

Spectroscopic and DFT investigations: Mesogenic alpha-Naphthyl derivatives with central cinnamate and ester linkages

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ABSTRACT

Two novel mesomorphic homologous series of cinnamates and esters with terminal naphthalene derivatives: (*E*)-naphthalen-1-yl 3-(4-(alkoxy)phenyl)acrylate (**I**) and naphthalen-1-yl 4-(alkoxy)benzoate(**II**), were prepared and analyzed by standard spectroscopic characterization like UV, FT-IR, NMR, DSC, POM, and DFT studies. All the compounds with varying alkyl chain length exhibit mesomorphism with naphthalene attachment at the other terminal. In series I, *n*-ethoxy to *n*-butyloxy derivatives exhibit a monotropic nematic mesophase, whereas *n*-propyloxy and *n*-butyloxy derivatives exhibit a monotropic smectic A mesophase. Schlieren nematic and Smectic A mesophase commence from *n*-pentyloxy derivatives as enantiotropic and persist up to the last member synthesized. In series II, *n*-ethoxy to *n*-butyloxy derivatives are non-mesogenic, while both monotropic smectic A mesophase and schlieren nematic mesophase commence from *n*-pentyloxy derivatives as enantiotropic and persist up to the last member synthesized. Comparison with other homologous help to evaluate the effects of central cinnamate/ester linkage on mesomorphism, polarizability. We also use length/breadth (**L/B**) ratio from the MM2 models to gain understanding of the steric effect of the terminal naphthalene moiety. Furthermore, all the derivatives were geometrically optimized via time-dependent density functional theory (TD-DFT) at the B3LYP/6-31 G (d,p) computation also recorded the polarizability, interaction energy, HOMO – LUMO orbital energy gap.

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1. Introduction

Terminal groups greatly affect and help enhance the thermal stability, for example by modifying the phase transition via a change in the molecular polarizability rather than by changing the breadth of molecule. Polarity is greatly affected by the presence of terminal groups in the molecule. Hird and Gray et al. [1] have reported that terminally substituted derivatives exhibit a more stable mesophase than others. Several studies have reported that the terminal substituent conjugated with the ring, affect the mesophase to varying extent and the size of substituent is more pronounced [2–4]. The molecular polarizability can be increased by introducing a terminal naphthalene group without disturbing the molecular breadth. A substances with unique flow capacity and optical properties can be treated as a liquid crystal (LC). The thermotropic liquid crystalline materials show the characteristics in between of solid crystalline and liquid state [5]. Gray and Imrie et al. [6,7] reported that the mesophase transition temperature can be regulated

by changing the chain length. Moreover, polarity and the presence of dipoles are also key factors for increasing the mesophase stability. Further, Goodby et al. [8,9] have reported that LC molecule's architectural design also plays an important role in affecting its mesophase stability. Yamaguchi et al. [10,11] have synthesized a set of molecules and reported that different structural configurations can be achieved via different modes of attachments. Yoshizawa et al. [12,13] investigated the nematic phase with layered pattern in U-shaped and Y-shaped molecules. et al. [14,15] discovered the moieties with variable molecular configurational arrangements, which provide additional importance to the field of liquid crystals. Prajapati et al. [16,17] have synthesized H-shaped and λ-shaped liquid crystalline compounds with polar substituents. Prajapati et al. [18] have also reported dimeric liquid crystalline compounds. Patel et al. [19] have reported the shape variant azo diester and evaluated the effect of the terminal methyl/methoxy substituents.

Thermal stability, mesophase temperature variation, anisotropic ordering can be achieved with the help of different terminal and lateral linking group [20–22]. Doshi and Prajapati [23] studied the mesomorphism dependence on the lateral substitution in novel azoester series. Recently, Patel and Thakur [24] reported that aromatic esters are best suited to achieve thermal stability and a that

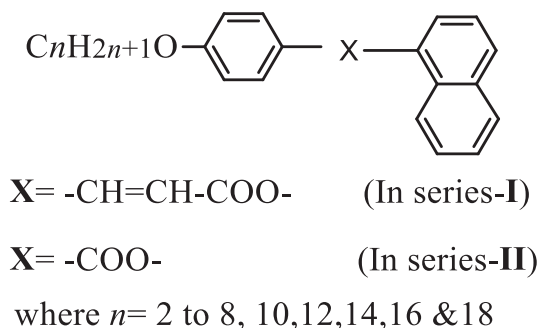
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the attachment of ester group between the two aromatic rings enhances the double bond character.

In addition to substitution of the terminal groups, different central linkages can perturb the linearity and co-planarity of molecule via the polar or steric effects. The steric or polar changes at lateral position via introduction of $-\text{COO}-$, $-\text{CH}=\text{CH}-$, $-\text{CH}=\text{CH}-\text{COO}-$, $-\text{CH}=\text{N}-$ etc. as central linkages are known to reduce the thermal stability [25,26]. Vora and Prajapati [27] reported the effect of changes at the lateral positions like thiol. Prajapati et al. used mesogenic homologous series of Schiff base esters containing the naphthalene moiety to investigate the effect of lateral methyl [28], methoxy [29] and chloro [30] substitutions on mesomorphism. The effect of these changes at lateral positions have also been reported in several studies [31,32]. Vora and Prajapati [33,34] investigated esters of 4-(4'-*n*-alkoxy-benzoyloxy)benzoic acid and α -methyl cinnamates. Prajapati and Pandya [35] reported homologous series of azo/esters having ethoxy ethyl terminal chain. Prajapati et al. [36–39] reported a series of Schiff's base ester containing compounds with methoxyethyl, ethoxyethyl and chloroethyl terminal groups and evaluated their effect on mesomorphism. Earlier, our group also reported mesogenic cinnamates with ethyl-substituted terminal chain. Prajapati and Patel [40] reported a series containing cinnamates at the center and the terminal group substituted with an ethyl chain and studied their dielectric relaxation properties. Recently, Prajapati and Patel [41] evaluated the effect of central cinnamoyloxy linkage and butyloxyethyl chain as terminal linkage on the mesophase behavior.

A study by Gray et al. [42] reported a comprehensive understanding of the changes in phase transition temperature due to the variation in the length of the terminal alkyl chain. In order to regulate the melting and clearing temperature as well as mesophase temperature range, various different structural factors can also be employed. For example, the introduction of a cyano group [43], the introduction of double bonds into the terminal chains [44,45], or the introduction of fluorine-containing terminal [46] or lateral [47] units. All these changes were shown to have a great impact on the transition temperature and the mesogenic properties. Symmetry lowering controls the transition temperature and temperature ranges of the liquid crystal [48,49]. A large number of naphthalene derivatives with rich mesomorphism are reported in literature [50]. Many mesogenic Schiff's base of arylidene 2, 6-, 1, 5- and 1, 4-diaminonaphthalenes were reported by Wiegand [51]. Coates and Gray [52] reported conversions of 6-*n*-alkyl/alkoxy-naphthalene-2-carboxylic acids to 4-*n*-alkyl/alkoxyphenyl esters. Chamchaang [53] prepared symmetrical as well as unsymmetrical stilbenes following the process of pyrolysis of aryl cinnamates. Phenol, thiols, amines and alcohol undergo acylation by introducing Indium (III) chloride as a catalyst in organic synthesis [54]. Sondern [55] explained the formation of α -naphthol esters of *p*-methoxycinnamic acid from oil of *Kaempferia galanga* L. Jiang et al. [56] developed a convenient one-pot synthetic route of making aryloxy alkyl esters using different types of phenolic esters and halogenated alcohols. Phenolic esters play an important role in many agro and pharma companies. Prajapati and Patel [57] synthesized terminally substituted naphthyl derivatives with introduction of ester and azomethine/azo at central position. Li et al. [58] reported many bioactive obtained natural products while synthesizing functional polymers. Sultan et al. [59] prepared two series of naphthyl derivatives with ester and azo central linkages and studied the effect of lateral fluoro atom. Previously, Ahmed et al. [60] investigated the mesophase behavior by inverting the ester group of three ring azo/ester containing derivatives. The introduction of lateral methyl group along with the replacement of ester phenyl ring by naphthyl groups was also studied [61]. Ahmed et al. prepared four rings with azo/ester/azo linkage and studied the effect of incorporating lateral bromo sub-



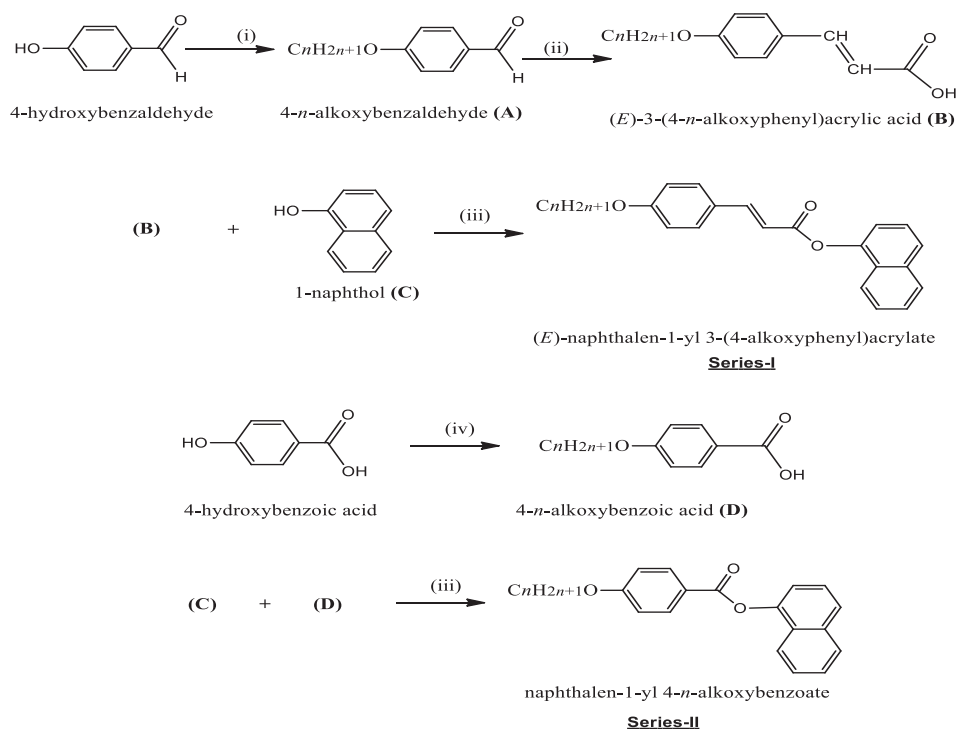
Scheme 1. The general formula shown in the scheme 1.

stituent [62]. Ahmed et al. [63] have studied the effect of changing an azo group with an azomethine group and mesophase behavior of four-ring azo/ester/azomethine compounds. The mesophase behavior of a new sequence of Schiff base/esters, 4-((2'-or 3'-fluorophenylimino)methyl)phenyl-4'-alkoxy benzoates, was investigated [64]. Vora and Prajapati [65] synthesized the mesogenic homologous series of azomesogens without lateral substituent, synthesis and plasmonic photo characterization of azo groups by Yoshioka et al. [66]. Prajapati et al. [67] reported the effect of lateral chloro groups on naphthyl azo-mesogens. Jadav et al. [68] studied the effect of naphthalene moiety on mesomorphism via homologous series of azo-esters containing two naphthalene nuclei. Prajapati et al. [69] reported mesogenic homologous series of Schiff base cinnamates and also studied the effect of an ethylene linking group (cinnamoyl linkage) and a naphthalene moiety on the mesomorphism. Prajapati et al. [70] investigated the phase transition behavior of two new mesogenic homologous series of salicylaldehydes with the naphthalene moiety as metallo-mesogens of both series of ligands containing the Cu (II) atom also, more importantly the liquid crystalline properties were studied by texture observations of synthesized compounds containing naphthalene moiety. Naphthalene ring increases the breadth of the molecules, which thus decreases the mesogenic properties as it is the interesting aromatic moiety. In continuation of our research work on liquid crystalline naphthalene derivatives and also on cinnamic acid derivatives, we have synthesized two new mesogenic terminal naphthalene based homologous series. In our present study, new (E)-naphthalen-1-yl 3-(4-(alkoxy)phenyl)acrylate (**I**) and naphthalen-1-yl 4-(alkoxy)benzoate (**II**) compounds have been synthesized to analyze the effect of naphthalene moiety with cinnamoyl/ester central linkage on mesomorphism and also studied the polarity change and stereo effect on stereo configuration due to the terminal naphthalene attachment, which support the disruption in the linearity of the molecule and affects the thermal stability. The structural formula for two new naphthalene series is shown in Scheme 1.

2. Experimental

2.1. Materials

4-hydroxybenzoic acid, 4-hydroxybenzaldehyde, *n*-bromoalkane, potassium hydroxide (KOH), potassium carbonate (K_2CO_3), malonic acid, piperidine, 1-naphthol, N,N'-dicyclohexylcarbodiimide (DCC), 4-dimethyl aminopyridine (DMAP), and Tetrahydrofuran (THF) were used as received. Solvents like ethanol, pyridine, dichloromethane (MDC) and acetone were dried and distilled before use.



Reagents and conditions: (i) R-Br, Anhydrous K_2CO_3 , Dry acetone (ii) Malonic acid, Dry pyridine, Pipyridine (iii) 1-Naphthol, DCC, DMAP, Dry THF (iv) R-Br, KOH, ethanol

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

2.2. Measurements

Microanalysis of the derivatives was performed and which are quite similar to the calculated one. UV-Vis spectra were recorded on Perkin Elmer UV/Vis spectrometer Lambda 35 with WinLab software. Infrared (IR) spectra were recorded by making KBr pellets with Shimadzu IR-408 spectrophotometer. 1H NMR spectra were recorded with Perkin-Elmer R-32 spectrometer using standard internal reference solution tetramethylsilane (TMS). The δ (ppm) symbol was used for chemical shifts; the solvent $CDCl_3$ was used for all of the compounds. Polarizing optical microscopy was used to determine different phases appeared during transition and were recorded using a polarizing microscope (LeitzLaborlux 12 POL) equipped with heating stage. The transition enthalpies were recorded by using cryo-DSC model DSC 822^c, Mettler Toledo, Switzerland, having star^e software system in g^{-1} at a scanning rate of $5^\circ C \text{ min}^{-1}$ with pure indium as a standard for calibration. Different textures were examined by using polarizing optical microscope.

Scheme 2 depicts the synthetic route to compounds of series I and series II.

Different n -alkyl bromides were treated with 4-hydroxybenzoic acid to synthesize 4- n -alkoxybenzoic acids [A] by employing a Williamson's ether synthesis protocol [71].

By using method of Vyas and Shah [72] 4- n -alkoxybenzaldehydes [B] were prepared from 4-hydroxybenzaldehyde.

With the help of reported method given by Gray and Jones [73], *trans*-4- n -alkoxycinnamic acids [C] from 4- n -alkoxybenzaldehydes and malonic acid can easily be synthesized.

0.1 mole of *trans*-4- n -alkoxycinnamic acids (B) (for series I), 0.1 mole of 4- n -alkoxybenzoic acids (D) (for series II), 0.1 mole of 1-naphthol (C), 0.1 mol of DCC [74], 0.01 mole of DMAP were completely dissolved in dry THF (an organic solvent) and left overnight

for constant stirring at room temperature. The quick thin-layer chromatography check was performed using TLC sheets coated with silica gel to confirm the completion of reaction before filtration by detecting spots with a UV-lamp. The final compound was collected and the insoluble solid, left over the filter paper was discarded. The pure compound was extracted using petroleum ether ($60-80^\circ C$) following column chromatography using proportion (95:5) of petroleum ether and ethyl acetate on silica gel. The repeated crystallization was performed on elute with ethanol after removing the excess solvent till constant transition temperature were obtained and also using TLC plates (thin layer chromatography Merck Kiesel gel 60, F_{254} pre-coated plates) again for purity check. Yield was 65–70%.

2.3. Computational methods

For both Series I and Series II, derivatives were generated by varying the $-OC_nH_{2n+1}$ group in the range of $n = 1-6, 8, 10$ and 12 . The ab-initio calculations were performed using the density function theory (DFT) as implemented in Gaussian quantum chemistry package [75]. The geometry of derivatives of Series I and Series II molecules were optimized in gas phase at the B3LYP/6-31 G (d, p) level of theory. During the energy and geometry optimizations, no symmetry constraint was imposed. Harmonic frequency calculations were carried out at the same level of theory to characterize the stationary points, with no imaginary frequency indicating a stationary point. The same procedure was used to optimize 1-naphthol and water molecule, to enable the computation of stabilization energy. The molecular orbital energies were generated and visualized at the same level of theory using Gauss View. Further, Time-dependent DFT (TDDFT) [76] calculations were performed for Series I and Series II members ($n = 1-6$) at the B3LYP/6-31 G (d, p) level of theory as implemented in Gaussian09. The UV-VIS spectra

corresponding to these molecules were generated and interpreted by visualizing the associated molecular orbital.

3. Characterization

The spectroscopic analysis like UV, FT-IR, ^1H NMR and DSC of all the compounds was found to be in accordance with the proposed structure. As a prior investigation, the mesophase exhibited by the compounds of the present series were analyzed by the optical microscopic studies. The liquid crystalline phases were observed by using a polarizing optical microscope. The compound is sandwiched between the two, glass slide and a cover slip at heating and cooling rate is $2\text{ }^\circ\text{C min}^{-1}$ respectively.

Series I: (E)-naphthalen-1-yl 3-(4-propyloxyphenyl)acrylate

UV Spectrum (MDC) nm: 272 and 317.

IR spectrum (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2906, 2825, 1720 ($-\text{COO}-$), 1629 ($-\text{CH}=\text{CH}-$), 1525, 1506,

1485, 1224, 1187, 1062, 967, 825.

^1H NMR spectrum (400 MHz): δ 1.04 (t, 3H, $-\text{CH}_3$), 1.82–1.86 (m, 2H, $\text{Ar}-\text{O}-\text{C}-\text{CH}_2-$), 3.99 (t, 2H at $-\text{O}-\text{CH}_2-$), 6.64–6.67 (d, 1H, $\text{Ar}-\text{CH}=\text{CH}-$), 6.94–6.96 (d, 2H, $\text{Ar}-\text{H}$ at C-3 and C-5), 7.31–7.33 (d, 1H, $=\text{CH}-\text{COO}-$), 7.47–7.51 (d, 3H of naphthalene ring system at C-3, C-4 and C-5), 7.57–7.59 (d, 2H, $\text{Ar}-\text{H}$ at C-2 and C-6), 7.75–7.94 (d, 3H of naphthalene ring system at C-6' C-7' and C-8), 7.96 (s, 1H of naphthalene ring system at C-2').

Series I: (E)-naphthalen-1-yl 3-(4-butyloxyphenyl)acrylate

UV Spectrum (MDC) nm: 271 and 321.

IR spectrum (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2927, 2854, 1734 ($-\text{COO}-$), 1638 ($-\text{CH}=\text{CH}-$), 1602, 1512,

1302, 1223, 1166, 1123, 948, 839.

^1H NMR spectrum (400 MHz): δ 0.99 (t, 3H, $-\text{CH}_3$), 1.49–1.57 (m, 2H, $\text{Ar}-\text{O}-\text{C}-\text{CH}_2-$), 1.77–1.82 (m, 2H, $\text{Ar}-\text{O}-\text{C}-\text{C}-\text{CH}_2-$), 4.03 (t, 2H at $-\text{O}-\text{CH}_2-$), 6.64–6.67 (d, 1H, $\text{Ar}-\text{CH}=\text{CH}-$), 6.93–6.95 (d, 2H, $\text{Ar}-\text{H}$ at C-3 and C-5), 7.31–7.33 (d, 1H, $=\text{CH}-\text{COO}-$), 7.47–7.52 (d, 3H of naphthalene ring system at C-3, C-4 and C-5), 7.56–7.58 (d, 2H, $\text{Ar}-\text{H}$ at C-2 and C-6), 7.75–7.94 (d, 3H of naphthalene ring system at C-6' C-7' and C-8), 7.95 (s, 1H of naphthalene ring system at C-2').

Series I: (E)-naphthalen-1-yl 3-(4-decyloxyphenyl)acrylate

UV Spectrum (MDC) nm: 257 and 320.

IR spectrum (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2939, 2846, 1729 ($-\text{COO}-$), 1627 ($-\text{CH}=\text{CH}-$), 1600, 1571, 1509, 1472, 1301, 1254, 1172, 967, 810.

^1H NMR spectrum (400 MHz): δ 0.86 (t, 3H, $-\text{CH}_3$), 1.26–1.42 (m, 12H, 6 x $-\text{CH}_2-$), 1.71–1.75 (m, 4H, $\text{Ar}-\text{O}-\text{C}-\text{CH}_2-$), 4.04 (t, 2H at $-\text{O}-\text{CH}_2-$), 6.90 (d, 1H, $\text{Ar}-\text{CH}=\text{CH}-$), 7.01–7.04 (d, 2H, $\text{Ar}-\text{H}$ at C-3 and C-5), 7.37–7.39 (d, 1H, $=\text{CH}-\text{COO}-$), 7.55–7.60 (d, 3H of naphthalene ring system at C-3, C-4 and C-5), 7.80–7.83 (d, 2H, $\text{Ar}-\text{H}$ at C-2 and C-6), 7.88–8.03 (d, 3H of naphthalene ring system at C-6' C-7' and C-8), 8.03 (s, 1H of naphthalene ring system at C-2').

Series I: (E)-naphthalen-1-yl 3-(4-dodecyloxyphenyl)acrylate

UV Spectrum (MDC) nm: 260 and 321.

IR spectrum (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2918, 2850, 1730 ($-\text{COO}-$), 1628 ($-\text{CH}=\text{CH}-$), 1600, 1570, 1511,

1471, 1287, 1252, 1173, 965, 827.

^1H NMR spectrum (400 MHz): δ 0.86 (t, 3H, $-\text{CH}_3$), 1.25–1.42 (m, 16H, 8 x $-\text{CH}_2-$), 1.71–1.74 (m, 4H, $\text{Ar}-\text{O}-\text{C}-\text{CH}_2-$), 4.04 (t, 2H at $-\text{O}-\text{CH}_2-$), 6.89 (d, 1H, $\text{Ar}-\text{CH}=\text{CH}-$), 7.01–7.03 (d, 2H, $\text{Ar}-\text{H}$ at C-3 and C-5), 7.37–7.39 (d, 1H, $=\text{CH}-\text{COO}-$), 7.55–7.60 (d, 3H of naphthalene ring system at C-3, C-4 and C-5), 7.80–7.83 (d, 2H, $\text{Ar}-\text{H}$ at C-2 and C-6), 7.85–8.03 (d, 3H of naphthalene ring system at C-6' C-7' and C-8), 8.04 (s, 1H of naphthalene ring system at C-2').

Series I: (E)-naphthalen-1-yl 3-(4-tetradecyloxyphenyl)acrylate

UV Spectrum (MDC) nm: 268 and 325.

IR spectrum (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2918, 2849, 1729 ($-\text{COO}-$), 1629 ($-\text{CH}=\text{CH}-$), 1601, 1571, 1511,

1470, 1291, 1257, 1175, 965, 821.

^1H NMR spectrum (400 MHz): δ 0.85 (t, 3H, $-\text{CH}_3$), 1.24–1.41 (m, 20H, 10 x $-\text{CH}_2-$), 1.71–1.74 (m, 4H, $\text{Ar}-\text{O}-\text{C}-\text{CH}_2-$), 4.04 (t, 2H at $-\text{O}-\text{CH}_2-$), 6.89 (d, 1H, $\text{Ar}-\text{CH}=\text{CH}-$), 7.01–7.03 (d, 2H, $\text{Ar}-\text{H}$ at C-3 and C-5), 7.37–7.39 (d, 1H, $=\text{CH}-\text{COO}-$), 7.55–7.60 (d, 3H of naphthalene ring system at C-3, C-4 and C-5), 7.80–7.82 (d, 2H, $\text{Ar}-\text{H}$ at C-2 and C-6), 7.85–8.03 (d, 3H of naphthalene ring system at C-6' C-7' and C-8), 8.04 (s, 1H of naphthalene ring system at C-2').

Series I: (E)-naphthalen-1-yl 3-(4-octadecyloxyphenyl)acrylate

UV Spectrum (MDC) nm: 273 and 321.

IR spectrum (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2914, 2818, 1715 ($-\text{COO}-$), 1628 ($-\text{CH}=\text{CH}-$), 1602, 1509, 1427, 1298, 1239, 1178, 919, 820.

^1H NMR spectrum (400 MHz): δ 0.87 (t, 3H, $-\text{CH}_3$), 1.24–1.45 (m, 28H, 14 x $-\text{CH}_2-$), 1.57–1.82 (m, 4H, $\text{Ar}-\text{O}-\text{C}-\text{CH}_2-$), 4.02 (t, 2H at $-\text{O}-\text{CH}_2-$), 6.67 (d, 1H, $\text{Ar}-\text{CH}=\text{CH}-$), 6.94–6.95 (d, 2H, $\text{Ar}-\text{H}$ at C-3 and C-5), 7.31–7.32 (d, 1H, $=\text{CH}-\text{COO}-$), 7.48–7.59 (d, 3H of naphthalene ring system at C-3, C-4 and C-5), 7.75–7.77 (d, 2H, $\text{Ar}-\text{H}$ at C-2 and C-6), 7.87–7.94 (d, 3H of naphthalene ring system at C-6' C-7' and C-8), 7.95 (s, 1H of naphthalene ring system at C-2').

Series II: naphthalen-1-yl 4-n-hexyloxybenzoate

UV Spectrum (MDC) nm: 260.

IR spectrum (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2924, 2853, 1736 ($-\text{COO}-$), 1603, 1527, 1458, 1279, 1226, 1120, 996, 804.

^1H NMR spectrum (400 MHz, CDCl_3): δ 0.90 (t, 3H, $-\text{CH}_3$), 1.33–1.38 (m, 4H, 2x $-\text{CH}_2-$), 1.46–1.50 (m, 2H, $\text{Ar}-\text{O}-\text{C}-\text{CH}_2-$), 1.73–1.84 (m, 2H, $\text{Ar}-\text{O}-\text{C}-\text{C}-\text{CH}_2-$), 4.05 (t, 2H at $-\text{O}-\text{CH}_2-$), 6.97–6.99 (d, 2H, $\text{Ar}-\text{H}$ at C-3 and C-5), 7.33–7.46 (d, 3H of naphthalene ring system at C-3, C-4 and C-5), 7.58–7.60 (d, 2H, $\text{Ar}-\text{H}$ at C-2 and C-6), 7.61–7.64 (d, 3H of naphthalene ring system at C-6' C-7' and C-8), 8.16 (s, 1H of naphthalene ring system at C-2').

Series II: naphthalen-1-yl 4-n-octyloxybenzoate

UV Spectrum (MDC) nm: 261.

IR spectrum (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2912, 2822, 1722 ($-\text{COO}-$), 1598, 1509, 1473, 1269, 1231, 1172, 982, 887.

^1H NMR spectrum (400 MHz, CDCl_3): δ 0.89 (t, 3H, $-\text{CH}_3$), 1.25–1.38 (m, 8H, 4x $-\text{CH}_2-$), 1.46–1.50 (m, 2H, $\text{Ar}-\text{O}-\text{C}-\text{CH}_2-$), 1.72–1.84 (m, 2H, $\text{Ar}-\text{O}-\text{C}-\text{C}-\text{CH}_2-$), 4.04 (t, 2H at $-\text{O}-\text{CH}_2-$), 6.96–6.99 (d, 2H, $\text{Ar}-\text{H}$ at C-3 and C-5), 7.33–7.46 (d, 3H of naphthalene ring system at C-3, C-4 and C-5), 7.58–7.61 (d, 2H, $\text{Ar}-\text{H}$ at C-2 and C-6), 7.62–7.64 (d, 3H of naphthalene ring system at C-6' C-7' and C-8), 8.15 (s, 1H of naphthalene ring system at C-2').

Series II: naphthalen-1-yl 4-n-tetradecyloxybenzoate

UV Spectrum (MDC) nm: 262.

IR spectrum (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2926, 2854, 1720 ($-\text{COO}-$), 1602, 1512, 1451, 1250, 1226, 1173, 993, 805.

^1H NMR spectrum (400 MHz, CDCl_3): δ 0.88 (t, 3H, $-\text{CH}_3$), 1.32–1.36 (m, 20H, 10 x $-\text{CH}_2-$), 1.46–1.49 (m, 2H, $\text{Ar}-\text{O}-\text{C}-\text{CH}_2-$), 1.76–1.84 (m, 2H, $\text{Ar}-\text{O}-\text{C}-\text{C}-\text{CH}_2-$), 4.04 (t, 2H at $-\text{O}-\text{CH}_2-$), 6.97–6.99 (d, 2H, $\text{Ar}-\text{H}$ at C-3 and C-5), 7.35–7.46 (d, 3H of naphthalene ring system at C-3, C-4 and C-5), 7.58–7.61 (d, 2H, $\text{Ar}-\text{H}$ at C-2 and C-6), 7.62–7.64 (d, 3H of naphthalene ring system at C-6' C-7' and C-8), 8.15 (s, 1H of naphthalene ring system at C-2').

Series II: naphthalen-1-yl 4-n-hexadecyloxybenzoate

UV Spectrum (MDC) nm: 257.

IR spectrum (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2922, 2849, 1723 ($-\text{COO}-$), 1600, 1573, 1510, 1471, 1245, 1221, 1153, 999, 842.

^1H NMR spectrum (400 MHz, CDCl_3): δ 0.89 (t, 3H, $-\text{CH}_3$), 1.25–1.40 (m, 24H, 12 x $-\text{CH}_2-$), 1.44–1.49 (m, 2H, $\text{Ar}-\text{O}-\text{C}-\text{CH}_2-$), 1.66–1.86 (m, 2H, $\text{Ar}-\text{O}-\text{C}-\text{C}-\text{CH}_2-$), 4.05 (t, 2H at $-\text{O}-\text{CH}_2-$), 6.97–6.99 (d, 2H, $\text{Ar}-\text{H}$ at C-3 and C-5), 7.35–7.46 (d, 3H of naphthalene ring system at C-3, C-4 and C-5), 7.58 (d, 2H, $\text{Ar}-\text{H}$ at C-2 and C-6), 7.60–7.64 (d, 3H of naphthalene ring system at C-6' C-7' and C-8), 8.15 (s, 1H of naphthalene ring system at C-2').

4. UV- visible and IR spectra

Solutions were prepared with concentration of 1×10^6 with dichloromethane (MDC) solvent. During the photochemical studies, the UV-visible scans represents that all the compounds consist of four absorption bands 200–235 nm, 240–255 nm, 265–272 nm, 280–345 nm. In case of **C₁₀** (I), **C₁₂** (I), two peaks have been observed with absorption maxima of 256 nm, 320 nm and 260 nm, 321 nm. In case of **C₈** (II), **C₁₄** (II), peaks observed with absorption maxima of 261 nm and 262 nm. The first two weak absorption bands of series I coming at 240–255 nm, 265–272 nm may be ascribed as $\pi \rightarrow \pi^*$ transition, arises just from HOMO $\rightarrow$ LUMO transition within the phenyl ring. From the recorded UV data it may be concluded that the derivatives lead to the π -extended opening system and is an accountable factor for the appropriate absorption spectra from 280 to 345 nm. The sharper absorption band for series I with λ_{max} at 320 nm and 321 nm appearing in region of 280–345 nm as the mesogenic part is affected by the π - electronic system due to increased conjugation, due to $\pi \rightarrow \pi^*$ transition of aromatic ring [77]. While the weak absorption band for series II appearing with λ_{max} at 261 nm and 262 nm may be due to the $n \rightarrow \pi^*$ located on the central ester group.

IR gives the information about the frequency of specific functional groups present in the series. The IR spectrum (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ indicates the absorption bands appearing in the region of 2950–2901 (C–H stretching of alkane), in region of 2860–2810 (C–H stretching of $(-\text{CH}_2)_n$ group of alkoxy chain), 1740–1710 (C = O stretching of carbonyl carbon) and strong medium band appear in region of 1638–1600 ($-\text{CH}=\text{CH}$ stretching of alkene conjugated with $-\text{COO}$ for series I only), 1570, 1512, 1509 (C = C stretching of aromatic ring), the regions of 1472, 1302, 1280 covers strong intensity C–O stretching band of carboxy ($>\text{CO}$) group both in series I and series II. While the strong intense absorption bands can be seen in region of 1734–1715 ($-\text{COO}-$), 1638–1627 ($-\text{CH}=\text{CH}-$) for series I and in region of 1736–1720 ($-\text{COO}-$) for series II.

5. Results and discussion

Optical microscopy studies

The optical microscopic study concluded that the mesophase exhibited by compounds of series I and II as a primary inves-

tigation found consistent with the previous results. On cooling, isotropic liquids of series I, *n*-ethyloxy to *n*-butyloxy derivatives formed small droplets that coalesced to the classical schlieren texture of the nematic phase as monotropically. On further cooling, *n*-propyloxy and *n*-butyloxy derivatives also gave focal conic texture characteristic of smectic A mesophase as monotropically. The derivatives from *n*-pentyloxy to *n*-hexadecyloxy, exhibit both nematic and smectic A mesophase enantiotropically while the last homologue *n*-octadecyloxy ($n = 18$) of series I gave only focal conic texture characteristic of smectic A (SmA) mesophase enantiotropically.

In series II, *n*-ethyloxy to *n*-butyloxy derivatives are non-mesogenic. On cooling, isotropic liquids of series II, *n*-pentyloxy to *n*-octadecyloxy derivatives exhibit schlieren texture of the nematic phase observed as monotropically. On further cooling, *n*-pentyloxy to *n*-octadecyloxy derivatives exhibit focal conic texture characteristic of smectic A (SmA) mesophase as monotropically (Fig. 1).

Mesomorphic behavior

Series I: (E)-naphthalen-1-yl 3-(4-*n*-alkoxyphenyl)acrylate(I)

Mesomorphic behavior was observed in all twelve synthesized derivatives. Ethoxy to *n*-butyloxy derivatives exhibited monotropic nematic mesophase, while *n*-propyloxy and *n*-butyloxy derivatives showed monotropic smectic A mesophase. Derivatives from *n*-pentyloxy to *n*-hexadecyloxy exhibited enantiotropic nematic mesophase, whereas enantiotropic smectic A mesophase from *n*-pentyloxy upto the last *n*-octadecyloxy derivative. The transition temperatures for these derivatives are mentioned in Table 1. The number of carbon atoms in the alkoxy chain when plotted against the transition temperatures (Fig. 2), showed that as the length of the terminal alkoxy tail increases, the transition temperatures drop sharply moving from crystal to isotropic, resulting in the enantiotropic nature of the present series from *n*-pentyloxy onwards to the last derivative. The decrease in nematic to isotropic phase transition temperatures was observed as the terminal alkoxy chain length increases up to *n*-hexyloxy, followed by a pronounced odd-even effect till the last derivative. smectic A to nematic phase transition temperatures exhibited falling tendency up to *n*-octyloxy derivatives and then rose up to *n*-dodecyloxy derivatives exhibiting a strong odd even effect.

Series II: naphthalen-1-yl 4-*n*-alkoxybenzoates(II)

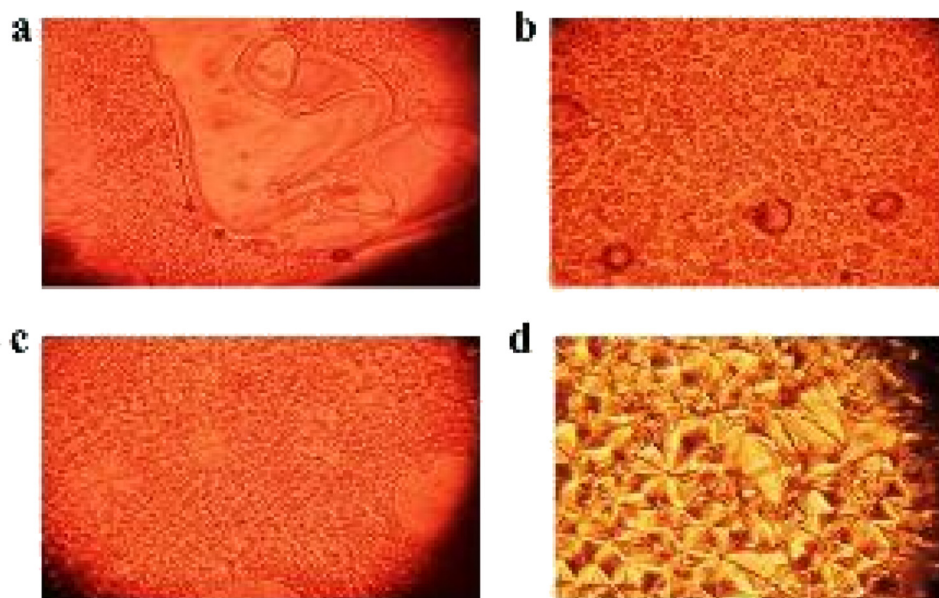
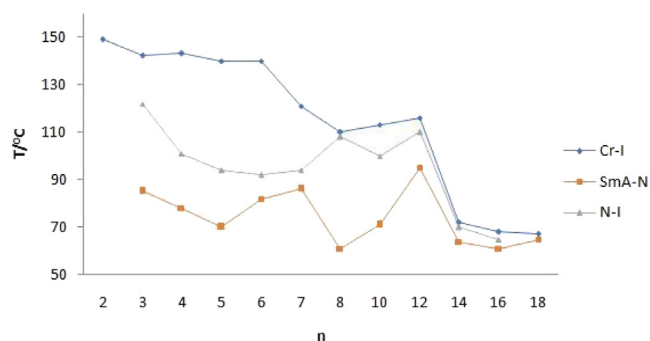


Fig. 1. POM images of representative compounds: (a) after cooling from isotropic liquids (Series I; $n = 3$) at 142 °C; (b) schlieren texture of nematic mesophase (Series I; $n = 3$) at 122 °C; (c) nematic at 101 °C for (Series I; $n = 4$); (d) smectic A at 78 °C (Series I; $n = 4$).

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

Series I	n	Transition temperature during heating °C			
		R = C _n H _{2n+1}	Smectic A	Nematic	Isotropic
1	2	C ₂ H ₅ –	–	(142)	149
2	3	C ₃ H ₇ –	(85)	(122)	142
3	4	C ₄ H ₉ –	(78)	(101)	143
4	5	C ₅ H ₁₁ –	70	94	140
5	6	C ₆ H ₁₃ –	82	92	145
6	7	C ₇ H ₁₅ –	86	94	121
7	8	C ₈ H ₁₇ –	61		
	108	110			
8	10	C ₁₀ H ₂₁ –	71	100	113
9	12	C ₁₂ H ₂₅ –	94	110	116
10	14	C ₁₄ H ₂₉ –	64	70	72
11	16	C ₁₆ H ₃₃ –	61	65	68
12	18	C ₁₈ H ₃₇ –	65	–	67

(Cr= Solid Crystal, n= alkyl group); () indicates monotropy
 – Phase does not exist

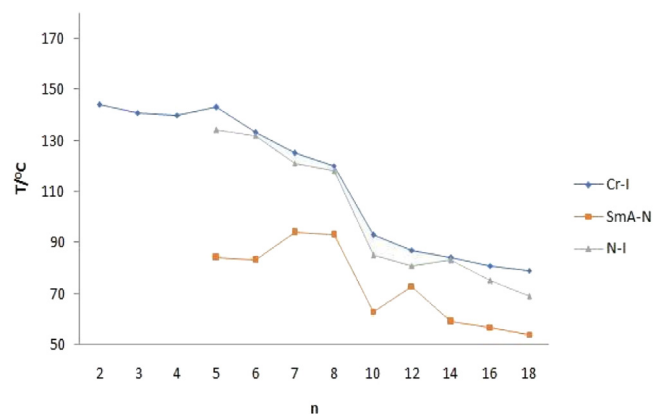
**Fig. 2.** The phase behavior for series I compounds, where n is number of carbon atom.**Table 2**
Transition temperatures (°C) of the series II compounds.

Series II	n	Transition temperature during heating °C			
		R = C _n H _{2n+1}	Smectic A	Nematic	Isotropic
13	2	C ₂ H ₅ –	–	–	144
14	3	C ₃ H ₇ –	–	–	141
15	4	C ₄ H ₉ –	–	–	140
16	5	C ₅ H ₁₁ –	(84)	(134)	143
17	6	C ₆ H ₁₃ –	(83)	(132)	133
18	7	C ₇ H ₁₅ –	(94)	(121)	125
19	8	C ₈ H ₁₇ –	(93)	(118)	120
20	10	C ₁₀ H ₂₁ –	(63)	(85)	93
21	12	C ₁₂ H ₂₅ –	(73)	(81)	87
22	14	C ₁₄ H ₂₉ –	(59)	(83)	84
23	16	C ₁₆ H ₃₃ –	(57)	(75)	81
24	18	C ₁₈ H ₃₇ –	(54)	(69)	79

(Cr= Solid Crystal, n= alkyl group); () indicates monotropy.
 – Phase does not exist.

In series II, twelve compounds were synthesized. Derivatives from *n*-ethoxy to *n*-butyloxy exhibited non-mesogenic behavior as derivatives directly converted to isotropic form, whereas derivative from *n*-pentyloxy to *n*-octadecyloxy exhibited both nematic mesophase and smectic A mesophase as monotorpically. Table 2 shows the temperatures at which the transition occurred. Fig. 3 shows the plot of transition temperatures for series II against the number of carbon atoms in the alkyl chain. The transition temperatures dropped with increasing alkoxy chain, except for the crystal-isotropic transition. The temperatures of both SmA-N and N-I transitions increased with the chain length.

With the increase in the terminal alkyl chain length, anisotropic properties increased, resulting in increasing T_{NI}, while the dilution of the core decreased the T_{NI}. Overall, T_{NI} was observed to be

**Fig. 3.** The phase behavior for series II compounds, where n is number of carbon atom.

dependent on the interaction strength of the core. In the present series, increasing molecular anisotropy favors the odd-even effect [78–83]. The thermotropic liquid crystal's molecular constitution is well understood to be extremely sensitive. The thermal stability and mesophase length as a measure of mesomorphism are correlated with the molecular constitution of the compounds to determine the effects of alterations in the molecular core on the mesogenic properties of a compound.

Differential Scanning Calorimetry studies

Differential Scanning Calorimetry (DSC) is employed for the detection of phase transitions. The quantitative analysis helped to understand the nature of different phases during phase transitions. In our present research work, heat enthalpies of compounds were measured by DSC for both two series. Data obtained from thermographs are recorded in Table 3. The enthalpy values of the phase transitions matched those with previously reported results [84], indicating the presence of a mesophase type. Next, DSC was used to measure the enthalpies of derivatives of both the series I and series II, using (cryo-DSC model DSC 822e, Mettler Toledo, Switzerland, having star^e software). The phase transition behavior was investigated by scanning from ambient temperature to 150 °C at a rate of 5 °C per minute and then cooling from 150 °C to 25 °C at a similar rate (i.e. 5 °C /min). On the heating scan, the differential calorimetry thermograms showed one endotherm for crystal to isotropic phase transition peak, and on the cooling scan, it showed the first exotherm for the isotropic to nematic mesophase transitions, and the second endotherm for the smectic mesophase to crystallization phase transitions for compounds of both series. When compounds melt to their isotropic temperature, their calorimetric values are extremely high when compared to when they transition from isotropic to crystal growth or any other phase transition. DSC thermogram values were cross confirmed with transition temperature readings obtained via POM and were found in close agreement with each other. A clear cut transition temperature of all studied compounds can be seen in DSC thermogram.

For series I, On the heating cycle, compounds C₁₄ showed two peaks at 64.39 °C (ΔH = 5.26 kJ/mol), 70.08 °C (ΔH = 5.54 kJ/mol) and 72 °C (ΔH = 9.75 kJ/mol) which corresponds to Cr–SmA, SmA–N, N–I respectively and a single peak at 57.43 °C (ΔH = 25.84 kJ/mol) which corresponds to I–N transitions on cooling. Compound C₁₂ on heating showed peaks at 94.91 °C (ΔH = 42.42 kJ/mol), 110.78 °C (ΔH = 38.06 kJ/mol) and 160 °C (ΔH = 13.46 kJ/mol) which corresponds to Cr–SmA, SmA–N, N–I respectively, and on cooling peaks at 72.78 °C (ΔH = 20.61 kJ/mol) and 71.89 °C (ΔH = 21.07 kJ/mol) which corresponds to I–N, N–SmA transitions can be observed. The thermograms of compound C₁₂ by differential calorimetry show three endotherms for the crys-

Table 3

DSC data readings for series I, II compounds.

Heating Scan (Endo) Phase transition temperature, t (°C), enthalpy, ΔH (KJ/mol) and entropy, ΔS (J/mol/K).						
n	Series I			Series II		
	Smectic A	Nematic	Isotropic	Smectic A	Nematic	Isotropic
2	—	142 ^a , 17.74, 42.74	149, 16.91, 40.07	—	—	144, *, *
3	85 ^a , 4.10, 11.45	122 ^a , 5.89, 14.91	142, 19.55, 47.10	—	—	141, *, *
4	78 ^a , 3.02, 8.60	101 ^a , 5.40, 14.43	143, 27.59, 66.32	—	—	140, 25.38, 61.45
5	70, 6.82, 19.88	94, 5.46, 14.87	140, 1.22, 2.95	84 ^a , 14.90, 41.73	134, 12.91, 31.71	143, 27.03, 64.97
6	82, 0.74, 2.08	92, 2.43, 6.65	145, 15.87, 37.96	83 ^a , 28.87, 81.09	132, 37.58, 92.79	133, 37.58, 92.56
7	86, 22.44, 62.50	94, 10.05, 27.38	121, 1.68, 4.26	94 ^a , 12.31, 33.54	121, 11.25, 28.55	125, 14.44, 36.28
8	61, 2.41, 7.21	108, 10.15, 26.64	110, 1.79, 4.67	93 ^a , 15.04, 41.09	11, 34.19, 87.44	120, 34.19, 86.99
10	71, 11.57, 33.63	100, 21.64, 58.01	113, 19.89, 51.52	63 ^a , 0.23, 0.69	85 ^a , 1.48, 4.13	93, 4.15, 11.33
12	94, 42.42, 115.5	110, 38.06, 99.37	116, *, *	73 ^a , 0.80, 2.31	81 ^a , 2.88, 8.13	87, 10.06, 27.94
14	64, 5.26, 15.60	70, 5.54, 16.15	72, 0.75, 28.26	59 ^a , 9.860, 29.69	83 ^a , 13.03, 36.60	84, 12.17, 34.08
16	61, 6.86, 20.53	65, 38.10, 112.7	68, 22.11, 64.83	57 ^a , 13.57, 41.12	75 ^a , 17.86, 51.32	81, 26.96, 76.15
18	65, 66.0, 195.4		67, 7.15, 21.02	54 ^a , 14.37, 43.94	69 ^a , 18.36, 53.6	79, *, *

[**] changes were too small to be calculated. ^a denotes monotropic.

tal to smectic A mesophase, smectic A to nematic mesophase and nematic to isotropic phase transition on heating scan, and three exotherm for isotropic to nematic mesophase transitions, nematic to smectic A and the third represents smectic A to crystallization on cooling scan. When the enthalpy changes for Cr-SmA, SmA-N, and N-I for the compounds listed in Table 3 are converted to entropy changes, it should be noted that they are very small, as expected for phase transitions [55]. For series II, the compounds C₁₂ in series II showed peak at 87.46 °C ($\Delta H = 10.06$ KJ/mol) corresponding to N-I transitions, respectively. Cooling the compound revealed three peaks for the I-N, N-SmA, and SmA-Cr transitions at 81.04 °C ($\Delta H = 2.88$ KJ/mol), 73.44 °C ($\Delta H = 0.800$ KJ/mol), and 70.67 °C ($\Delta H = 0.306$ KJ/mol), respectively. A clear difference can be seen in enthalpy and the entropy value of both the two series that the enthalpy values are higher in series II for lower alkoxy members than in series I while the medium alkoxy members acquire lesser enthalpy value in series II than in series I and are found correlating with the previous investigations done for dimeric liquid crystals with pyrene moieties [85–87]. Date et al. [88] observed that the decrease in width of nematic phase attributes increase in enthalpy change due to Sm-N transition. This could be due to the difference in planarity which influences intermolecular interactions, which in turn influence phase transition enthalpy in terms of alkoxy chain length. The enthalpy and entropy values for both the series can be observed in Table 3.

The mesophase length, thermal stability (SmA-N and N-I transition temperatures), and molecular structure of the *n*-dodecyloxy derivatives of present series I and II as well as structurally related series A [89] and B [89] are summarized in Table 4. The central cinnamoyloxy (-CH=CH-COO-) linkage is present in both series I and A, while series II and B have ester (-COO-) central linkage. The molecular structure of series I, A and series II, B molecules shown in Fig. 4 reveal that the central linkage is the only difference between two Series. Enantiotropic SmA and nematic mesophases are shown by Series I, while Series II exhibited monotropic SmA and nematic mesophase. The smectic mesophase length and thermal stability of series II were lowered by 7 °C and 21 °C than series I (Table 4). Comparison of series I with A showed minor differences in the smectic mesophase length and thermal stabilities of series I was observed to be lower by 4 °C and 1 °C than series A. Simi-

Table 4The mesophase length, phase transition and comparative molecular structure of *n*-dodecyloxy derivative of Series I, II and A, B.

Series	Mesophase Length/ °C		Thermal stabilities/ °C		Commencement of Smectic phase
	SmA	N	SmA-N	N-I	
I	21	15	94	110	C ₃
II	14	8	73	81	C ₅
A	25	18	95	113	C ₆
B	18	9	62	71	C ₁₀

larly, series II members showed lower smectic mesophase length and thermal stabilities by 4 °C and 11 °C than B. The nematic mesophase length and thermal stability of series I lower by 7 °C and 29 °C than series II and comparison with structurally related compounds of series A, minor differences in nematic mesophase length and thermal stabilities of series I were observed and both are lower by 3 °C. The nematic mesophase length and thermal stability of series II was lowered by 1 °C and 10 °C as compared to series B.

The energy-minimized ball and stick model (MM2 model derived from CS Chem draw) with length and breadth measurement, the molecular structure and transition temperature of *n*-dodecyloxy derivative of synthesized series I and series II were calculated and compared with structurally related series A and series B [89] (Fig. 4). In Series I, the length/breadth (*L/B*) ratio was (5.08), which is greater than for Series II (4.67). The decrease in the thermal stability of Series II than that of Series I and comparison with other two series could be attributed the mutual conjugation and steric factor. Increase in polarizability because of the presence of cinnamate group broaden the molecule, which makes the system non-planar. In addition to these factors, the lower thermal stability of series II might be responsible for achieving the monotropic nature of mesophase observed. The overall molecular breadth of series I was higher as compared with Series A; it can be seen from Fig. 4, that length/breadth (*L/B*) ratio for Series I (*L/B*: 5.08) is lower as compared with compound A (*L/B*: 6.93). Same changes were observed while comparing Series II and series B. Higher members of series II showed enantiotropic behavior, whereas B showed monotropic nematic and smectic mesophase.

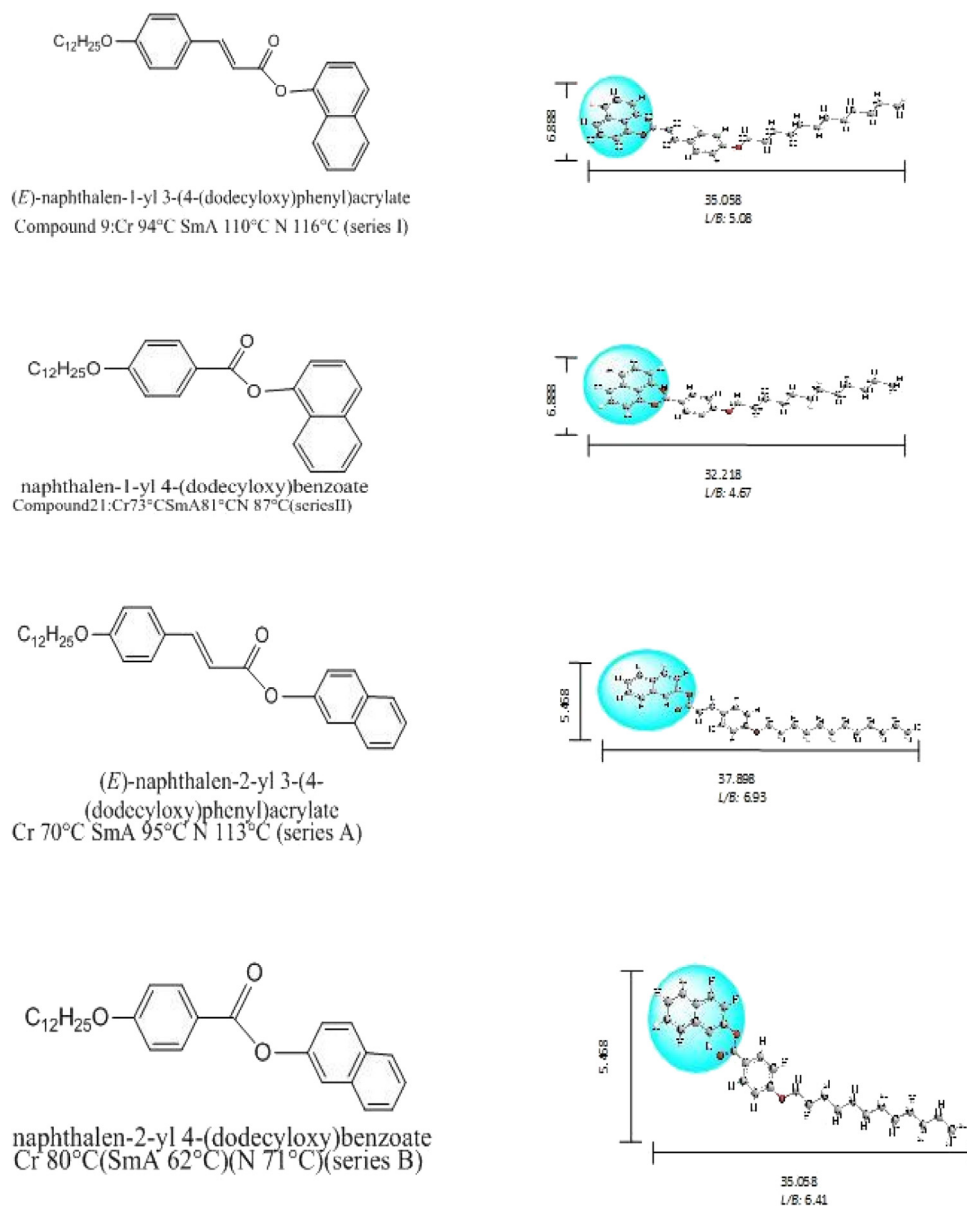


Fig. 4. Molecular structures and their names, transition temperatures and energy minimized ball and stick model (MM2 models with length/breadth ratio (L/B)) of present series I and II and structurally related series A and series B.

This aspect can be fully justified by length/breadth (L/B) ratio for Series II (L/B : 4.67) and is lower as compared with compound B (L/B : 6.41). 1-naphthol attachment at terminal site help in broadening of molecule, which may be due to the increase in thickness or increasing the breadth of molecule [90]. 2-naphthyl derivatives maintained linearity due to the substitution at the second position in naphthalene nucleus, increasing the smectic and nematic thermal stability. While the attachment at the first position in 1-naphthyl derivatives disrupts the linearity, decreasing both nematic and smectic mesophase thermal stability.

Due to the presence of a central cinnamoyloxy ($-\text{CH}=\text{CH}-\text{COO}-$) linkage, series I and A were longer and more polarizable than series II which is discussed in later section. The reduction in nematic and smectic thermal stabilities and the addition of a double increases the length and overall axial polarizability of rod-like molecules [91]. As a result, greater smectic and nematic mesophase range, as well as thermal stability, of series I could be explained in terms of polarizability and increased molecular length due to the addition of ($-\text{CH}=\text{CH}-$) units in the central linkages.

Table 4 shows that smectic and nematic mesophase length as well as thermal stabilities of series I are higher than those of series II, as it is obvious that the molecule of series I is little longer because of additional $-\text{CH}=\text{CH}-$ unit in the central linkage. After comparing series A and B with the present series, the mesophase length and thermal stabilities slightly differ.

DFT Calculations:

For both Series I and Series II, derivatives were generated by varying the $-\text{OC}_n\text{H}_{2n+1}$ group in the range of $n = 1-6, 8, 10$ and 12. All the generated derivatives were geometrically optimized at the B3LYP/6-31 G (d, p) level of theory. The optimized conformations for members of both series showed an unconventional deviation from a planar geometry (Fig. 5). Both series members showed a “twist” at connecting the naphthalene unit and the central cinnamoyloxy ($-\text{CH}=\text{CH}-\text{COO}-$) or ester ($-\text{COO}-$) linkage. However, the values of the “twist” angle were calculated to be higher for the alkoxybenzoate than for the alkoxybenzoate series. The higher deviation indicate that the series I members to be more thermally stable than the Series II members.

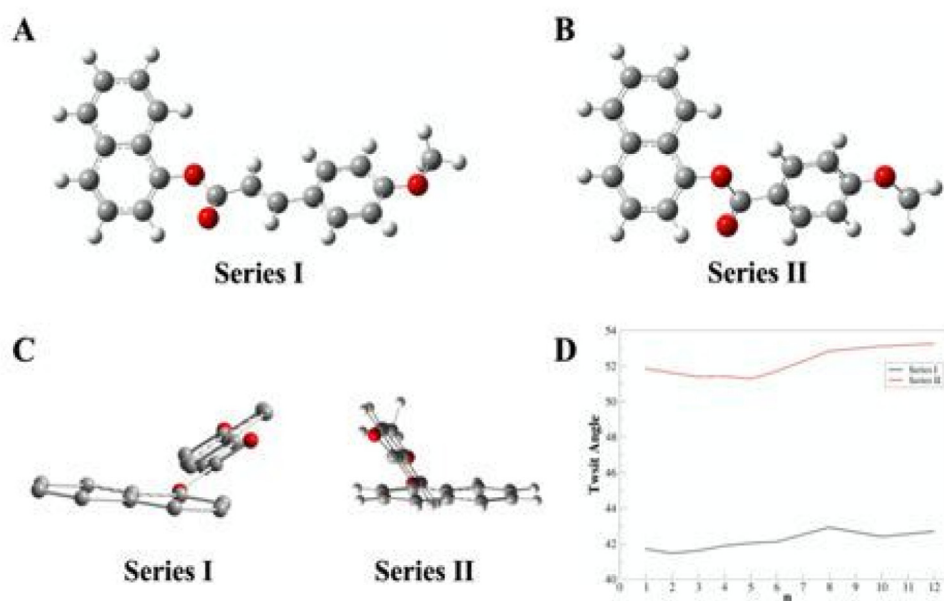


Fig. 5. The optimized geometry of Series I (A) and Series II (B) member with $n = 1$. The observed “twist” in the optimized geometry of both molecules (C). The “twist angle” values are shown for all members of Series I and II (D).

Table 5

Polarizability, interaction energy, HOMO – LUMO orbital energy gap as calculated at the B3LYP/6–31G(d, p) level of theory.

$-\text{OC}_n\text{H}_{2n+1}$	Polarizability (a.u.)		Interaction Energy, ΔE (kcal/mol)		$E_{\text{HOMO}} - E_{\text{LUMO}}$ (Hartree)	
	Series I	Series II	Series I	Series II	Series I	Series II
1	251.67	205.44	8.556	8.103	0.1634	0.1407
2	265.84	218.73	8.565	8.128	0.1637	0.1411
3	278.21	230.91	8.573	8.126	0.1638	0.1412
4	290.59	242.98	8.577	8.133	0.1638	0.1413
5	302.46	254.82	8.580	8.144	0.1638	0.1414
6	314.29	266.50	8.591	8.150	0.1639	0.1414
8	337.39	289.57	8.600	8.152	0.1642	0.1415
10	360.24	312.54	8.608	8.152	0.1642	0.1418
12	383.64	335.44	8.612	8.155	0.1643	0.1419

The stabilization energy values and polarizability values of each member of both series are shown in Table 5. Accordingly, the comparison of interaction energy for both series showed that the Series I members are energetically more stable than the respective Series II members (Table 5). Moreover, the length of the terminal alkoxy chains was observed to affect the stability of both series members. An excellent correlation was also observed between the polarizability and the terminal alkoxy chain length for both Series members: the polarizability increases with increase in the chain length (Table 5). Moreover, the polarizability values were computed to be higher for the Series I molecules than the corresponding Series II member.

The highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO) are visualized in Fig. 6 and the difference in their energy values are mentioned in Table 5. For Series I, the HOMO is major comprised by the π orbitals of the naphthyl ring, along with a smaller contribution of ethylenic linker, $-\text{HC}=\text{CH}-$ (Fig. 7). The LUMO is associated with the corresponding anti-bonding orbital of the connected phenyl ring. Whereas for Series II member, the HOMO is mainly localized by the π orbitals of the naphthyl unit, and a smaller contribution of π orbitals of $-\text{COO}$ linker. The LUMO is associated with the corresponding anti-bonding orbital of the phenyl ring.

The difference in HOMO – LUMO energy values showed higher value for Series I compounds than for Series II, indicating their higher thermal stability of the former. Additionally, the short ter-

minal alkoxy chain length had no discernible effect on the location of the electron densities of the MO's.

Further, we performed TD DFT calculations using Gaussian 09 for selected members of both Series to explain the UV data. The theoretical UV–VIS spectra for both series I and II were in excellent corroboration with the experimental data. Fig. 7 shows the vertical excitation energy and oscillator strength of two optically bright state as well as the associated molecular orbital with these excitations. In Series I, a sharp peak at 308.63 nm was observed, along with a weaker peak at 368.24 nm. Both optical bands are originated by the $\pi \rightarrow \pi^*$ excitation. The first theoretical band is located at 3.37 eV and associated oscillator strength is 0.2052. This excitation is mainly dominated by HOMO-LUMO transition. As discussed above, this transition involved the transfer of the electron from the naphthyl ring to the phenyl ring through the ethylenic linker. The second optical band is also dominated by the $\pi \rightarrow \pi^*$ excitation. The excitation energy is 4.02 eV and oscillator strength is 0.8206. This transition is dominated by HOMO-2 orbital to LUMO. The HOMO-2 is localized on the ethylenic linker and the π orbital of the phenyl group.

The effect of the lack of conjugation in Series II compound was clearly visible as in addition to a weak peak at 314.5 nm, a sharp peak at 260.5 nm was observed. The first theoretical band is located at 3.94 eV and oscillator strength is 0.1483. This excitation is mainly dominated by HOMO-LUMO transition. Therefore, as discussed above, it primarily involves transition from the localized π

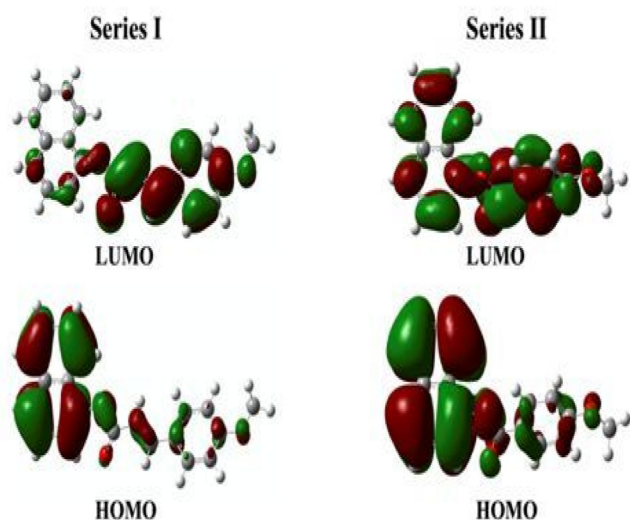


Fig. 6. HOMO and LUMO orbital for the Series I and Series II member ($n = 1$) calculated at the B3LYP/6-31 G (d, p) level of theory.

orbitals of the naphthyl ring to corresponding anti-bonding orbital of the phenyl ring. As compared to Series I, this transition was *blue shifted*. This is in line with the results of 1-D box quantum mechanical problem: “*decreasing the conjugation results into an increase of the excitation energy.*” Another optically bright transition is located at 4.76 eV and oscillator strength is 0.2243. This transition is dominated by HOMO-2 to LUMO. The HOMO-2 is localized on the π orbitals of the phenyl group.

Polarity plays an important role in the identification of mesophase stability which is mainly dependent on the intermolecular attraction, change in the alkoxy chain and electronic interaction between the terminal and lateral substituent affect the polar

stability. Different alkoxy groups still maintains the same dipole moment of all members [92]. The alkoxy chain with same polarity irrespective of its length do not disturb the electronic interactions between central ester carbonyl and alkoxy oxygen.

Comparing current prepared series mesophase behavior with previously made series [89], it was observed in series I that members (*n*-propyloxy & *n*-butyloxy) with shorter alkoxy chains show monotropic nematic and smectic mesophase while the longer-chain members (*n*-pentyloxy to *n*-hexadecyloxy) show both smectic and nematic phase enantiotropically, except *n*-octadecyloxy which exist only as enantiotropic smectic mesophase. Derivatives of series II from (*n*-pentyloxy to *n*-octadecyloxy) exhibited dimorphic behavior monotropically. All compounds with same central linkage, differing only at the terminal position, showed both smectic and nematic mesophase monotropically, with slight difference in mesophase temperatures. The terminal naphthalene group lead to a strong steric effect, which might be the reason for all homologs of 1-naphthyl derivatives to achieve monotropic behavior. The monotropic smecticA behavior in some of homologs might exist because of the weak end to end intermolecular forces as the layers can slide freely over one another. Moreover, the homologous that showed greater mesophase stability are 2-naphthyl (benzoates/cinnamates) just because of the reason of steric effect which is comparatively more in 2-naphthyl derivatives.

Another strong comparison could be made in terms of mesophase stability in 1-naphthyl series and 2-naphthyl [89].

2-naphthyl cinnamates > 1-naphthyl cinnamates

2-naphthyl benzoates > 1-naphthyl benzoates

Thus, we could draw a conclusion that, due to greater mutual conjugation between phenyl ring and the naphthalene moiety attached via cinnamate group ($-\text{CH}=\text{CH}-\text{COO}-$) rather than ester ($-\text{COO}-$) group, polarizability increases, making the molecule more stable. Mesophase stability is greatly affected by the presence of suitable central linking core like ($-\text{CH}=\text{CH}-\text{COO}-$) as well as by the steric effect arising from the presence of the naphthalene group at the terminal position. Due to this steric effect, terminal and lateral

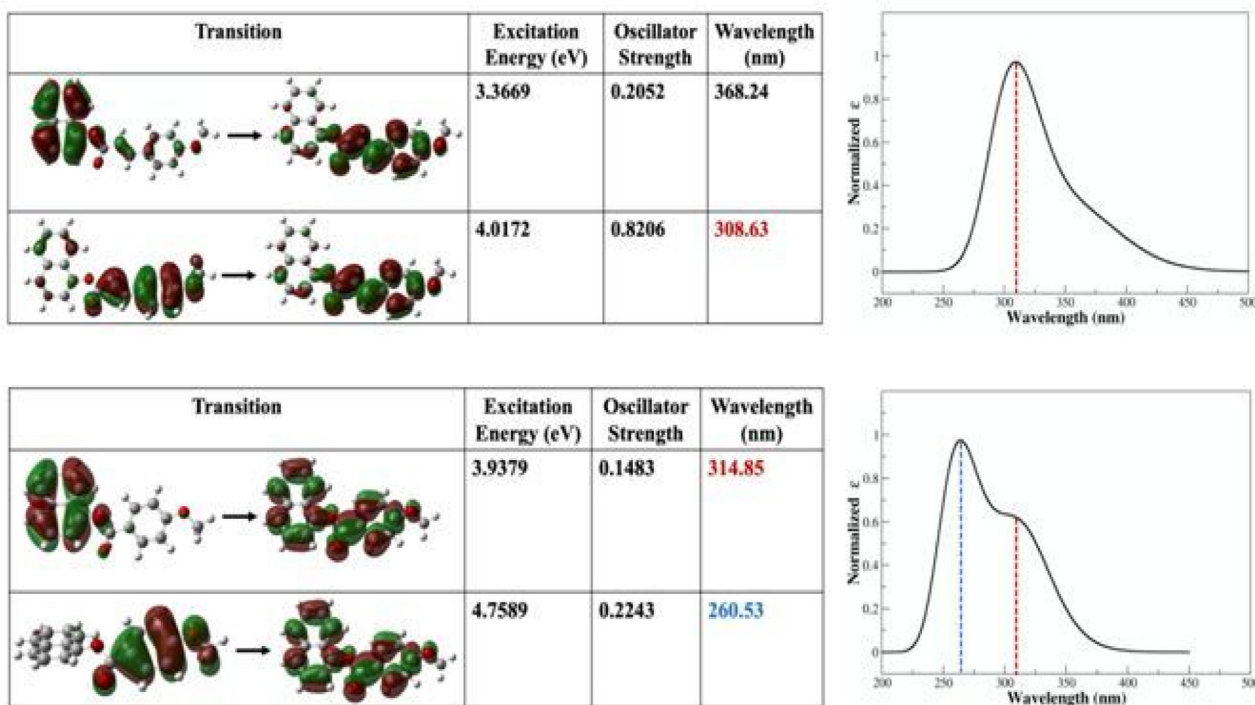


Fig. 7. Molecular orbital, excitation energy values, oscillator strength and excitation wavelength for the Series I and Series II member ($n = 1$) as observed from the TD-DFT calculations at the B3LYP/6-31 G (d, p) level of theory.

substituent widening of the core, which in turn increases the intermolecular separation, whereas reduction in lateral association follows the reduction in mesophase stability [93–95].

The major difference in mesomorphic properties of 2-naphthyl and 1-naphthyl derivatives is affiliated to the geometry of molecules. All compounds with *n*-alkoxy chains are isomeric but show slight difference in geometry via attachment through different positions.

Sometimes, addition of side groups adhering liquid crystalline properties may disturb the molecular packing. Generally, terminal and lateral substitution is the main reason for such kind of disruption. As concerned with the application part, mesomorphic properties greatly affected by the disruption in molecular packing. During terminal and lateral substitution, the nematic stability is directly proportional to the size of attached substituent rather than its polarity. Also smectic phase stability can be affected by substituting any polar group at the terminal and lateral substitution. Increasing the polarity may affect the lamellar packing [96].

After examining the molecular structure of 1-naphthol derivatives, we observed that the non-bonded side of oxygen of ($-C=O$) bond of the ester linkage ($-COO-$) for planar geometry is might come close to the hydrogen present at the ortho position of the terminal naphthyl group. The resulting steric and repulsive interactions force the molecule to twist around the ($-C-O-$) single bond. While the twist is small, it will help the terminal aromatic naphthyl ring to move out of plane of the central ($-C=O-$) as well as ($-CH=CH-COO-$) linkage. This may be due to the change in π -bond character and thus finally affecting the mutual conjugation along the whole molecule, reducing the co-planarity of molecule. The varying polarizability along the long axis is due to the change in position of aromatic ring with reference to the central linking core causing less participation of electrons in conjugation which thus in this direction leads to reduction in polarizability [97].

6. Conclusion

In this article, we have presented the synthesis and characterization of two new naphthalene-containing mesogenic homologous series. We have examined the changes in behavior via terminal attachments as varying alkyl chain, different central linkage and terminal naphthyl group respectively and evaluated the effect of terminal naphthyl moiety on mesomorphism. The homologs of series I from (*n*-ethoxy derivative) exhibit only monotropic nematic phase, from (*n*-propyloxy & *n*-butyloxy derivative) exhibit smectic as well as nematic phase monotropically while from (*n*-pentyloxy to *n*-hexadecyloxy derivative) derivatives exhibit enantiotropic mesophase while (*n*-octadecyloxy derivative) exhibit only enantiotropic smectic mesophase. In series II, first three derivatives exhibit non mesogenic behavior. Mesomorphic behavior start from *n*-pentyloxy and all the homologs of series II exhibit monotropic dimesomorphic behavior.

- The mesomorphic properties exhibited by the present series I and II exhibit larger mesophase thermal stability of series I as compared with those of series II due to increase in breadth of the molecule of series I.
- Thus we may conclude that due to the additional ($-CH=CH-$) units in the central linkages, the presence of cinnamoyloxy ($-CH=CH-COO-$) central linkages increases the molecule's mesophase length and polarizability when compared to series II ($-COO-$) central linkages. The comparison of interaction energy for both series showed that the Series I members are energetically more stable than the respective Series II members.
- The geometry of molecules of 2-naphthyl and 1-naphthyl derivatives creates a major difference in mesomorphic properties. Due to the steric effect, 2-naphthyl derivatives are more

stable than 1-naphthyl derivatives as 2-naphthyl derivatives acquire less steric interactions which in turn help the molecules to become planar and finally provides stability.

- Mesomorphism affected by steric and repulsive interaction, π -bond character and terminal naphthalene moiety.

Declaration of competing interest

The authors declare that they have no known competing financial interests.

Data availability

The data that has been used is confidential.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.molstruc.2022.134629](https://doi.org/10.1016/j.molstruc.2022.134629).

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