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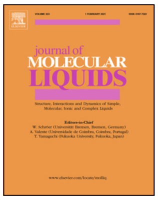

λ-shaped to T-shaped azo diester mesogens having methyl ($-CH_3$)/methoxy($-OCH_3$) terminal substituents with trisubstituted benzene

Yongfang Yao [a,b,c], Rohit R. Koshti [d], Akshay Vyas [d], Chetan B. Sangani [d], Yongtao Duan [a], Rakesh Kumar Ameta [d], Umesh P. Tarpada [e], H.N. Patel [d,*]

[a] *Henan Provincial Key Laboratory of Pediatric Hematology, Children's Hospital Affiliated to Zhengzhou University, Henan Children's Hospital, Zhengzhou Children's Hospital, Zhengzhou 450018, China*
[b] *School of Pharmaceutical Science, Zhengzhou University, Zhengzhou, Henan 450001, China*
[c] *Key Laboratory of Advanced Drug Preparation Technologies Zhengzhou University), Ministry of Education of China, Zhengzhou 450001, China*
[d] *Shri Maneklal M. Patel Institute of Sciences & Research, Kadi Sarvavishwavidyalaya, Gandhinagar, Gujarat, India*
[e] *Chemistry Department, Government Science College, Gandhinagar, Gujarat 382015, India*

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ABSTRACT

A two new homologous series of λ-shape to **T**-shape mesogenic azo diesters were synthesized, and their thermotropic properties were studied by differential scanning calorimetry and a hot-stage polarizing optical microscope. The difference between these two series is in the structure of terminal substituents methyl ($-CH_3$) for series **I** and methoxy ($-OCH_3$) for series **II** at one terminus. Structure variation from λ-shape to **T**-shape as we go from lower members to higher members is discussed. In the series **I**, methoxy to *n*-pentyloxy derivatives are non-mesogenic. *n*-hexyloxy derivative exhibits only monotropic nematic mesophase. *n*-heptyloxy to *n*-dodecyloxy derivatives exhibit monotropic smectic C mesophase. *n*-tetradecyloxy derivative exhibits enantiotropic SmA mesophase, whereas *n*-hexadecyloxy derivatives exhibit monotropic Smectic A mesophase. In series **II**, methoxy to *n*-hexyloxy derivatives are non-mesogenic. *n*-heptyloxy and *n*-octyloxy derivatives exhibit monotropic smectic C mesophase. Smectic A mesophase commences from the *n*-decyloxy derivative as a monotropic and persists up to the last member synthesized. The mesomorphic properties of the present series were compared with each other and with the structurally related mesogenic homologous series to evaluate the effect of methyl ($-CH_3$)/methoxy ($-OCH_3$) substituents as well as variation in the shape of the molecule by varying the alkoxy chain length of the bulky lateral substituent on mesomorphism.

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* Corresponding author.
E-mail address: hemant71patel@gmail.com (H.N. Patel).

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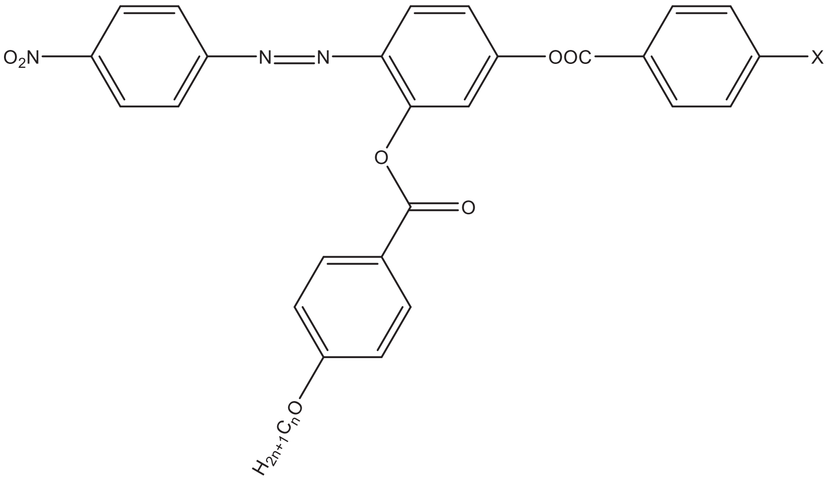
1. Introduction

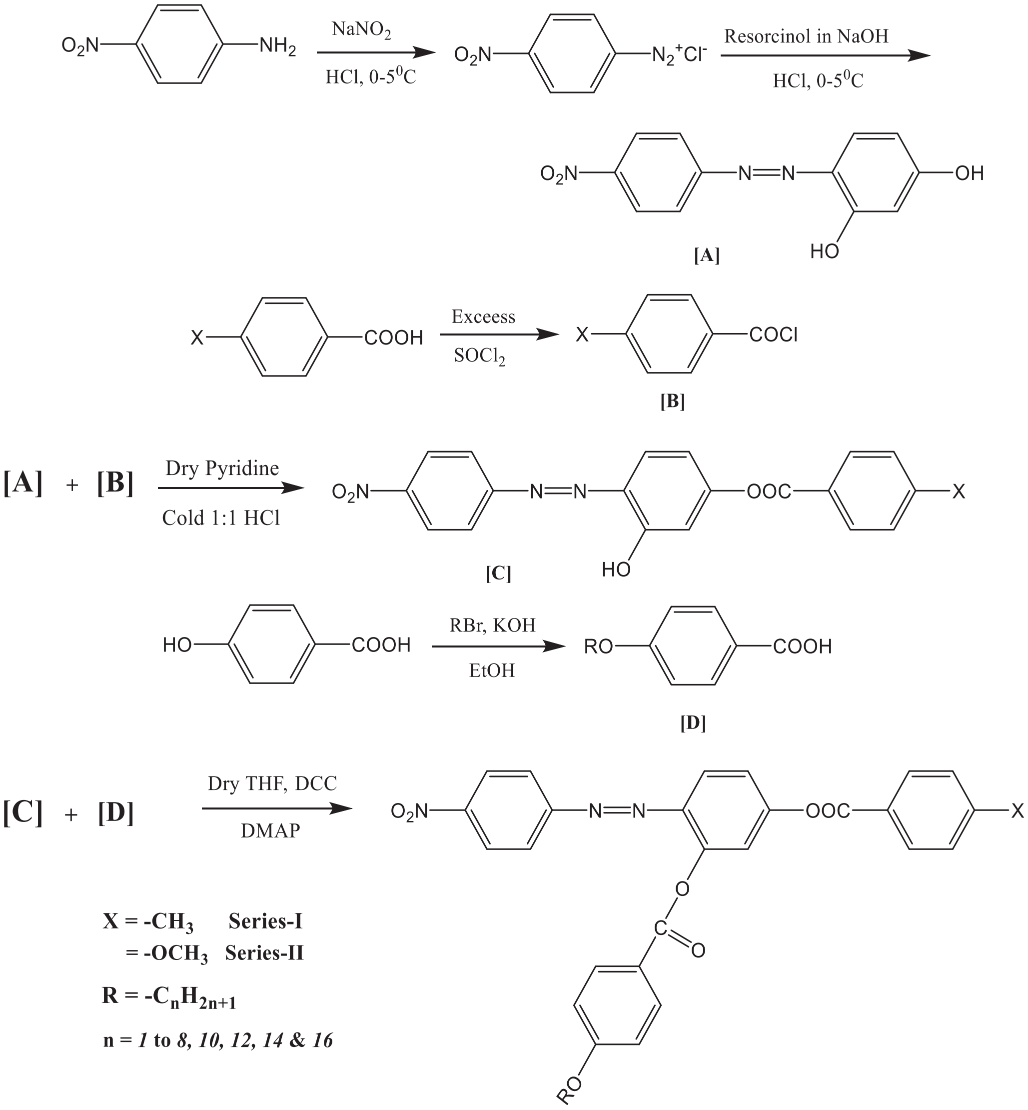
The supramolecular assemblies of disc-shaped molecules lead to the formation of discotic liquid crystals, discovered in Bangalore in 1977 by Chandrasekhar et al, for more than 30 years. However, this is relatively recent compared with the well-developed area of calamitic liquid crystal research [1-4]. Previously, discotic liquid crystal (LC) materials have received a great deal of attention due to their technological importance in low dimensional conductivity [5], electro optical display devices with optical compensation films [6,7], holographic data storages [8] and photovoltaic cells [9]. More research has been focused on the triphenylene structure due to its relative ease of synthesis [10-12] and its strong tendency to form columnar mesophases [10]. However, compounds based on a single benzene ring as the central core having different substituents increased in importance since 1977 following the pioneering work of Chandrasekhar et al. [1].(seeScheme 1.Scheme 2.)

Trisubstituted benzene mesogens molecules have a molecular assembly having versatility in their synthesis that encompasses various functional groups and structure the desired physical and chemical properties [13-16] Molecules with Smectic C, Nematic, Smectic A and columnar liquid crystalline phases [10,17-19]. The self-assembly in columnar phases allows the transport of electrons, protons and ions by building the molecular constitution in one dimension. The flexibility of the arms in the trisubstituted benzene mesogens forms aggregates of two or more molecules in a disc or a half disc, rising to a supramolecular columnar system by self-assembly resulted by conformational changes. This organization provides columnar liquid crystals with properties desirable for various applications like light-emitting diodes, photoconductive semi-



Series	X	n=
I	-CH3	*1-8*, *10*,*12*,*14* and *16*.
II	-OCH3	*1-8*, *10*,*12*,*14* and *16*.

Scheme 1. Core structure of azo diester mesogens.



Scheme 2. Synthetic route to series I and II compounds.

conductor devices, field-effect transistors, photovoltaic cells, gas sensors, memory devices and electro-optical and optical fibers [20,21]. Various molecules incorporating oxadiazole with symmetrical and non-symmetrical 1,3,5 tri substituted benzene as a central core have been synthesized, and their mesomorphic and photophysical properties studied [22-24].

Aside from the linear combination of two or more mesogenic entities linked via flexible spacers [25], other modes of interlinked have been adopted to prepare molecules of a variety of shapes such as banana-shaped [26-28], S-shaped [29,30], H-shaped [31-33], U-shaped [34,35], **T**-shaped [36,37], Y-shaped [38-40] and the λ-shaped mesogens [41-43]. Star-shaped liquid crystals usually have a core and symmetric or asymmetric mesogens as the side arms, which is kind of an unconventional liquid crystal. [44-48], which has led to the growing interest in the synthesis and application. The simplest star-shaped liquid crystals (LCs) composed of a small aromatic core unit surrounded by three mesogenic units have been the most commonly studied liquid crystalline materials [49-51]. The common mesophase of the star-shaped liquid crystals (LCs) is the columnar phase. In order to obtain cholesteric star-shaped liquid crystals (LCs), it is undoubtedly effective to use a chiral compound with multiple functional groups as the cores [52-55].

A large number of thermotropic liquid crystals have a rigid core made of two or more aromatic and /or aliphatic rings with one or more flexible different terminals as alkyl/alkoxy chains [56,57]. In general, the rings are linked with 1, 2, 4 units, generally producing a rod-like, lathe-like or disc-like structure. In general, a rigid, lateral substituent perturbs the orderings of liquid crystalline different phases [58-60], causing a significant depression in the phase transition, a reduction of the liquid crystal range, and destabilization of ordered smectic A phases. However, the effect of a lateral, flexible substituent like an alkoxy or alkyl chain is quite different [61-63]. A methyl or a methoxy substituent causes a strong decrease in the phase transition, but as the chain length increases, the effect of the perturbation diminishes. In fact, chains with three or more carbons perturb the molecular arrangement in the phase transition to about the same extent, as the lateral alkyl chain is supposed to be orientated along the long molecular axis. Until now, only compounds containing three phenyl rings have been shown to exhibit some different phase transition, if the lateral substituent is an alkyl or an alkoxy group. Recently molecular constitution [64] has attracted much attention for producing molecules of different shapes with rich mesogenic behaviour. A recent review of research work shows that a number of efforts have been going on for designing molecules of different shapes showing liquid crystalline behaviour. Reports in the literature have shown that the majority of the published work on bent shaped, U shaped, banana or V- shaped molecules based on rigid central 1, 3-phenylene and 2, 7-naphthalene cores self-assemble to yield molecular structures that show banana liquid crystalline mesomorphism [65]. The swallowed tailed compounds [66] have also been reported with interesting phase transitions. ''Janus-like'' supramolecular liquid crystals have been found with chiral nematic and chiral smectic A phases [67]. U-shaped molecule having layered structure in the nematic phase have been reported by Yoshizawa and Yamaguchi [68]. Berdague et al. [69] reported 1, 2, 4-trisubstituted benzene derivatives possessing azo-ester and ester linkages having terminal dodecyloxy substituents.

We [70] have reported the synthesis of two λ-shape (Trisubstituted Benzene Mesogens) mesogenic homologous series in which one series were having methyl and the other having ethoxy terminal. Mahajan et al. [71] have also reported the synthesis of two λ-shape mesogenic homologous series trisubstituted benzene derivatives having ester and amide linkages with chloro or methoxy terminal substituents. Vora and Prajapati [72] have reported a mesogenic homologous series containing three phenyl rings in the central core and substituted by a lateral acetyl group on the central benzene nucleus as the effect of lateral acetyloxy group on mesomorphism has not been studied extensively. The mesogenic homologous series with lateral acetyl group exhibited nematic mesomorphism, whereas homologous series with lateral aromatic branch exhibited smectogenic tendencies. Patel [73] have reported the synthesis of 1, 2, 4-trisubstituted benzene derivatives with azo-ester and ester linkages having the terminal nitro group. Nandedkar [74] has also reported the synthesis of 1,2,4- trisubstituted benzene derivative possessing azo-ester and ester linkages without any terminal group. Guan-YeowYeap et al. [75] have also reported the synthesis of λ-Shaped liquid crystal trimers having dual terminal cholesteryl exhibiting N*, SmA and cholesteric glassy phases. Mei Tian et al. [76] reported Mesomorphic properties of non-symmetric three-arm chenodeoxycholic acid-derived liquid crystals. Irina Carlescu et al. [77] reported star-shaped liquid crystals based on 1,3,5-trihydroxy benzene with pendant alkyloxylated azobenzene arms.

In this present study, we have synthesized two new mesogenic homologous series containing tri substituted benzene in the central core with azo diester linkage and having nitro substituents, with the lateral *n*-alkoxy chain and methyl ($-CH_3$)/methoxy ($-OCH_3$) terminal groups. The mesomorphic properties of these two series having the following general structural formula were compared with each other as well as other structurally related compounds to evaluate the effect of different terminal group and shape of molecule by changing the lateral alkyl chain length.

2. Experimental

2.1. Materials

4-Nitroaniline, Benzene-1,3-diol, 4-methylbenzoic acid, 4-methoxybenzoic acid, 4-Hydroxybenzoic acid, *n*-bromoalkane, N, N′-Dicyclohexylcarbodiimide (DCC), 4-Dimethylaminopyridine (DMAP), Tetrahydrofuran (THF) thionyl chloride ($SOCl_2$), dry pyridine, pottasium hydroxide (KOH), ethyl alcohol were used as receivd. Distillation and drying of solvent were done prior to using them. Column chromatography was done on Acme's silica gel (100–200 mesh) as a stationary phase. Thin layer chromatography (TLC) was performed on aluminum sheets pre-coated with silica gel (Merck, Kiesel 60F254 pre-coated). Shimadzu IR-408 spectrophotometer was used to record the infrared spectra (IR) using potassium bromide (KBr) pellets. Proton nuclear magnetic resonance(^{1}H NMR) spectra were recorded on a Bruker Avance Neo-spectrometer (400 MHz) using Deuterated chloroform ($CDCl_3$) as a solvent and tetramethyl silane (TMS) as internal reference standard. The chemical shifts are quoted as δ (ppm) downfield from the reference. The phase appearance and phase transition were determined by thermal polarizing optical microscopy using a polarizing microscope equipped with a heating stage. The enthalpies of phase transitions, reported in $J.g^{-1}$, were measured using differential scanning calorimeter (DSC) Shimadzu DSC-60 plus system, with a scanning rate of 10 ℃ min^{-1}. The instrument was calibrated using pure indium as a standard.

2.2. Synthesis

2.2.1. Preparation of 4-((4-nitrophenyl) diazenyl) benzene-1,3-diol [a]

Dissolve 0.036 Mole of 4-nitroaniline in a warm mixture of 14 ml of concentrated hydrochloric acid and 14 ml of water contained in a 500 ml beaker. Place the beaker in a crushed ice salt bath and cool to 0–5 °C whilst stirring vigorously; 4-nitroaniline hydrochloride will separate in a finely divided crystalline form. Add a cold solution of 0.054 mol of sodium nitrite in 10 ml of water slowly, stirring to an endpoint with potassium iodide starch paper. Do not allow the temperature of the solution to rising above 10 °C. Dissolve 0.035 mol of benzene-1–3-diol in a solution of 7 g of sodium hydroxide in 30 ml of water, cool in ice, add the diazotized solution slowly, and stir. Then add cooled concentrated hydrochloric acid slowly and with vigorous stirring to the cold mixture until it is strongly acid to congo red paper. The colour will change from violet to dark red-brown. Filter with gentle suction, wash with water until free from acid and dry upon filter paper in the air. The yield is 0.034 Mole (75%). It was crystallized from glacial acetic acid till constant melting point was obtained. M. P. 198–201 °C (Reported [73] M. P. 202 °C).

2.2.2. 4-methyl (–CH3)/methoxy (–OCH3) benzoyl chloride [b]

4-methyl ($-CH_3$)/methoxy ($-OCH_3$) benzoyl chloride was prepared by treating corresponding acids with excess of thionyl chloride under reflux for 2 h [78].

2.2.3. **3-hydroxy-4-((4-nitrophenyl) diazenyl) phenyl 4-methyl** ($-CH_3$)/**methoxy** ($-OCH_3$) **benzoate [c]**

0.01 Mole of 4-((4-nitrophenyl) diazenyl) benzene-1,3-diol **[A]** was dissolved in 12 ml of dry pyridine and was added dropwise with constant shaking to cold 0.01 mol of 4-methyl ($-CH_3$)/ methoxy ($-OCH_3$) benzoyl chloride. The mixture was then warmed

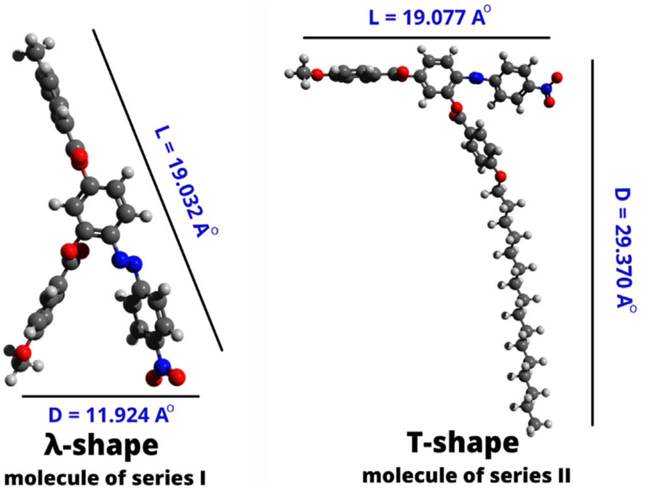


Fig. 1. λ-shape molecular of series I*1* and T-shape molecular of series II*16*.

on water bath for approximately 30–45 min and was allowed to stand overnight. It was acidified with cold 1:1 hydrochloric acid and precipitates obtained were filtered and washed with water, followed by washings of cold dilute sodium hydroxide solution and cold water. The 3-hydroxy-4-((4-nitrophenyl) diazenyl) phenyl 4–4-methyl (–CH_3)/methoxy (–OCH_3) benzoate was crystallized two to three times from glacial acetic acid until constant transition temperatures were (Cr 186 ℃ N 236 ℃ I) obtained. Yield: 72%. Elemental analysis: Found C 63.51, H 3.86, N 11.523%, $C_{20}H_{15}N_3O_5$ requires C 63.67, H 3.98, N 11.15%. IR Spectrum (KBr) $V_{max/cm-1}$: 3200–3600 (–OH phenolic), 2921, 1749 (–COO-), 1605 (-N = N-), 1512 (–NO_2), 1344, 1255, 1168, 1010, 916, 896, 840, 758, 658 cm^{-1}.

2.2.4. 4-n-Alkoxybenzoic acids [d]

4-*n*-alkoxybenzoic acids [**D**] were synthesized from 4-hydroxybenzoic acid by employing a Williamson's ether synthesis protocol [79].

2.2.5. **3-((4-alkoxybenzoyl) oxy)-4-((4-nitrophenyl) diazenyl) phenyl 4-methyl** (–CH_3) **/methoxy** (–OCH_3) **benzoate (series-I/ Series-II)**

0.01 Mole of 3-hydroxy-4-((4-nitrophenyl) diazenyl) phenyl 4–4-methyl (–CH_3)/methoxy (–OCH_3) benzoate **[C]**, 0.01 mol of 4-*n*-alkoxy benzoic acids **[D]**, 0.01 mol of DCC [80] and 0.001 mol of DMAP were dissolved in dry THF and stirred at room temperature for 36 h. The insoluble solid was removed through filtration. The solution was chromatographed on silica gel using petroleum ether (60–80 °C) ethyl acetate mixture (96:4) as eluent. Removal of solvent from the eluate afforded a solid material which was crystallized two–three times from methanol. The purities of all these synthesized compounds were checked by thin layer chromatography (Merk-kiesel gel 60F254 pre-coated plates). Yield: 36–41%. The elemental analysis of all the synthesized compounds was found to be satisfactory.

The UV, IR and ^1H NMR spectral data of representative compounds were found to be consistent with the proposed structure.

2.3. Spectroscopic characterization

3-((4-octyloxybenzoyl) oxy)-4-((4-nitrophenyl) diazenyl) phenyl 4-methyl benzoate

UV spectrum (MDC) nm: 225 and 365. IR Spectrum (KBr) $V^{-1}_{max/cm}$: 2920, 1734 (–COO-), 1604 (-N = N-), 1521, 1508, (–NO_2), 1342, 1251, 1238, 1168, 1102, 1064, 968, 890, 856, 749, 684. ^1H NMR spectrum (400 MHz): δ 0.92 (t, 3H, –CH_3), 1.25–1.56 (m, 10*H*, 5 × –CH_2-), 1.80 (quant., 2H-O-C-CH_2-), 2.47(s, 3H, Ar-CH_3), 4.04 (t, 2H, Ar-O-CH_2-), 7.05 (d, 2H, ArH), 7.11 (s ,1H, ArH), 7.22 (d ,2H, ArH), 7.26 (d ,1H, ArH), 7.80 (d, 2H, ArH), 8.03 (d, 2H, ArH), 8.05 (d, 1H, ArH), 8.15–8.30 (d, 4H, ArH).

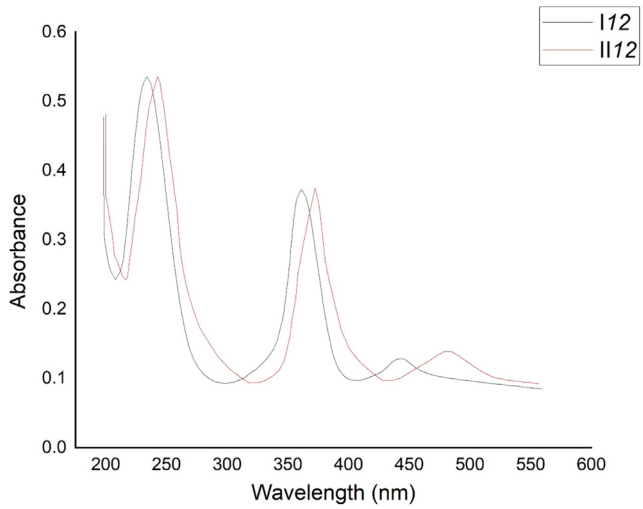


Fig. 2. UV–Vis absorption spectra of compounds I*12* and II*12* in THF.

2.3.1. 3-((4-dodecyloxybenzoyl) oxy)-4-((4-nitrophenyl) diazenyl) phenyl 4-methyl benzoate

UV spectrum (MDC) nm: 225 and 365. IR spectrum (KBr) $V^{-1}_{max/cm}$:2958, 2920, 1742 (–COO-), 1605 (-N = N-), 1521, 1509, (–NO_2), 1342, 1251, 1238, 1168, 1102, 1064, 968, 890, 856, 749, 684. ^1H NMR spectrum (400 MHz): δ 0.91 (t, 3H, –CH_3), 1.24–1.56 (m, 18H, 9 × –CH_2-), 1.78 (quant., 2H-O-C-CH_2-), 2.48(s, 3H, Ar-CH_3), 4.02 (t, 2H, Ar-O-CH_2-), 7.06 (d, 2H, ArH), 7.12 (s ,1H, ArH), 7.23 (d ,2H, ArH), 7.26 (d ,1H, ArH), 7.80 (d, 2H, ArH), 8.02 (d, 2H, ArH), 8.05 (d, 1H, ArH), 8.13–8.30 (d, 4H, ArH).

2.3.2. 3-((4-tetradecyloxybenzoyl) oxy)-4-((4-nitrophenyl) diazenyl) phenyl 4-methyl benzoate

UV spectrum (MDC) nm: 225 and 365. IR spectrum (KBr) $V^{-1}_{max/cm}$: 2960, 2920, 2850, 1741 (–COO-), 1604 (-N = N-), 1527, 1510 (–NO_2), 1471, 1450, 1342, 1259, 1168, 1093, 1051, 844, 800, 759, 688. ^1H NMR spectrum (400 MHz): δ 0.89 (t, 3H, –CH_3), 1.25–1.57 (m, 22H, 11 × –CH_2-), 1.80 (quant., 2H, -O-C-CH_2-), 2.49 (s, 3H, ArCH_3), 4.04 (t, 2H, Ar-O-CH_2-), 7.03 (d, 2H, ArH), 7.12 (s ,1H, ArH), 7.22 (d ,2H, ArH), 7.25 (d ,1H, ArH), 7.81 (d, 2H, ArH), 8.02 (d, 2H, ArH), 8.06 (d, 1H, ArH), 8.14–8.31 (d, 4H, ArH).

2.3.3. 3-((4-hexadecyloxybenzoyl) oxy)-4-((4-nitrophenyl) diazenyl) phenyl 4-methyl benzoate

UV spectrum (MDC) nm: 225 and 365. IR spectrum (KBr) $V^{-1}_{max/cm}$: 2960, 2920, 2850, 1741 (–COO-), 1606 (-N = N-), 1527, 1512 (–NO_2), 1471, 1450, 1342, 1259, 1168, 1093, 1051, 844, 800, 759, 688. ^1H NMR spectrum (400 MHz): δ 0.89 (t, 3H, –CH_3), 1.25–1.58 (m, 26H, 13 × –CH_2-), 1.80 (quant., 2H, -O-C-CH_2-), 2.49 (s, 3H, ArCH_3), 4.04 (t, 2H, Ar-O-CH_2-), 7.05 (d, 2H, ArH), 7.10 (s ,1H, ArH), 7.21 (d ,2H, ArH), 7.25 (d ,1H, ArH), 7.81 (d, 2H, ArH), 8.04 (d, 2H, ArH), 8.07 (d, 1H, ArH), 8.11–8.30 (d, 4H, ArH).

2.3.4. 3-((4-pentyloxybenzoyl) oxy)-4-((4-nitrophenyl) diazenyl) phenyl 4-methoxy benzoate

UV spectrum (MDC) nm: 266 and 368. IR spectrum (KBr) $V^{-1}_{max/cm}$: 2920, 2832, 1732 (–COO-), 1606 (-N = N-), 1525, 1510, (–NO_2), 1344, 1255, 1168, 1105, 1010, 916, 898, 840, 758, 658. ^1H NMR spectrum ((400 MHz): δ 0.93 (t, 3H, –CH_3), 1.25–1.57 (m, 4H, 2 × –CH_2-), 1.80 (quant., 2H, -O-C-CH_2-), 4.00–4.10 (m, 5H, Ar-O-CH_2- and Ar-OCH_3), 7.10 (d, 2H, ArH), 7.30 (d, 2H, ArH), 7.40 (s, 1H, ArH), 7.52 (d, 1H, ArH), 7.80 (d, 2H, ArH), 8.04 (d, 1H, ArH), 8.15 (d, 4H, ArH), 8.30 (d, 2H, ArH).

2.3.5. 3-((4-heptyloxybenzoyl) oxy)-4-((4-nitrophenyl) diazenyl) phenyl 4-methoxy benzoate

UV spectrum (MDC) nm: 266 and 368. IR (KBr) $V^{-1}_{max/cm}$: 2941, 2920, 2832, 2852, 1734 (–COO-), 1608 (-N = N-), 1525, 1510 (–NO_2), 1475, 1396, 1342, 1238, 1165, 1105, 1008, 916, 898, 840, 758, 684. ^1H NMR spectrum (400 MHz): δ 0.92 (t, 3H, –CH_3), 1.25–1.57 (m, 8H, 4 × –CH_2-), 1.81 (quant., 2H, O-C-CH_2-), 4.00–4.15 (m, 5H, Ar-O-CH_2- and Ar-OCH_3), 7.10 (d, 2H, ArH), 7.30 (d, 2H, ArH), 7.40 (s, 1H, ArH), 7.54 (d, 1H, ArH), 7.70(d, 2H, ArH), 8.05 (d, 1H, ArH), 8.15 (d, 4H, ArH), 8.30 (d, 2H, ArH).

2.3.6. 3-((4-dodecyloxybenzoyl) oxy)-4-((4-nitrophenyl) diazenyl) phenyl 4-methoxy benzoate

UV spectrum (MDC) nm: 266 and 368. IR spectrum (KBr) $V^{-1}_{max/cm}$: 2920, 2832, 1736 (–COO-), 1606 (-N = N-), 1525,1510

Table 1
Transition temperatures (°C) of the series I compound.

Compound No.	R = $-C_nH_{2n+1}$ n =	Cr		SmC		SmA		N		I
1	*1*	•	191							•
2	*2*	•	181							•
3	*3*	•	186							•
4	*4*	•	175							•
5	*5*	•	170							•
6	*6*	•	160					(•	110)	•
7	*7*	•	80	(•	50)					•
8	*8*	•	77	(•	57)					•
9	*10*	•	85	(•	80)					•
10	*12*	•	83	(•	79)					•
11	*14*	•	80			•	105			•
12	*16*	•	82			(•	72)			•

() = monotropic value.

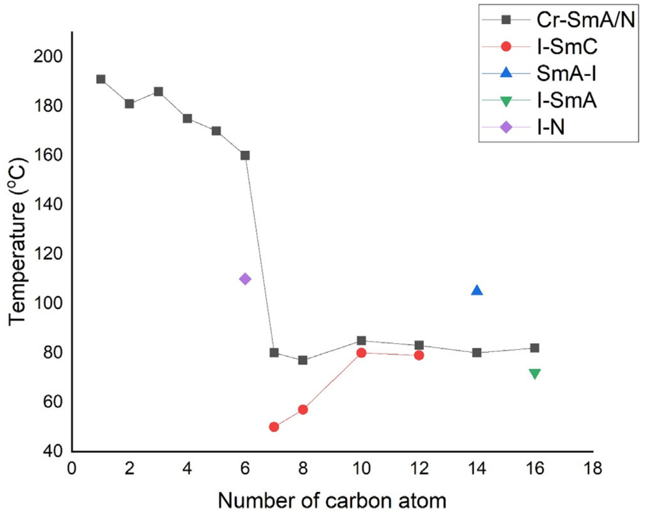


Fig. 3. The phase behavior of series I.

($-NO_2$), 1475, 1396, 1253, 1165, 1008, 916, 898, 758, 658. ^1H NMR spectrum (400 MHz): δ 0.83 (t, 3H, $-CH_3$), 1.18–1.49 (m, 18H, 9 × $-CH_2$-), 1.74 (quant., 2H, -O-C-CH_2-), 4.00–4.10 (m ,5H, Ar-O-CH_2- and Ar-OCH_3), 7.04 (d, 2H, ArH), 7.25 (d, 2H, ArH), 7.40 (s, 1H, ArH), 7.52 (d, 1H, ArH), 7.71 (d, 2H, ArH), 7.95 (d, 1H, ArH), 8.17 (d, 4H, ArH), 8.32 (d, 2H, ArH).

2.3.7. 3-((4-hexadecyloxybenzoyl) oxy)-4-((4-nitrophenyl) diazenyl) phenyl 4-methoxy benzoate

UV spectrum (MDC) nm: 266 and 368. IR spectrum (KBr) $V^{-1}_{max/cm}$: 2920, 2832, 2850, 1741(−COO-), 1604(-N = N-), 1527, 1510 ($-NO_2$), 1471, 1342, 1317, 1255, 1234, 1141, 1093, 1051, 1006, 900, 804. ^1H NMR spectrum (400 MHz): δ 0.86 (t, 3H, $-CH_3$), 1.27–1.49 (m, 26H, 13 × $-CH_2$-), 1.81 (quant., 2H, -O-C-CH_2-), 4.00–4.15 (m, 5H, Ar-O-CH_2- and Ar-OCH_3), 7.05 (d, 2H, ArH), 7.30 (d, 2H, ArH), 7.35 (s, 1H, ArH), 7.54 (d, 1H, ArH), 7.70 (d, 2H, ArH), 8.05 (d, 1H, ArH), 8.15(d, 4H, ArH), 8.36 (d, 2H, ArH).

3. Results and discussion

3.1. Effect of molecular constitution on mesomorphism

In all trans conformation, from the molecular shape of the series **I** and **II** it was observed that the molecules are neither rod-like nor disc-like but of λ-shape to **T**-shape. In thermotropic liquid crystal formation of mesophase is highly sensitive to the molecular configuration which can be correlated with thermal stability and mesophase length. Fig. 1 summarizes the molecular structure and dimensions of series **I** and **II**.

The molecular geometry of series **I** and **II** contains three phenyl rings linked by ester (–COO-) and azo (-N = N-) with central rigid ring, lateral *n*-alkoxy phenyl group and terminal methyl phenyl/ methoxy phenyl groups are attached to the meta and para position of central core ring with reference to the azo (-N = N-) group. The terminal methyl ($-CH_3$) /methoxy ($-OCH_3$) branch in series **I** and **II** seems to be affects the immergence of the mesophase and its thermal stability to a greater extent than the lateral *n*-alkoxy group, presumably due to the effect of its increased width. The L/ D ratio in series **I** (1.596) is lower than that in series **II** (1.629) due to the presence of methyl ($-CH_3$) group in series **I** and methoxy ($-OCH_3$) group in series **II**. Representative λ-shape molecule of series **I** and **T**-shape molecule of series **II** with length and diameter are shown in Fig. 1. As the lateral *n*-alkoxy chain length increases the

Table 2
Transition temperatures (°C) of the series II compound.

Compound No.	R = $-C_nH_{2n+1}$ n =	Cr		SmC		SmA		I
1	*1*	•	175					•
2	*2*	•	160					•
3	*3*	•	145					•
4	*4*	•	137					•
5	*5*	•	129					•
6	*6*	•	118					•
7	*7*	•	107	(•	72)			•
8	*8*	•	102	(•	77)			•
9	*10*	•	101			(•	79)	•
10	*12*	•	100			(•	85)	•
11	*14*	•	98			(•	89)	•
12	*16*	•	100			(•	60)	•

() = monotropic value.

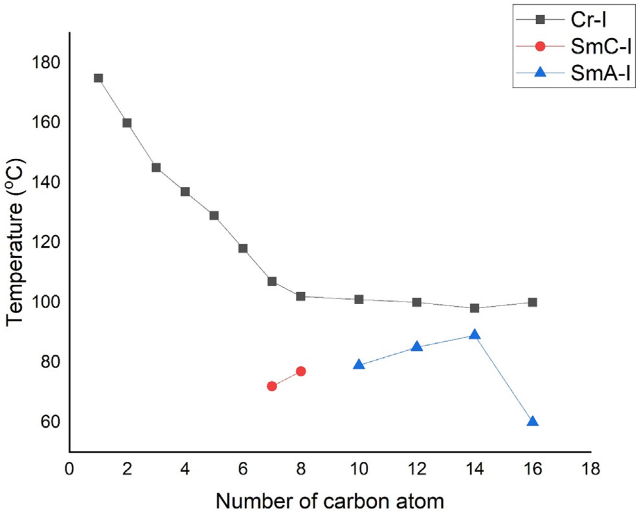


Fig. 4. The phase behavior of series II.

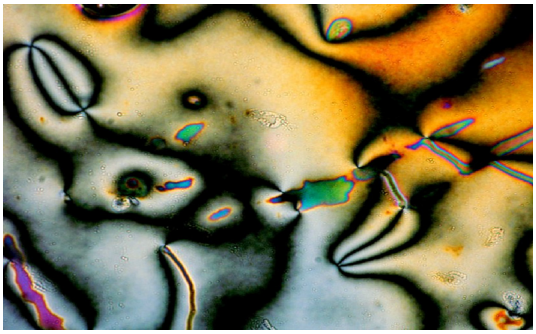


Fig. 5. *n*-hexyloxy derivative on cooling from isotropic liquid showed classical schlieren nematic texture at 100 ℃

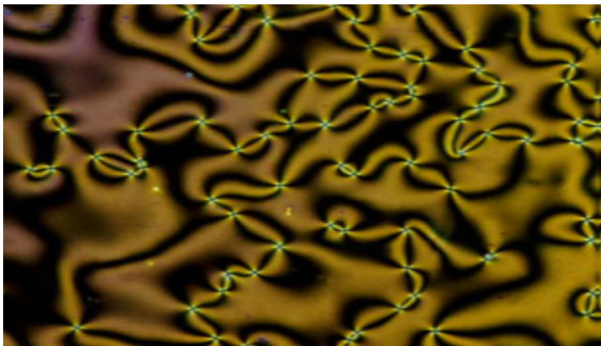


Fig. 6. *n*-dodecyloxy derivative showed smectic C mesophase on cooling from isotropic liquid at 75 ℃.

width of the molecules increases and the shape of molecule changes from λ-shaped to **T**-shaped which lowers the L/D ratio. This decrease in L/D ratio affects the formation of mesophase and thermal stability. Terminal attraction between the molecules prevails the smectic C/smectic A and nematic mesophase formation due to intermolecular attraction. As the lateral alkyl chain length increase the total polarizability enhances and the terminal attraction to lateral attraction ratio decreases. Under such conditions the molecules will adhere and strictly maintains the layered structure, although they might moderately acquire a fluid condition, and layered smectic C/ smectic A structure is maintained, giving rise to a smectic mesophase.

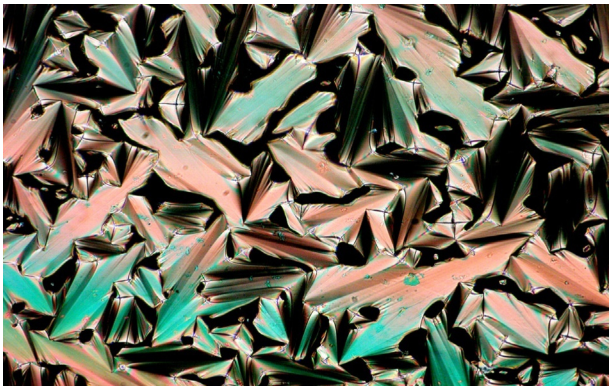


Fig. 7. *n*-hexadecyloxy derivative showed focal conic smectic A mesophase at 68 ℃ on cooling from the isotropic liquid.

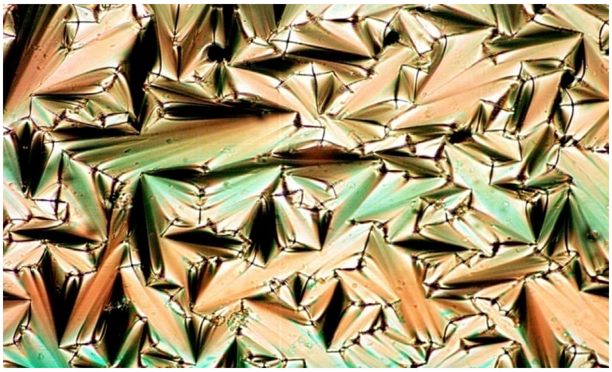


Fig. 8. *n*-tetradecyloxy derivative on cooling from the isotropic liquid showed focal conic smectic A mesophase at 81 ℃.

Lateral methoxy derivative of both the series **I** and **II** were found to be of λ-shape, as the number of carbon increases in lateral alkoxy chain the L/D ratio of the ascending molecules decreases and shape of the molecule changes from λ-shape to **T**-shape. For present series **I** it was observed that at about 1.351 L/D ratio mesomorphism immerges due to the mesogenic core and the lateral alkoxy chain interaction, whereas for series **II** threshold L/D ratio was about 1.442. Whereas for lower members **I***1*-**I***5* and **II***1*-**II***6* inheriting λ-shape, due to the short lateral alkoxy chain length weak intermolecular interaction between mesogenic core and the lateral alkoxy chain length as well as terminal nitro (–NO_2) and methyl (–CH_3)/methoxy (–OCH_3) prevents the formation of intercalation which in result prevents formation of mesophase. Increasing the lateral alkoxy chain length changes the molecular changes from λ-shape to **T**-shape and increase the interaction between terminal nitro (–NO_2), methyl (–CH_3)/methoxy (–OCH_3), mesogenic core and the lateral alkoxy chain, which favors the formation of intercalated structure.

3.2. Spectroscopic investigation

The presence of azo (-N = N-) groups leads to the possibly of photo-isomerization and photochromic behaviour. Preliminary studies of the photochemical properties were therefore conducted in solution. Chloroform solutions of concentration, 1×10^{-6} for dodecyl derivative of both the series were prepared for determination of UV–Vis absorption spectra. The λ-shaped to **T**-shaped mesogenic compounds of series **I** displayed three primary absorption

Table 3
DSC data for series I and II compounds.

Series-I	Heating Temp ℃ [$\Delta H/Jg^{-1}$, $\Delta S/Jg^{-1}\ K^{-1}$]		Cooling Temp ℃ [$\Delta H/Jg^{-1}$, $\Delta S/Jg^{-1}\ K^{-1}$]			
	SmA	Iso	N	SmA	SmC	Cr
6		159.6[13.09, 0.0302]	110.3[6.83, 0.0178]			78.6[8.05, 0.0228]
7		80.2[16.74, 0.0473]			49.7[5.09, 0.0157]	34.4[10.43, 0.0336]
8		76.8[10.27, 0.0293]			57.1[6.01, 0.0182]	37.7[13.61, 0.0438]
10		84.9[21.32, 0.0595]			79.8[8.97, 0.0254]	61.8[11.97, 0.0357]
12		83.3[17.02, 0.0472]			79.3[3.01, 0.0085]	64.7[13.14, 0.0397]
14	80.4[0.73, 0.0020]	105.6[14.81, 0.0391]		104.2[2.89, 0.0076]		73.8[19.04, 0.0549]
16		81.9[19.46, 0.2307]		72.5[8.55, 0.0247]		50.9[7.94, 0.02450]
Series-II						
7		106.3[33.59, 0.0885]			71.8[5.18, 0.2082]	51.1[23.82, 0.0734]
8		102.6[40.11, 0.1067]			77.4[1.73, 0.0049]	55.7[35.01, 0.1065]
10		101.1[42.79, 0.1137]		78.9[6.17, 0.0175]		62.4[36.17, 0.1082]
12		99.7[29.67, 0.0715]		84.7[7.82, 0.0218]		64.3[29.34, 0.0869]
14		98.0[35.92, 0.0968]		89.2[5.23, 0.0144]		75.5[15.62, 0.0448]
16		100.4[19.04, 0.0509]		60.1[9.12, 0.0273]		40.9[36.69, 0.1168]

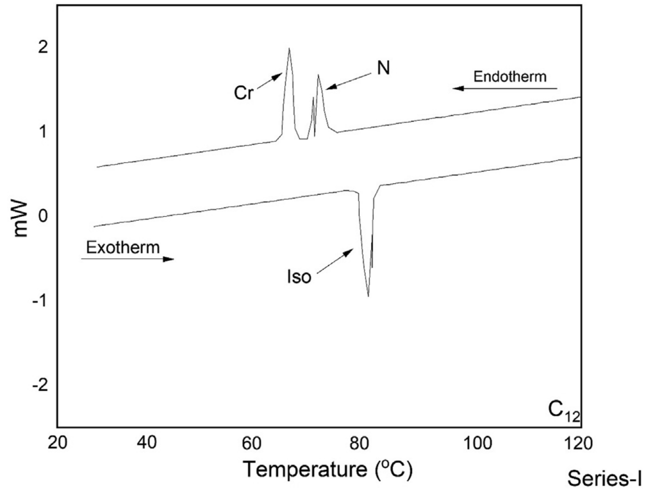


Fig. 9. DSC plots of series I, compound *12*.

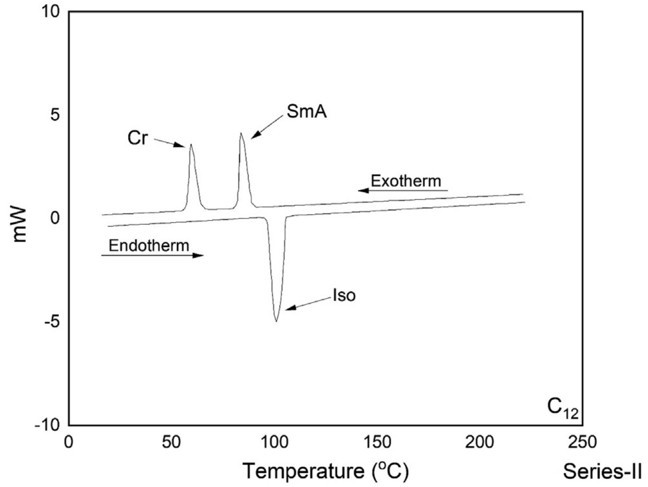


Fig. 10. DSC plots of series II, compound *12*.

maxima, at 225 nm, 365 nm and 470 nm; compounds of series **II** also showed three primary absorption maxima at 266 nm, 368 nm and 475 nm (Fig. 2). The λ-shaped to **T**-shaped azo (-N = N-) compounds in the *trans*-form showed a strong band at 365–368 nm attributed to π–π* transition, and a weak band at 470–475 nm due to n–π* transition. The *trans*-form is much more stable than the *cis*-form, but each isomer can be transformed into the other by irradiation of light of the appropriate wavelength. In general, on irradiation with UV light azobenzene compounds are characterized by a reversible transformation from the more stable trans- to the less stable *cis*-form. Photochemical trans–*cis*-trance isomerization by reorientation of azobenzene group can be induced by means of linearly polarized light [81-84].

The IR spectrum (λmax/cm^{-1}) show absorption bands in the region of 2960–2920 due to C-H stretching, in region of 1732–1741 due to carbonyl (C = O of ester) stretching vibration. The strong intensity stretching band in the region of 1604–1608 arising due to azo (-N = N-) group. Strong intensity C-O stretching band in the region of 1278–1282 and 1251–1269 arising in series **I** and **II** respectively, due to aromatic ester (O = C-O-Ar). In Series **I** there is only one the lateral alkoxy group (-OR) while in series **II** there is one the lateral alkoxy (-OR) and one terminal methoxy (–OCH$_3$), which in para direction to azo group (-N = N-) of central ring. This methoxy (–OCH$_3$) group creates asymmetric ether system which gives rise to additional frequency in the region of 2832 in series **II**. In the ^{1}H NMR spectrum, fifteen aromatic protons appear in the form of seven doublets (d) in the region of 8.11–8.31, 8.05–8.07, 8.02–8.04, 7.80–7.81, 7.25–7.26, 7.21–7.23 and 7.02–7.06, while one proton appear in the form of one singlet (s) in the region of δ 7.10–7.12 for series **I,** 7.52–7.40 for series **II**. One oxy-methylene of the lateral alkoxy chain (-OR) and terminal methyl (–CH$_3$) group resonate in the region of δ 4.02–4.04 as triplet and δ 2.47–2.49 as singlet in series **I**. Oxy-methylene of the lateral alkoxy chain (-OR) and terminal methoxy (–OCH$_3$) protons resonate in the region of δ 4.00–4.15 as a multiplate in series **II**. One methylene (O-C-CH$_2$) protons resonate in the region δ 1.74–1.81 as a quartered. One methyl group (–CH$_3$) attached to chiral carbon (C*) of ester chain (–COO-) and rest of the methylene protons of the lateral alkoxy chain resonate in the region δ 1.18–1.58 as a multiplate. Methyl group (–CH$_3$) of the lateral alkoxy chain (-OR) resonate in the region of δ 0.83–0.93 as triplet.

As a preliminary investigation, the mesophases exhibited by compounds of series **I** and **II** were concluded by the optical microscopic studies.

3.3. The phase behavior and mesomorphic properties of series I and II

3.3.1. 3-((4-alkoxybenzoyl) oxy)-4-((4-nitrophenyl) diazenyl) phenyl 4-methyl benzoate

In the series **I** methoxy to *n*-pentyloxy derivatives are non-mesogenic. *n*-Hexyloxy derivative exhibits only monotropic nematic mesophase. *n*-Heptyloxy to *n*-dodecyloxy derivatives

Table 4
The comparison of mesophase length (℃), thermal stabilities (℃) and molecular structure of *n*-dodecyloxy derivative of series **I** and **II**, Series **A** to **D.**

Series	Mesophase length		Thermal stability		Commencement of smectic phase
	SmA	N	SmA-I	N-I	
I	21	–	79	–	C_7
II	23	–	85	–	C_7
A	37	–	105	–	C_7
B	–	9	–	80	–
C	23.3	26	41.4	–	C_{12}
D	21	–	58	–	C_8

exhibit monotropic smectic C mesophase. *n*-tetradecyloxy derivative exhibits enantiotropic SmA mesophase whereas *n*-hexadecyloxy derivatives exhibits monotropic Smectic A mesophase. The transition temperatures are recorded in table 1. The plot of transition temperatures against the number of carbon atoms in the alkoxy chain is given in Fig. 3 from which it can be noticed that the SmC-I transition temperatures increase as the series ascended which levels off slightly for *n*-dodecyloxy derivative, whereas it exhibits a falling tendency for SmA-I transition temperatures in the higher homologues.

3.3.2. 3-((4-alkoxybenzoyl) oxy)-4-((4-nitrophenyl) diazenyl) phenyl 4-methoxy benzoate

In the series **II** methoxy to *n*-hexyloxy derivatives are non-mesogenic. *n*-Heptyloxy and *n*-octyloxy derivatives exhibit monotropic smectic C mesophase. Smectic A mesophase commences from *n*-decyloxy derivative as a monotropic and persist up to the last member synthesized. The transition temperatures are recorded in table 2. The plot of transition temperatures against the number of carbon atoms in the alkoxy chain is given in Fig. 4 from which it can be noticed that the crystal-isotropic transition temperatures exhibit a tendency to decrease with increase in the length of terminal alkoxy tail except for *n*-tetradecyloxy derivative. Smectic C to isotropic transition temperatures exhibited little rising tendency. SmA-I transition temperatures exhibited rising tendency which levels off for the last homologue synthesized.

3.3.3. Microscopic observation for series I and II

All mesogenic compounds of series **I** was found monotropic except *n*-tetradecyl derivative SmA mesophase which was found enantiotropically mesogenic. *n*-hexyloxy derivative (n = *6*) formed small droplets that coalesced to the classical schlieren texture of the nematic phase. *n*-heptyloxy to *n*-dodecyloxy derivatives exhibited schlieren texture of smectic C mesophase. Rest of the higher homologues of series **I** (n = *14* and *16*) gave only focal-conic texture characteristic of smectic A mesophase. *n*-hexyloxy derivative on cooling from isotropic liquid showed classical schlieren nematic texture at 100 ℃ (Fig. 5), *n*-dodecyloxy derivative showed smectic C mesophase on cooling from isotropic liquid at 75 ℃ (Fig. 6), and *n*-hexadecyloxy derivative showed focal conic smectic A mesophase at 68 ℃ (Fig. 7) on cooling from the isotropic liquid.

Mesogens of series **II** were also found to be monotropically mesogenic where methoxy to *n*-hexyloxy derivatives found non mesogenic, *n*-heptyloxy and *n*-octyloxy derivative exhibited schlieren texture of smectic C mesophase and rest of the higher homologues *n*-decyloxy to *n*-hexadecyloxy exhibited only focal-conic texture characteristic of smectic A mesophase. *n*-tetradecyloxy derivative on cooling from the isotropic liquid showed focal conic smectic A mesophase at 81 ℃ (Fig. 8).

3.4. Calorimetric studies

Thermograms for all mesogenic compounds of series **I** and **II** were recorded to confirm the microscopic reading and the type of mesophase. The enthalpy changes with respect to phase transitions are also observed. Data of these DSC analyses are recorded in table 3. Representative thermogram of *n*-dodecyloxy of series **I** is shown in Fig. 9 where peak of crystal to isotropic appeared at 83.3 ℃ with a ΔH of 17.02 Jg^{-1} and ΔS of 0.0472 Jg^{-1} K^{-1} on heating cycle, while peak of isotropic to Smectic C appeared at 79.3 ℃ with a ΔH of 3.01 Jg^{-1} and ΔS of 0.0085 Jg^{-1} K^{-1} and peak of Smectic C to crystal appeared at 64.7 ℃ with a ΔH of 13.14 Jg^{-1} and ΔS of 0.0397 Jg^{-1} K^{-1} on cooling cycle, similarly peak of crystal to isotropic appeared at 99.7 ℃ with a ΔH of 29.67 Jg^{-1} and ΔS of 0.0715 Jg^{-1} K^{-1} on heating cycle, while peak of isotropic to Smectic A appeared at 84.7 ℃ with a ΔH of 7.82 Jg^{-1} and ΔS of 0.0218 Jg^{-1} K^{-1} and peak of Smectic A to crystal appeared at 64.3 ℃ with a ΔH of 29.34 Jg^{-1} and ΔS of 0.0869 Jg^{-1} K^{-1} on cooling cycle thermogram of *n*-dodecyloxy of series **II** which is shown in Fig. 10. Enthalpy changes of the various transitions agree well with the existing related literature value.

3.5. Mesogenic properties and molecular constitution:

Table 4 summarizes comparison of smectic mesophase range, transition temperatures and molecular structure of *n*-dodecyloxy derivative of the series **I** and **II** respectively as well as structurally related known compounds **A** [73], **B** [74], **C** [69] and **D** [43]. All the compound (n = *7–16*) of series **I** and **II** are monotropic smectogenic with the exception of the *n*-hexyloxy derivative of series **I** which is monotropic nematogenic because of the presence of less polar methyl (–CH_3) terminal group. The smectic range of series **I** (n = *12*) is about 21 °C whereas that of series **II** (n = *12*) is 23 °C. However, the Sm-I transition temperatures of both the series are almost the same. This is understandable as the molecular constitution of series **I** and **II** differ only at one terminus. The molecule of series **I** has methyl group (–CH_3) at one terminus whereas molecule of series **II** has methoxy group (–OCH_3) at the same terminus.

Reference to table 4 also shows that the smectic mesophase length of series **I** and **II** is lower by 16 °C and 14 °C and smectic mesophase thermal stabilities is lower by 26 °C & 20 °C, respectively when compared that of series **A**. The molecular structure of series **I**, **II** and series **A** differ at one terminus only. The molecules of series **I** and **II** have terminal methyl group (–CH_3) and methoxy group (–OCH_3) respectively at one terminus whereas molecules of series **A** have –OR (-$OC_{12}H_{25}$) group at the terminus. Gray [85] has explained that the addition of each methylene group increases the polarizability of the molecules. Hence the higher mesophase length and the thermal stabilities of series **A** may be due to the presence of longer alkoxy chain (-OR).

Series **I** and **II** are smectogenic whereas series **B** is nematogenic. Moreover, the smectic mesophase length & thermal stabilities of series **I** and **II** are much higher as compared to the nematic mesophase length and thermal stabilities of series **B**. The main difference in the molecular structures of series **I** & **II** and series **B** is that the series **I** and **II** all are having less polar methyl (–CH_3) and methoxy (–OCH_3) group terminal group whereas series **B** has no terminal substituent at one end. Probably the presence of less polar methyl group (–CH_3) and methoxy group (–OCH_3) dipole in series **I** and **II** are responsible for the smectogenic properties as well as lower mesophase length & thermal stabilities of the present series **I** and **II** as compared to series **B**. This is also reflected in comparison of series **I** and **II** with series **C**. Table 4 indicates that the thermal stabilities of series **I** and **II** are higher compared to series **C** even though it contains longer dodecyloxy chain. However, the smectic mesophase length of series **I** and **II** are little lower as compared to series **C**. One should keep in mind that the mesophase length is also partly depend on the crystal-mesophase transitions.

It's also seen that the smectic mesophase length of series **I** and **II** is higher by 0 °C and 2 °C and smectic mesophase thermal stabilities is higher by 21 °C & 27 °C, respectively when compared that of series **D**. The molecular structure of series **I**, **II** and series **D** differ at one terminus and lateral chloro substituent only. The molecules of series **I** and **II** have methyl group ($-CH_3$) and methoxy group ($-OCH_3$) respectively at one terminus whereas molecules of series **D** have alkoxy (-OR) ($-OC_{12}H_{25}$) group at the terminus and lateral chloro group (–Cl) meta to the nitro group ($-NO_2$).

Due to the presence of terminus the *n*-alkoxybenzoyl substituent, which may be responsible for the slightly lower smectic A to isotropic transition temperature of series **D**. The range and thermal stability of the mesophase is the more important factor in relating mesomorphic behaviour to chemical constitution, since the chemical grouping gives rise to intermolecular attractions, which in turn determine the lower mesophase range and thermal stability. Gray [85] has explained that the addition of each methylene group increases the polarizability of the molecules. Hence the higher mesophase length and lower the thermal stabilities of series **D** may be due to the presence of longer alkoxy chain.

lateral chloro group (–Cl) meta to the nitro group ($-NO_2$), whereas the position meta to the nitro group ($-NO_2$) in series **I** and **II** is unsubstituted. The lateral substitution in the molecule normally decreases the thermal stability of both the smectic and nematic mesophases, as a result of the broadening effect and forcing the molecules apart. It seems that in series **D**. Lateral chloro (–Cl) substituents which do not broaden the molecule enhance liquid crystalline thermal energy; the thermal stability of the smectic phase is properly enhanced when the substituent is dipolar. Gray [85] has explained that a compound which requires more thermal energy to disorganize the molecular arrangement of the smectic mesophase will be more thermally stable.

4. Conclusion

Twenty-four new mesogenic λ-shaped to **T**-shaped homologues with less polar methyl ($-CH_3$) and methoxy ($-OCH_3$) substituents have been synthesized. Some of the compounds have been characterized by elemental analysis and standard spectroscopic methods.

The lower members of series **I** and **II** are non-mesogenic. Middle members of series **I** and **II** exhibit monotropic smectic C mesophase and the higher members exhibit monotropic smectic A mesophases. The mesomorphic properties of the present series were compared with each other and with the structurally related mesogenic homologous series to evaluate the effect of methyl ($-CH_3$) /methoxy ($-OCH_3$) terminal substituent's as well as variation of shape of the molecule by changing the chain length of bulky lateral alkyl substituent on mesomorphism. The mesogenic homologous series with less polar methyl ($-CH_3$) and methoxy ($-OCH_3$) substituents exhibited liquid crystalline properties with good mesomorphism having monotropic smectic C, smectic A and nematic mesophase with lower length and thermal stabilities.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] S. Chandrasekhar, B.K. Sadashiva, K.A. Suresh, Liquid Crystals of disk-like molecules, Pramana. 9 (1977) 471–480, https://doi.org/10.1007/BF02846252.
[2] F. Reinitzer, Contributions to the knowledge of cholesterol, Monatsh. Chem. 9 (1888) 421–441, https://doi.org/10.1007/BF01516710.
[3] F. Reinitzer, Contributions to the knowledge of cholesterol, Liquid Crystals 5 (1) (1989) 7–18, https://doi.org/10.1080/02678298908026349.
[4] O. Lehmann, Über fliessende Krystalle, Z. Phys. Chem. 4 (1889) 462–467, https://doi.org/10.1515/zpch-1889-0434.
[5] A.M. van de Craats, N. Stutzmann, O. Bunk, M.M. Nielsen, M. Watson, K. Müllen, H.D. Chanzy, H. Sirringhaus, R.H. Friend, Meso-Epitaxial Solution-Growth of Self-Organizing Discotic Liquid-Crystalline Semiconductors, Adv. Mater. 15 (6) (2003) 495–499, https://doi.org/10.1002/adma.200390114.
[6] G.G. Nair, D.S.S. Rao, S.K. Prasad, S. Chandrasekhar, S. Kumar, Electrooptic and Viewing Angle Characteristics of a Display Device Employing a Discotic Nematic Liquid Crystal Mol, Cryst. Liq. Cryst. 397 (1) (2003) 245–252, https://doi.org/10.1080/714965605.
[7] K. Kawata, Orientation Control and Fixation of Discotic Liquid Crystal, Chem. Rec. 2 (2) (2002) 59–80, https://doi.org/10.1002/(ISSN)1528-069110.1002/tcr.v2:210.1002/tcr.10015.
[8] J. Contzen, G. Heppke, H.S. Kitzerow, D. Kruerke, H. Schmid, Storage of laser-induced holographic gratings in discotic liquid crystals, Appl. Phys. B: Lasers Opt. 63 (6) (1996) 605–608, https://doi.org/10.1007/BF01831000.
[9] L. Schmidt-Mende, A. Fechtenkotter, K. Mullen, E. Moons, R.H. Friend, J.D. MacKenzie, Self-organized discotic liquid crystals for high-efficiency organic photovoltaics, Science 293 (2001) 1119–1122, https://doi.org/10.1126/science.293.5532.1119.
[10] S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hägele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel, M. Tosoni, Discotic Liquid Crystals: From Tailor-Made Synthesis to Plastic Electronics, Angew. Chem., Int. Ed. 46 (26) (2007) 4832–4887, https://doi.org/10.1002/(ISSN)1521-377310.1002/anie.v46:2610.1002/anie.200604203.
[11] S. Kumar, Self-organization of disc-like molecules: chemical aspects Chem, Soc. Rev. 35 (1) (2006) 83–109, https://doi.org/10.1039/B506619K.
[12] Bushby RJ, Lozman, OR. Curr. Opin. Discotic liquid crystals 25 years on. Colloid Interface Sci. 2002;7:343–354. DOI: 10.1016/S1359-0294(02)00085-7
[13] M. Lehmann, Star mesogens (Hekates)-tailor-made molecules for programming supramolecular functionality, Chem. Eur. J. 15 (15) (2009) 3638–3651, https://doi.org/10.1002/chem.200802625.
[14] Lehmann M, Gearba RI, Koch MHJ, et al. Semiflexible star-shaped mesogens asnonconventional columnarliquid crystals. Chem Mater. 2004;16:374–376. DOI:10.1021/cm034487x.
[15] A. Zelcer, B. Donnio, C. Bourgogne, F.D. Cukiernik, D. Guillon, Mesomorphism of hybrid siloxane-triphenylene star-shaped oligomers, Chem. Mater. 19 (8) (2007) 1992–2006, https://doi.org/10.1021/cm062949b10.1021/cm062949b.s001.
[16] L. de Campo, M.J. Moghaddam, T. Varslot, N. Kirby, R. Mittelbach, T. Sawkins, S. T. Hyde, Nanocompartmentalization of soft materials with three mutually immiscible solvents: synthesis and self-assembly of three-arm star-polyphiles, Chem. Mater. 27 (3) (2015) 857–866, https://doi.org/10.1021/cm503981t.
[17] A.L. Kanibolotsky, I.F. Perepichka, P.J. Skabara, Starshaped π-conjugated oligomers and their applications in organic electronics and photonics, Chem. Soc. Rev. 39 (2010) 2695–2728, https://doi.org/10.1039/b918154g.
[18] Y.-H. Ooi, G.-Y. Yeap, C.-C. Han, H.-C. Lin, K. Kubo, M.M. Ito, Synthesis and smectogenic properties of novel phloroglucinol-based star-shaped liquid crystals containing three peripheral alkyloxylatedschiff base arms, Liq. Cryst. 40 (4) (2013) 516–527, https://doi.org/10.1080/02678292.2012.761734.
[19] A.S. Achalkumar, U.S. Hiremath, D.S.. Rao, S.K. Prasad, C.V. Yelamaggad, Selfassembly of hekates-tris(N-salicylideneaniline)s into columnar structures: synthesis and characterization, J. Org. Chem. 78 (2) (2013) 527–544, https://doi.org/10.1021/jo302332u.

[20] C. Tschierske, Development of structural complexity by liquid-crystal self-assembly, Angew. Chem. Int. Ed. Engl. 52 (34) (2013) 8828–8878, https://doi.org/10.1002/anie.201300872.

[21] S. Huo, R. Mroz, J. Carroll, Negishi coupling in the synthesis of advanced electronic, optical, electrochemical, and magnetic materials, Org. Chem. Front. 2 (4) (2015) 416–445, https://doi.org/10.1039/C4QO00322E.

[22] E. Westphal, M. Prehm, I.H. Bechtold, C. Tschierske, H. Gallardo, Room temperature columnar liquid crystalline phases of luminescent non-symmetric star-shaped molecules containing two 1,3,4-oxadiazole units, J. Mater. Chemc. 1 (48) (2013) 8011, https://doi.org/10.1039/c3tc31704h.

[23] S.K. Pathak, B. Pradhan, R.K. Gupta, M. Gupta, S.K. Pal, A.S. Achalkumar, Aromatic π-π driven supergelation, aggregation induced emission and columnar self-assembly of star-shaped 1,2,4-oxadiazole derivatives, J. Mater. Chem. C. 4 (27) (2016) 6546–6561, https://doi.org/10.1039/C6TC01939K.

[24] P.J. Stackhouse, A. Wilson, D. Lacey, M. Hird, Synthesis and properties of novel columnar liquid crystals based on symmetrical and non-symmetrical 1,3,5-trisubstituted benzene derivatives, Liq. Cryst. 37 (9) (2010) 1191–1203, https://doi.org/10.1080/02678292.2010.490647.

[25] C.T. Imrie, P.A. Henderson, G.-Y. Yeap, Liquid crystal oligomers: going beyond dimers, Liq. Cryst. 36 (6-7) (2009) 755–777, https://doi.org/10.1080/02678290903157455.

[26] G. Pelzl, S. Diele, W. Weissflog, Banana-shaped compounds – a new field of liquid crystals, Adv. Mater. 11 (1999) 707–724, https://doi.org/10.1002/(SICI)1521-4095(199906)11:9<707::AID-ADMA707>3.0.CO;2-D.

[27] S. Balamurugan, P. Kannan, K. Yadupati, A. Roy, Electrooptical switching studies on 1,3-phenylene based banana shaped liquid crystals, J. Mol. Struct. 1001 (1-3) (2011) 118–124, https://doi.org/10.1016/j.molstruc.2011.06.027.

[28] F. Osman, G.Y. Yeap, A. Nagashima, et al., Structure property and mesomorphic behavior of S-shaped liquid crystal oligomers possessing two azobenzene moieties, Liq. Cryst. 43 (2016) 1283–1292, https://doi.org/10.1080/02678292.2016.1169562.

[29] F. Ogasawara, H. Kasai, Y. Nagashima, T. Kawaguchi, A. Yoshizawa, Structureproperty correlations of novel S-shaped liquid crystal oligomers, Ferroelectrics 365 (1) (2008) 48–57, https://doi.org/10.1080/00150190802062908.

[30] M. Kołpaczyńska, K. Madrak, J. Mieczkowski, E. Górecka, D. Pociecha, H-shaped liquid crystalline dimers, Liq. Cryst. 38 (2) (2011) 149–154, https://doi.org/10.1080/02678292.2010.531403.

[31] Prajapati AK, Varia MC. H-shaped symmetrical twin liquid crystalline compounds with polar-terminal substituents. Liq Cryst. 2013;40:1151–1158. DOI: 10.1080/02678292.2013.819945.

[32] J. Han, Q. Wang, J. Wu, L.-R. Zhu, Synthesis and liquid crystalline property of H-shaped 1,3,4-thiadiazole dimers, Liq. Cryst. 42 (1) (2015) 127–133, https://doi.org/10.1080/02678292.2014.966792.

[33] Y.-K. Kim, R. Breckon, S. Chakraborty, M. Gao, S.N. Sprunt, J.T. Gleeson, R.J. Twieg, A. Jákli, O.D. Lavrentovich, Properties of the broad-range nematic phase of a laterally linked H-shaped liquid crystal dimer, Liq. Cryst. 41 (9) (2014) 1345–1355, https://doi.org/10.1080/02678292.2014.920930.

[34] Attard GS, Douglass AG. U-shaped dimeric liquid crystals derived from phthalic acid. Liq Cryst. 1997;22:349–358. DOI: 10.1080/026782997209423.

[35] A. Yamaguchi, M. Watanabe, A. Yoshizawa, Odd-even effects in the phase transition behaviour of novel U-shaped liquid crystals, Liq. Cryst. 34 (5) (2007) 633–639, https://doi.org/10.1080/02678290701292355.

[36] M. Sato, A. Yoshizawa, F. Ogasawara, Novel T-shaped chiral oligomers with a wide temperature range of a blue phase, Mo.l Cryst. Liq. Cryst. 475 (1) (2007) 99–112, https://doi.org/10.1080/15421400701679939.

[37] M.C. Varia, S. Kumar, A.K. Prajapati, T-shaped non-symmetrical twin liquid crystalline compounds, Liq. Cryst. 39 (8) (2012) 933–942, https://doi.org/10.1080/02678292.2012.687780.

[38] A. Yoshizawa, M. Nakata, A. Yamaguchi, Phase transition behaviour of novel Y-shaped liquid crystal oligomers, Liq. Cryst. 33 (5) (2006) 605–609, https://doi.org/10.1080/02678290600617462.

[39] P.K. Challa, S. Chakraborty, R. Breckon, C. Zhang, S. Pardaev, R.W. Twieg, A. Jákli, S.N. Sprunt, J.T. Gleeson, Viscoelastic properties of a branched liquid crystal in the nematic phase, Liq. Cryst. 41 (6) (2014) 747–754, https://doi.org/10.1080/02678292.2014.889235.

[40] S. Kashima, Y. Takanishi, J. Yamamoto, A. Yoshizawa, Flexible taper-shaped liquid crystal trimer exhibiting a modulated smectic phase, Liq. Cryst. 41 (12) (2014) 1752–1761, https://doi.org/10.1080/02678292.2014.950353.

[41] A. Yamaguchi, I. Nishiyama, J. Yamamoto, H. Yokoyama, A. Yoshizawa, Unusual smectic phases organized by novel λ-shaped mesogenic molecules, J. Mater. Chem. 15 (2) (2005) 280–288, https://doi.org/10.1039/B406716A.

[42] Ganatra KJ, Bhoya UC. Study of homologous series of azomesogens with lateral aromatic branch. Mol Cryst Liq Cryst. 2008;487:110–116. DOI: 10.1080/15421400802221904.

[43] Prajapati AK, Varia MC. λ-shaped azomesogens with polar chloro- and nitro-substituents. Liq Cryst. 2010;37:1083–1090. 10.1080/02678292.2010.489153.

[44] F.A. Olate, M.L. Parra, J.M. Vergara, J. Barberá, M. Dahrouch, Star-shaped molecules as functional materials based on 1,3,5- benzenetriesters with pendant 1,3,4-thiadiazole groups: liquid crystals, optical, solvatofluorochromic and electrochemical properties, Liq. Cryst. 44 (7) (2017) 1173–1184, https://doi.org/10.1080/02678292.2016.1269369.

[45] S. Roth, M. Lehmann, Mesogenic origami–fourarmed, star-shaped mesogens as precursors for functional liquid crystal materials, Liq. Cryst. 44 (12–13) (2017) 1830–1851, https://doi.org/10.1080/02678292.2017.1346209.

[46] L.-L. Lai, C.-H. Lee, L.-Y. Wang, K.-L. Cheng, H.-F. Hsu, Star-shaped mesogens of triazine-based dendrons and dendrimers as unconventional columnar liquid crystals, J. Org. Chem. 73 (2) (2008) 485–490, https://doi.org/10.1021/jo701990w10.1021/jo701990w.s001.

[47] Y.-H. Ooi, G.-Y. Yeap, C.-C. Han, H.-C. Lin, K. Kubo, M.M. Ito, Synthesis and smectogenic properties of novel phloroglucinol-based starshaped liquid crystals containing three peripheral alkyloxylated Schiff base arms, Liq. Cryst. 40 (4) (2013) 516–527, https://doi.org/10.1080/02678292.2012.761734.

[48] Dan Shu Yao, Jun He, Guo Hua Li, Qian Xu, Ying Gang Jia, Fan Bao Meng, Synthesis and mesomorphism of novel star-shaped liquid crystals containing donor-acceptor groups, Appl. Mech. Mater. 395-396 (2013) 72–75, https://doi.org/10.4028/www.scientific.net/AMM.395-396.72.

[49] Y. Shimizu, A. Kurobe, H. Monobe, N. Terasawa, K. Kiyohara, K. Uchida, Calamitic and discotic mesophases formed by kinetically controlled rod–disc alternation of molecular shape in a triphenylene–azobenzene mesogenic system, Chem. Commun. (14) (2003) 1676–1677, https://doi.org/10.1039/B301862H.

[50] B. Pradhan, S.K. Pathak, R.K. Gupta, M. Gupta, S.K. Pal, A.S. Achalkumar, Star-shaped fluorescent liquid crystals derived from s-triazine and 1,3,4-oxadiazole moieties, J. Mater. Chem. C. 4 (25) (2016) 6117–6130, https://doi.org/10.1039/C6TC01260D.

[51] B.G. Kim, S. Kim, S.Y. Park, Star-shaped discotic nematic liquid crystal containing 1,3,5-triethynylbenzene and oxadiazole-based rigid arms, Tetrahedron Lett. 42 (14) (2001) 2697–2699, https://doi.org/10.1016/S0040-4039(01)00245-3.

[52] M. Tian, B.-Y. Zhang, Y.-H. Cong, N. Zhang, D.-S. Yao, Mesomorphic properties of multi-arm liquid crystals containing glucose and sorbitol as cores, J. Mol. Struct. 923 (1-3) (2009) 39–44, https://doi.org/10.1016/j.molstruc.2009.01.049.

[53] M. Tian, B.-Y. Zhang, Y.-H. Cong, X.-Z. He, H.-S. Chu, X.-Y. Zhang, Cholesteric starshaped liquid crystals induced by a maltose core: synthesis and characteristics, Liq. Cryst. 37 (11) (2010) 1373–1379, https://doi.org/10.1080/02678292.2010.517325.

[54] M. Tian, B.-Y. Zhang, Y.-H. Cong, X.-Z. He, B. Zhang, Mesomorphic properties of chiral nematic star-shaped liquid crystals containing melitose as cores, J. Mo.l Struct. 937 (1-3) (2009) 131–135, https://doi.org/10.1016/j.molstruc.2009.08.026.

[55] M. Tian, S.-J. Wu, X.-W. Tian, D.-S. Yao, C.-L. Li, J.-S. Hu, B.-Y. Zhang, Mesomorphic properties of chiral three-arm liquid crystals containing 1,2,4-butanetriol as core, J. Mol. Struct. 1107 (2016) 202–213, https://doi.org/10.1016/j.molstruc.2015.11.040.

[56] Demus, D. Plenary Lecture. One hundred years of liquid-crystal chemistry: Thermotropic liquid crystals with conventional and unconventional molecular structure. Liq. Crystals, 1989;5: 75-110. DOI: 10.1080/02678298908026353; Demus, D. 100 Years Liquid Crystal Chemistry. Mol. Cryst. Liq. Cryst. 1988;165:45-84. DOI: 10.1080/00268948808082196.

[57] Gray GW, Liquid Crystals and Plastic Crystals (Ellis Horwood), Halsted press (1974)..

[58] Osman MA, Mol. Cryst. Liq. Cryst., Molecular Structure and Mesomorphic Properties of Thermotropic Liquid Crystals. III. Lateral Substituents.1985;128;45-63. DOI: 10.1080/00268948508082187.

[59] E. Bui, J.P. Bayle, F. Perez, L. Liebert, J. Courtieu, Synthèse de complexes nématiques du cuivre à partir de ligands substitués par des halogens, Liq. Cryst. 8 (1990) 513, https://doi.org/10.1080/02678299008047366.

[60] W. Weissflog, D. Demus, Compounds with lateral long-chain substituents—a new molecule structure concept for thermotropic liquid crystals Crystal Res, Tech. 18 (1983), https://doi.org/10.1002/crat.2170180127.

[61] C.T. Imrie, L. Taylor, The preparation and properties of low molar mass liquid crystals possessing lateral alkyl chains, Liq. Cryst. 6 (1989) 1–10, https://doi.org/10.1080/02678298908027317.

[62] H.T. Nguyen, C. Destrade, J. Malthete, New biforked mesogen series, Liq. Cryst. 8 (1990) 797–811, https://doi.org/10.1080/02678299008047390.

[63] W. Weissflog, D. Demus, Liquid-crystalline compounds with lateral aromatic branches, Liq. Cryst. 3 (1988) 275–284, https://doi.org/10.1080/02678298808086374.

[64] J.W. Goodby, G.H.I. Mehl, M. Saez, R.P. Tuffin, G. Mackenzie, R.A. Auzely-Velty, T. Benvegu, D. Plusquellec, Liquid crystals with restricted molecular topologies: supermolecules and supramolecular assemblies, Chem. Commun. 19 (1998) 2057–2070, https://doi.org/10.1039/A802762E.

[65] Shen D, Pelzl DS, Wirth GI, Tschierske C. Designing banana-shaped liquid crystals without Schiff's base units: m-terphenyls, 2,6-diphenylpyridines and V-shaped tolane derivatives. J. Mater. Chem., 1999;9:661-672. DOI: 10.1039/A808275H; Takezoe H, Takanishi Y. Bent-Core Liquid Crystals: Their Mysterious and Attractive World. Jpn. J. Appl. Phys., 2006;45(2A):597. DOI: 10.1143/JJAP.45.597.

[66] M. Massalska-Arodz, H. Stettin, H. Kresse, Dielectric Low-Frequency Relaxation in a Swallow-Tailed Liquid Crystal, Mol. Cryst. Liq. Cryst. 177 (1989) 155–161, https://doi.org/10.1080/00268948908047779.

[67] I.M. Saez, J.W. Goodby, Design and properties of "Janus-like" supermolecular liquid crystals, Chem. Commun. (2003) 1726–1727, https://doi.org/10.1039/B305152H.

[68] A. Yoshizawa, A. Yamaguchi, Kinetically induced intermolecular association: unusual enthalpy changes in the nematic phase of a novel dimeric liquid-crystalline molecule, Chem. Commun. (2002) 2060, https://doi.org/10.1039/B204901P.

[69] P. Berdague, J.P. Bayle, Mei-Sing Ho, B.M. Fung, New laterally aromatic branched liquid crystal materials with large nematic ranges, Liq. Cryst. 14 (1993) 667–674, https://doi.org/10.1080/02678299308027746.

[70] R.A. Vora, A.K. Prajapati, J.B. Kevat, K.K. Raina, Mesogenic properties and the effect of 1,2,4-trisubstitution on the central benzene nucleus of a three-ring mesogens, Liq. Cryst. 28 (2001) 983–989, https://doi.org/10.1080/02678290110048273.

[71] R. Mahajan, H. Nandedkar, S.S. Denial, Liquid Crystals Posessing 1,2,4-Trisubstituted Benzene Derivatives, Mol. Cryst. Liq. Cryst. 368 (2001) 697–707, https://doi.org/10.1080/10587250108030003.

[72] R.A. Vora, A.K. Prajapati, Azomesogens with 1,2,4-trisubstituted benzene moiety, Bull. Mater. Sci. 25 (2002) 355–358, https://doi.org/10.1007/BF02704132.

[73] M.Ph. Patel, D. Thesis, 'Synthesis and Evalution of Liquid Crystals with Low Molecular mass and High molecular mass (Polymers)', The M, S. University of Baroda, Vadodara, India, 2000.

[74] H.Ph. Nandedkar, D. Thesis, "Synthesis and Characterization of Liquid Crystals with Flexible and Rigid Spacer" The M, S., University of Baroda, Vadodara, India, 1999.

[75] G.Y. Yeap, Y.H. Ooi, λ-Shaped liquid crystal trimers with dual terminal cholesteryl moieties: synthesis and concomitant of N*, SmA and cholesteric glassy phases, Liq, Cryst. 45 (2017) 204–218, https://doi.org/10.1080/02678292.2017.

[76] X.S. Chen, H.Z. Tao, L. Dong, J.S. Hu, D.S. Yao, M. Tian, Mesomorphic properties of non-symmetric three-arm chenodeoxycholic acid-derived liquid crystals, Liq. Cryst. 46 (2018) 442–453, https://doi.org/10.1080/02678292.2018.1508768.

[77] I. Carlescu et al., Self-assembled star-shaped liquid crystals based on 1,3,5-trihydroxybenzene with pendant alkyloxylated azobenzene arms, Liq. Cryst. 47 (12) (2020) 1852–1862, https://doi.org/10.1080/02678292.2020.1747648.

[78] A.K. Prajapati, H.M. Pandya, Azomesogens with methoxyethyl tail: Synthesis and characterization, J. chem. Sci. 117 (2005) 255–261, https://doi.org/10.1007/BF02709295.

[79] J.S. Dave, R.A. Vora, in: Liquid Crystals and Ordered Fluids, Plenum Press, New York, 1970, p. 477.

[80] A. Hassen, V. Alexanian, Direct room temperature esterification of carboxylic acids, Tetra. Lett. 19 (46) (1978) 4475–4478, https://doi.org/10.1016/S0040-4039(01)95256-6.

[81] M. Eich, J.H. Wendorff, B. Reck, H. Ringsdorf, Reversible digital and holographic optical storage in polymeric liquid crystals, Macromol. Rapid Commun. 8 (1) (1987) 59–63, https://doi.org/10.1002/marc.1987.030080111.

[82] M. Eich, J.H. Wendorff, Erasable holograms in polymeric liquid crystals, Macromol. Rapid Commun. 8 (9) (1987) 467–471, https://doi.org/10.1002/marc.1987.030080909.

[83] U. Wiesner, N. Renolds, C. Boeffel, H.W. Spiess, Photoinduced reorientation in liquid-crystalline polymers below the glass transition temperature studied by time-dependent infrared spectroscopy, Macromol. Rapid Commun. 12 (8) (1991) 457–464, https://doi.org/10.1002/marc.1991.030120801.

[84] U. Wiesner, N. Renolds, C. Boeffel, H.W. Spiess, An infrared spectroscopic study of photo-induced reorientation in dye containing liquid-crystalline polymers, Liq. Cryst. 11 (2) (1992) 251–267, https://doi.org/10.1080/02678299208028986.

[85] Gray GW. Molecular structure and properties of liquid crystals. Academic press, London (1962)..