.5, 123.4, 124.4, 128.7, 129.2, 131.4, 134.6, 144.7, 147.6, 151.4, 155.2, 159.8, 162.4, 163.1, 168.1. Selected IR bands (cm<sup>-1</sup>):  $\nu$  2848, 2917, 1726, 1603, 1474, 1502, 1254–1023, 1138.Anal. Calcd for C<sub>50</sub>H<sub>65</sub>N<sub>3</sub>O<sub>4</sub>. C, 77.78%; N, 5.44%; H, 8.49%. Found: C, 77.18%; N, 5.01%; H, 8.11%.

**2.4.4. 6d**: Yield: 68%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 8.71 (s, Ar-CH = N-, 1H), 7.94–7.92 (d, J = 7.8 Hz, aromatic-H, 2H), 7.90 (d, J = 7.54 Hz, aromatic-H, 6H), 7.52 (m, 5H, aromatic-H), 7.11–7.08 (d, J = 7.43 Hz, aromatic-H, 2H), 7.07–7.06 (d, J = 7.43 Hz, aromatic-H, 2H), 7.52 (d, J = 12.5 Hz, olefinic-H, 1H), 6.46 (d, J = 11.7 Hz, olefinic-H, 1H), 4.01–3.98 (t, 4H, J = 8.2 Hz, -OCH<sub>2</sub>), 1.77–1.72

(m, 4H, aliphatic-CH<sub>2</sub>), 1.38–1.25 (m, aliphatic-CH<sub>2</sub>, 36H), 0.99–0.97 (t, 6H, J = 6.4 Hz, aliphatic-CH<sub>3</sub>).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) $\delta$ /ppm:14.01, 22.9, 26.4, 28.7, 29.0, 31.6, 69.6, 115.3, 121.7, 123.3, 124.5, 128.6, 129.1, 131.3, 134.5, 144.7, 147.6, 151.5, 155.2, 159.9, 162.4, 163.0, 168.0. Selected IR bands (cm<sup>-1</sup>):  $\nu$  2850, 2918, 1724, 1602, 1473, 1503, 1251, 1025, 1147.Anal Calcd for C<sub>52</sub>H<sub>69</sub>N<sub>3</sub>O<sub>4</sub>.C, 78.06%; N, 5.25%; H, 8.69%.Found: C, 77.86%; N, 5.01%; H, 7.42%.

# 2.4.5. Synthesis of 4-(((E)-4-(((E)-3-(4-(hexyloxy)phenyl)acryloyl)oxy)benzylidene)amino) phenyl 4-(hexyloxy)benzoate (7a)

Yield: 71%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 8.70 (s, Ar-CH = N-, 1H), 8.12–8.04 (d, J = 7.6 Hz, aromatic-H, 2H), 7.52 (d, J = 7.5 Hz, aromatic-H, 6H), 7.37–7.32 (m, 5H, aromatic-H), 7.15 (d, J = 7.5 Hz, aromatic-H, 2H), 7.18–7.08 (d, J = 7.6 Hz, aromatic-H, 2H), 7.43 (d, J = 11.7 Hz, olefinic-H, 1H), 6.74–6.71 (d, J = 11.5 Hz, olefinic-H, 1H), 4.02–3.98 (t, 4H, J = 8.2 Hz, OCH<sub>2</sub>), 1.74–1.72 (m, 4H, aliphatic-CH<sub>2</sub>), 1.52–1.21 (m, aliphatic-CH<sub>2</sub>, 24H), 1.02–0.98 (t, 6H, J = 6.7 Hz, aliphatic-CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) $\delta$ /ppm:14.1, 22.8, 26.5, 28.6, 29.1, 31.5, 69.6, 114.6, 115.3, 119.2, 121.7, 122.7, 123.6, 128.6, 129.0, 131.2, 132.3, 134.5, 135.8, 144.6, 146.4, 150.4, 155.2, 163.9, 167.1, 168.1. Selected IR bands (cm<sup>-1</sup>):  $\nu$  2847, 2922, 1729, 1606, 1494, 1254–1028, 1127. Anal Calcd for C<sub>41</sub>H<sub>45</sub>NO<sub>6</sub>.C, 76.02%; N, 2.16%; H, 7.00%. Found: C, 75.32%; N, 2.01%; H, 6.48%.

**2.4.6.** 7b:Yield: 69%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 8.68 (s, Ar-CH = N-, 1H), 8.12– 8.08 (d, J = 7.6 Hz, aromatic-H, 2H), 7.7 (d, J = 7.4 Hz, aromatic-H, 6H), 7.36–7.31 (m, 5H, aromatic-H), 7.16 (d, J = 7.6 Hz, aromatic-H, 2H), 7.19–7.14 (d, J = 7.4 Hz, aromatic-H, 2H), 7.47 (d, J = 11.7 Hz, olefinic-H, 1H), 6.72–6.70 (d, J = 11.4 Hz, olefinic-H, 1H), 4.02–3.98 (t, 4H, J = 8.4 Hz, OCH<sub>2</sub>), 1.76–1.72 (m, 4H, aliphatic-CH<sub>2</sub>), 1.50–1.24 (m, aliphatic-CH<sub>2</sub>, 28H), 1.02–0.98 (t, 6H, J = 6.7 Hz, aliphatic-CH<sub>3</sub>).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) $\delta$ /ppm: 14.2, 22.7, 26.6, 28.5, 29.2, 31.4, 69.5, 114.6, 115.3, 119.2, 121.7, 122.7, 123.4, 128.5, 129.1, 131.3, 132.2, 134.5, 135.6, 144.6, 146.5, 150.4, 155.2, 163.8, 167.2, 168.1. Selected IR bands (cm<sup>-1</sup>): v2856, 2925, 1731, 1606, 1499, 1254, 1026, 1102.Anal Calcd for C<sub>43</sub>H<sub>49</sub>NO<sub>6</sub>.C, 76.42%; N, 2.07%; H, 7.31%. Found: C, 76.02%; N, 1.76%; H, 6.82%.

**2.4.6.** 7c: Yield: 73%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 8.69 (s, Ar-CH = N-, 1H), 8.12– 8.05 (d, J = 7.4 Hz, aromatic-H, 2H), 7.51 (d, J = 7.5 Hz, aromatic-H, 6H), 7.37–7.34 (m, 5H, aromatic-H), 7.16 (d, J = 7.6 Hz, aromatic-H, 2H), 7.19–7.12 (d, J = 7.6 Hz, aromatic-H, 2H), 7.51 (d, J = 11.4 Hz, olefinic-H, 1H), 6.71–6.68 (d, J = 11.4 Hz, olefinic-H, 1H), 4.02–3.98 (t, 4H, J = 8.4 Hz, OCH<sub>2</sub>), 1.74–1.70 (m, 4H, aliphatic-CH<sub>2</sub>), 1.51–1.21 (m, 32H, aliphatic-CH<sub>2</sub>), 1.0–0.98 (t, 6H, J = 6.5 Hz, aliphatic-CH<sub>3</sub>).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) $\delta$ /ppm:14.1, 22.6, 26.5, 28.6, 29.1, 31.5, 69.6, 114.5, 115.4, 119.2, 121.5, 122.8, 123.4, 128.4, 129.1, 131.4, 132.3, 134.2, 135.6, 144.6, 146.4, 150.3, 155.2, 163.7, 167.2, 168.1.Selected IR bands (cm<sup>-1</sup>):  $\nu$  2854, 2928, 1725, 1608, 1494, 1262, 1016, 1108. Anal Calcd for C<sub>45</sub>H<sub>53</sub>NO<sub>6</sub>. C, 76.78%; N, 1.99%; H, 7.59%. Found: C, 75.67%; N, 1.27%; H, 6.85%.

**2.4.7.** 7d: Yield: 72%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 8.71 (s, Ar-CH = N-, 1H), 8.11– 8.09 (d, J = 7.5 Hz, aromatic-H, 2H), 7.54 (d, J = 7.6 Hz, aromatic-H, 6H), 7.35–7.35 (m, 5H, aromatic-H), 7.17 (d, J = 7.74 Hz, aromatic-H, 2H), 7.16–7.06 (d, J = 7.52 Hz, aromatic-H, 2H), 7.42 (d, J = 11.6 Hz, olefinic-H, 1H), 6.75–6.71 (d, J = 11.6 Hz, olefinic-H, 1H), 4.01–3.99 (t, 4H, J = 8.3 Hz, OCH<sub>2</sub>), 1.76–1.71 (m, 4H, aliphatic-CH<sub>2</sub>), 1.51–1.23 (m, 36H, aliphatic-CH<sub>2</sub>), 1.01–0.99 (t, 6H, J = 6.4 Hz, aliphatic-CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) $\delta$ /ppm:14.0, 22.9, 26.4, 28.7, 29.0, 31.6, 69.6, 114.7, 115.3, 119.1, 121.7, 122.9, 123.6, 128.6, 129.0, 131.1, 132.3, 134.5, 135.8, 144.7, 146.4, 150.5, 155.1, 163.9, 167.1, 168.0. Selected IR bands (cm<sup>-1</sup>):



Scheme 1. Synthesis of liquid crystalline compounds.

*v* 2853, 2929, 1729, 1608, 1502, 1258, 1029, 1107. Analysis Calcd for C<sub>47</sub>H<sub>57</sub>NO<sub>6</sub>. C, 76.78%; N, 1.99%; H, 7.59%. Found: C, 75.56%; N, 1.37%; H, 6.67%.

# 3. Results and discussion

#### 3.1. Synthesis and characterization

Scheme 1 illustrates the procedure employed for the synthesis of two series of azo and ester linkage of Schiff base containing chromophores with both end containing different alkoxy cinnamate esters. The synthesized compounds were characterized by means of FT-IR, <sup>1</sup>H, <sup>13</sup>C NMR, and elemental analysis. The Fourier transform infrared (FT-IR) spectroscopic analyses, <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopy confirmed the synthesis of compounds. The compound **6d** displays intensive characteristic absorption band around 1622–1629 cm<sup>-1</sup>attributed to azomethine bond. The chemical shift of protons was detected in the <sup>1</sup>H NMR spectrum, ratio values of integrals perfectly agree with calculated ones for the proposed structure. The FT-IR, <sup>1</sup>H, and <sup>13</sup>C-NMR spectra of compounds were provided in Supporting Information.

#### 3.2. Thermotropic behavior

The compounds **6a–d** and **7a–d** displayed thermotropic calamitic mesophases on heating and cooling cycles in the DSC and POM investigations.

The POM textures of **6d** and **7d** are exhibited in Figures 1 and 3 The DSC curves of **6d** indicated a crystalline melting endotherm at 164.4 °C (enthalpy changes  $\delta H = 22.6$  kJ mol<sup>-1</sup>) and Nematic–isotropic phase transition at 269.2 C (1.3 kJ mol<sup>-1</sup>) on heating, as well as an isotropic-Nematic and Nematic – Smectic-C transition at 238.4 °C and 178.5 °C (-0.7 kJ mol<sup>-1</sup>). Finally, the crystallization at 131.5 °C (-33.5 kJ mol<sup>-1</sup>) on cooling, as displayed in Figure 2. Taking into account on the observations, DSC exothermic peaks were assigned to



**Figure 1.** POM textures (20X) of compound **6d** (a) Nematic texture on heating to 247.5 °C; (b) Schlieren texture of Nematic on heating to 258 °C; (c) Nematic droplets which form by coalescence Schlieren texture on cooling to 262.4 °C; (d) Smectic C phase on cooling at 196 °C.



Figure 2. DSC curves of compounds 6d and 7d.



Figure 3. POM textures (20X) of Schiff base azo compound 7d (a) oily streak texture on cooling to 264 °C; (b) broken fan-shaped texture at 221 °C; (c) Smectic-C texture on cooling to 185 °C.

Compound	Heating	Cooling cycle
6a	Cr 166.7 (31.5) N 259.1 (1.6) I	l 254.7 (-0.2) N 244.4 (1.4) SmA 169.4 (-0.5) Cr 139.6 (-20.5)
6b	Cr 165.4 (28.5) N 263.2 (1.5) I	l 258.4 (-0.3) N 245.6 (1.6) SmA 172.7 (-0.6) Cr 137.4 (-24.5)
6c	Cr 166.7 (24.3) N 266.1 (1.4) I	l 259.7 (-0.4) N 240.4 (1.9) SmC 175.4 (-0.8) Cr 134.5 (-26.2)
6d	Cr 164.4 (22.6) N 269.2 (1.3) I	l 263.4 (-0.4) N 238.4 (2.3) SmC 178.5 (-0.7) Cr 131.5 (-33.5)
7a	Cr 143.7 (29.4) N 264.1 (1.6) I	l 259.7 (-2.3) N 237.4 (-0.8) SmA 135.4 (-0.4) Cr 78.6 (-13.7)
7b	Cr 141.7 (26.4) N 268.1 (1.5) I	l 264.7 (-1.7) N 232.4 (-1.1) SmA 138.4 (-0.6) Cr 75.2 (-15.4)
7c	Cr 138.8 (24.4) N 272.3 (0.8) l	l 269.2 (—1.4) N 229.6 (—1.5) SmC 142.5 (—1.0) Cr 70.5 (—16.8)
7d	Cr 136.2 (23.3) N 275.4 (0.7) l	l 270.4 (—0.9) N 225.6 (—1.7) SmC 146.7 (—1.3) Cr 60.4 (—18.3)

**Table 1.** Phase transition temperatures ( $T/^{\circ}C$ ) and enthalpies ( $\delta H/J g^{-1}$ ) obtained from DSC scans of **6a–d** and **7a–d**.

Cr = Crystal, N = Nematic, SmA = Smectic A, SmC = Smectic C, I = Isotropic.

Isotropic–Nematic, Nematic–Smectic-C, and Smectic-C–crystalline transitions, respectively (Table 1). In the first heating scan, compound **6d** of POM observation did not reveal significant changes corresponding to first endothermic peak, while at the temperature corresponding to second endothermic peak, a clear, fluid Nematic texture displayed (Figure 1a and b), which further transformed into an isotropic liquid (at a temperature corresponding to highest temperature endothermic peak). Based on these observations, first endothermic peak was ascribed to a solid–solid transition, second endothermic peak to a Nematic–isotropic transition.

In the first cooling scan, Nematic droplets appeared from isotropic liquid (Figure 1c), forming by coalescence an unstable Schlieren texture which very rapidly transformed into a Smectic-C texture (Figure 1d). The DSC thermogram in Figure 2 exhibited a crystalline melting at 136.2 °C ( $H = 23.3 \text{ kJ mol}^{-1}$ ) and Nematic-isotropic phase at 275.4 °C (0.7 kJ mol<sup>-1</sup>) on heating for 7d, as well as an isotropic-Nematic and Nematic-Smectic-C transition at 225.6 °C and 146.7 °C ( $-1.3 \text{ kJ mol}^{-1}$ ) finally crystallization at 60.4 °C ( $-18.3 \text{ kJ mol}^{-1}$ ) on cooling. The first heating/cooling cycle is similar to compound 7d, the only difference being the weaker first endothermic peak (7d) compared with compound 6d, attributed to difference between crystalline state obtained by crystallization from molten state and recrystallization from solvent, respectively. The enthalpy values recorded by DSC are in accordance with values usually observed for characteristic crystalline–Nematic, Nematic–Isotropic, Nematic–Smectic-C, and Smectic-C–Crystalline transitions, verifying the presence of a Nematic and Smectic-C mesophase [33].

On cooling, isotropic liquids of series I and II compounds with n = 6 and 8 formed small droplets that coalesced to Schlieren texture of SmA phase while, n = 10 and 12 derivative exhibited only focal conic texture characteristic of Smectic-C mesophase when cooled from isotropic liquid. The remaining lower members of compound **6a–6b** and **7a–7b** exhibit from above similar observation of Nematic and Smectic-A mesophase occur with wide transition temperature. This is attributed to flexibility of increased alkyl chain length whereas the phase transition sequence from isotropic from cooling as Isotropic–Nematic–Smectic-A–Crystal. The **7c** and **7d** alone exhibit Smectic-C texture because of increasing alkyl chain length (n = 10 and 12). It is noticed that crystal mesophase transition temperatures decreases with increase in length of terminal alkoxy chain length. The Nematic-isotropic transition temperatures also decreases with increase in number of carbon atoms in the alkoxy chain, whereas it exhibits a tendency for rising Smectic-C–Nematic transition temperature in ascending series, which levels off slightly in the higher homologues, when terminal alkoxy chain attractions are more prominent.



Figure 4. Absorption spectrum of compound 7a.

The molecules of series I and II have cinnamate connected to Schiff base with azo and ester linkages have addition of double bond in the system which increases length and polarizability of rod like molecules. The presence of this double bond system (cinnamate group) increases the length of polarizability of rod like molecules and enhances mesophase thermal stability. Therefore, greater mesophase thermal stability of the present series I and II may be explained in terms of greater molecular length and polarizability of molecule resulting from additional -CH=CH- units in central linkage. The overall polarizability is enhanced with increase of alkyl chain length as the series is ascended. The ratio of terminal attractions to lateral attractions decreases as the series is ascended; the net result is that the lateral attractions gain dominance over the terminal attractions. The molecules under such conditions will observe, strictly maintaining layered structure, although they might partially attain a fluid condition. It revealed that alkyl chain length from tenth member onwards; purely Smectic-C mesophase is exhibited. The overall polarizability of the molecules is enhanced as the length of alkyl chain at one end increases, contributing to exhibit Smectic-C textures. However, the ratio of terminal to lateral attractions is also low at certain stage the thermal vibration break down the orientation of molecules without giving them a chance for adopting Nematic orientation. Thus, Smectic-C mesophase alone prevails from dodecyloxyderivative.

#### 3.3. Photophysical properties

Photophysical properties of synthesized compounds have been investigated using UV-visible spectroscopy of the compound containing azo moiety in the diluted solutions, to have an insight into the electronic structure generated by chromophores. Absorption spectrum of compound were obtained from its absorption band is summarized in Table S6 and a spectrum is shown in Figure 4.

The absorption spectra of compounds were carried out in tetrahydrofuran solution. The azo linkage containing compounds was irradiated with UV light (365 nm), the band corresponding to  $\pi - \pi^*$  and  $n - \pi^*$  transitions decreases with increasing irradiation time [28]. In Figure 4, the band corresponding to isomerized product increases by increasing the irradiating time, which confirmed photoisomerization at various time intervals has occurred in the

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range of 385–550 nm. The UV-vis absorption spectrum of compound in solution is characterized by three absorption bands: an absorption band at longer wavelength 260-440 nm range corresponding to  $\pi - \pi^*$  transition of the mesogen. The **7a** irradiated at 365 nm, E–Z isomerization, resulting with a dramatic decrease in the absorption band from 379 nm is ascribed to  $\pi - \pi^*$  transition of the trans (E) isomer in azo group. The further very weak absorption band also found in the visible region around 487 nm, appropriate to  $n-\pi^*$  transition of cis (Z) isomer in the azo group was gradually increased by reaching photostationary state 80 sec. After 80 sec illumination, there is no change in absorption spectrum confirms photo-saturation of E-Z (trans-cis) isomerization process. The isobestic points were observed at 340 and 450, corresponding to trans-cis isomerization as these suggesting that only two isomers obtained. In Figure 4 for another band absorption exhibit the compound containing cinnamate unit in double bond undergo isomerization around at 273 nm. The absorption spectra are similar for all the compounds because of their similar molecular structure; the only difference is in the alkyl chain, which does not alter the electronic transitions [6, 34]. At the same time, we have tried for reversible photo isomerization in the dark condition for several min for 7a, with same concentration of tetrahydrofuran solution. The transformed cis isomer (Z) was not converted into trans form (E). The transformed cis isomer (Z) is not converted into trans form (E) ascribed to the imine (-CH=N-) group restricts electron delocalization on cinnamate moiety and chemical structure of chromophores attained the anisotropic interaction between the liquid crystals and unchanged trans isomer of azo group.

# 4. Conclusion

Novel thermotropic liquid crystalline rod shaped molecules containing Schiff base of azo and ester linkages have been synthesized and characterized. The mesophase range of present series I and II for those of structurally related compounds that have been depend on rod shaped and attributed to high polarizability of the molecule. The structural aspects strongly enhance phase transition behavior of Schiff's base compounds. The mesophases of rod like molecules have very high thermal stability and isotropic temperature of > 275 °C depending on the presence of olefinic double bond enhances the length of polarizability. Interestingly, change in orientation of outer ester group in lengthening of arm in the compounds in I series led to decrease in clearing temperature. The effect of terminal alkoxy containing azobenzene moiety, central linkage with spacer attached also plays a crucial role in the formation of mesophase. The duration required for exhibiting photoisomerization phenomena mainly related with chemical structure of compounds.

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