



Solvent free Green Synthesis of Pyrazole Derivatives by Hydrothermal method and Characterization of their Liquid Crystalline Properties

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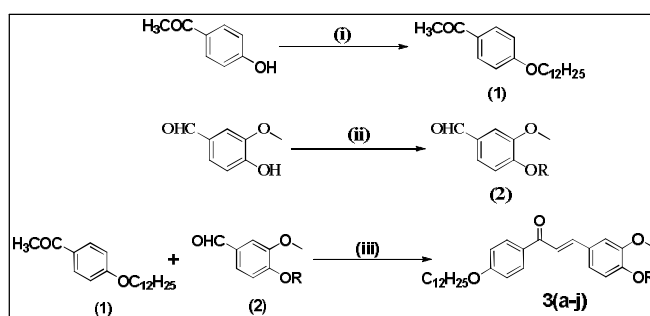
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ABSTRACT

Hydrothermal synthesis of a homologous series of unsymmetrical 3,5-disubstituted-1H-pyrazole derivatives is described. The synthesized compounds were characterized on the basis of mass, IR and NMR spectroscopy. The liquid crystalline properties of the synthesized compounds were investigated by Polarizing Optical Microscope (POM) and Differential Scanning Calorimetry (DSC). It is observed that most of members of the pyrazole derivatives exhibited both Nematic (N) and Smectic phases (S); while others are non-mesogenic.

Graphical Abstract



Synthetic route to the chalcones

Keywords: Heterocycle; Chalcone; Mesophase; Hydrothermal method; Phase transfer catalysis.

INTRODUCTION

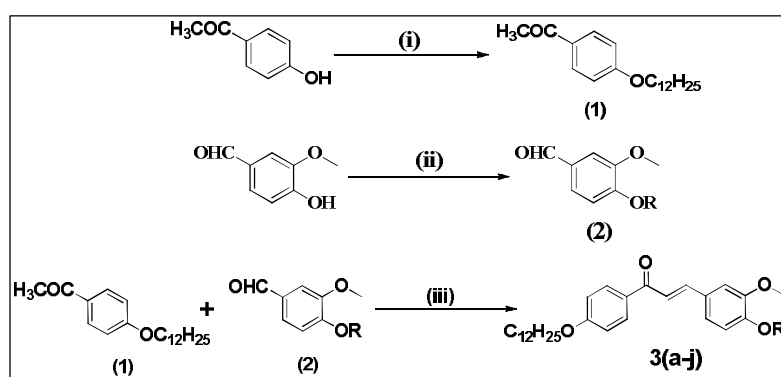
A wide variety of liquid crystalline compounds containing five-membered heterocycles have been synthesized to date [1-4]. The basic prime requirement to induce liquid crystalline properties in a substance is a suitable comprise of molecular rigidity and flexibility [5-8]. Molecular rigidity and

flexibility occurs as a consequence of the molecular shape, size and aromatic types of the central, terminal, lateral groups, their polarities, molecular polarity and polarizability, etc. During the past decades, a large number of liquid crystalline compounds containing heterocyclic units like isoxazole [9-12] pyrazole [13], thiadiazole [14] imidazole [15] triazole [16] pyridazine [17] units have been synthesized. Our interest in synthesizing pyrazole derivatives comes from the ease of synthesis with excellent mesomorphic behavior. The pyrazole ring incorporates a strong dipole moment which helps to increase the anisotropy of polarizability and consequently favor mesogenic behavior [18]. The attainment of mesogenic pyrazoles through the use of α,β -unsaturated ketones forms an easy way to prepare a molecular structure for the synthesis of non-polymer enantiotropic liquid crystalline materials. Our aim of this present work is the preparation of such compounds. Pyrazoles forms an important class of compounds in medicinal chemistry for their multifaceted pharmacological and medicinal applications [19, 20]. Indeed, some 3,5-disubstituted pyrazoles have demonstrated their ability to show liquid crystalline properties as themselves [21, 22] and with metal coordination [23].

MATERIALS AND METHODS

General procedure for the synthesis of 1-(4-(dodecyloxy)phenyl)ethanone and alkylated benzaldehyde (1 and 2)(Phase transfer catalysis): Mixture of p-hydroxy acetophenone (1 mmol) and dodecylbromide (1 mmol) was taken in a round bottomed flask containing about 25 mL of tetrahydrofuran (THF). Then tetra n-butyl ammonium bromide (TBAB, 1mmol) and powdered potassium hydroxide (1 mmol) were added and stirred at room temperature for 10 h. Reaction was monitored by TLC. The product 1-(4-(dodecyloxy)phenyl)ethanone (1) obtained was extracted into ether layer and it was dried over anhydrous Na_2SO_4 . Similarly, the above procedure was followed to obtain 4-alkylated-3-methoxybenzaldehyde (2) with a stirring for 6-12 h with different n-alkyl halides from 4-hydroxy-3-methoxybenzaldehyde.

General procedure for the synthesis of 1-(4-(dodecyloxy)phenyl)-3-(4-alkoxy-3-methoxyphenyl) prop-2-en-1-one (3a-j): The most common procedure to synthesize α, β -unsaturated ketones is the classic Claisen-Schmidt reaction by a well established method [24]. Synthesis involves the condensation of alkylated aromatic aldehyde (1 mmol) with 1-(4-(dodecyloxy)phenyl)ethanone (0.6 mmol) in ethanol and the reaction mixture was maintained in a cold water bath. 10 mL of 10% NaOH solution was added dropwise and the whole reaction mixture was stirred for 5 h at 40-50°C. After cooling, the crude product was filtered under suction and extracted into ether layer and it is concentrated to obtain pale yellow solid, which was further purified by repeated recrystallization from ethanol to get the unsymmetrical *O*-alkylated chalcones of **3a-j** series. In this scheme, all the compounds formed under the conditions described are obtained in good yields. The synthetic pathway to the target compound **3a-j** is depicted in scheme 1.

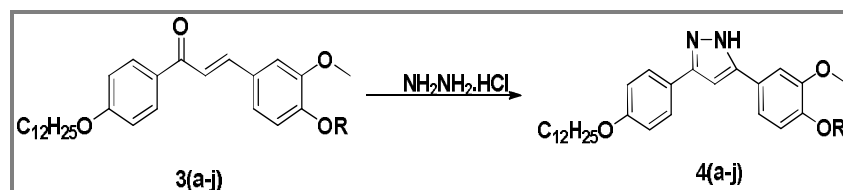


Reagents and Conditions: (i) n-dodecyl bromide, TBAB, THF, 10 h, rt;
(ii) R-Br, TBAB, THF, 6-12 h, rt, $\text{R}=\text{C}_n\text{H}_{2n+1}$ where $n=2-7,10,12,14,16$
(iii) $\text{C}_2\text{H}_5\text{OH}$, NaOH, 5h, 40-50°C.

Scheme 1. Synthetic route to the chalcones

Typical procedure for the Hydrothermal Synthesis of Pyrazole Derivative

General procedure for the synthesis of 3, 5-diarylpirazoles (4a-j): Mixture of synthesized α,β -unsaturated ketone 3a-j (1 mmol), hydroxylamine hydrochloride (1.5 mmol) and sodium acetate (1.5 mmol) were taken in a Teflon liner. Teflon liner was closed tightly and lowered inside a steel autoclave. The steel autoclave was kept in a pre-heated oven at 170°C for 16-32 h. Then the autoclave was taken out of the oven and allowed to attain room temperature. The product was extracted into 50 mL ethyl acetate, washed with brine, finally dried over anhydrous sodium sulfate and evaporated using rotavapour and it was further purified by column chromatography using ethylacetate and petroleum ether to obtain **4a-j** series as a pale yellow solid which is depicted in [scheme 2](#).



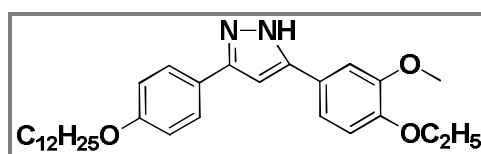
Where, R = C_nH_{2n+1} , $n = 2-7, 10, 12, 14, 16$

Scheme 2. Synthetic route to the pyrazoles

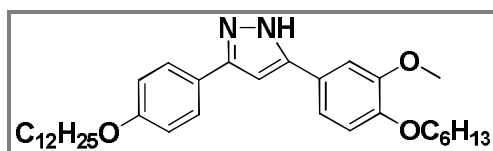
Characterization: All the common reagents procured from commercial supplies were used as such without any purification. The solvents were of analytical grade and were used without further purification. All the reactions were monitored by thin-layer chromatography (TLC) using silica gel 60 (Merck 60F254 0.25 mm thickness) and visualization under UV light. Melting points were recorded on SELACO melting point apparatus. For few representative compounds, IR spectra in the spectral range of 400-4000 cm^{-1} were recorded on Shimadzu FT-IR model 8300 spectrophotometers, ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded using Agilent-NMR using CDCl_3 and the chemical shift is recorded in ppm relative to TMS as an internal standard. Mass spectral analysis was registered in a mass spectrometer of Synapt G2 HDMS. The liquid crystalline properties, melting temperatures and transition temperatures were determined by using optical polarizing microscope in conjunction with LTS 420 Lincam hot stage of Olympus BX51 model. The mesophase type was determined by comparing the observed texture with the corresponding standards.²⁵ Samples were prepared as thin films between a glass slide and a glass cover slip. Transition temperatures and associated enthalpies were determined by differential scanning calorimetry (DSC), using DSC Mettler TA 4000 at a scanning rate of 10°Cmin⁻¹ with a controlled cooling accessory. The purity of the compounds was further confirmed by elemental analysis using Perkin CHN analyzer.

Selected data

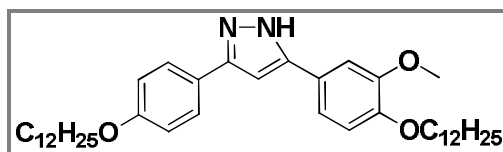
3-(4-(dodecyloxy)phenyl)-5-(4-ethoxy-3-methoxyphenyl)-1H-pyrazole (4a) FT-IR (cm^{-1}): 3454, 3250, 2917, 1738, 1613, 1583, 1304, 1251. ^1H NMR (DMSO, 400 MHz) δ : 0.88(t, -CH₃, 6H), 1.35(m, -CH₂, 12H), 1.44 (m, -CH₂, 4H), 1.80 (m, -CH₂, 4H), 3.94 (s, -OCH₃, 3H), 4.01(t, -OCH₂, 2H), 4.07(t, -OCH₂, 2H), 6.65 (d, 1H), 6.94 (m, ArH, 3H), 7.44 (d, J=8 Hz, ArH, 2H), 7.77 (d, J=8.8 Hz, ArH, 2H). 12.30 (br s, N-H, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 14.20, 14.70, 22.70, 25.90, 29.23, 29.56, 31.87, 56.12, 64.89, 68.72, 98.36, 108.50, 111.12, 114.93, 114.98, 119.28, 119.87, 122.90, 128.20, 130.20, 150.40, 150.67, 159.40, 162.04, 169.35. LCMS: 479.56 [M+H]⁺. Elemental Analysis (%): Calcd for $\text{C}_{30}\text{H}_{42}\text{N}_2\text{O}_3$ C, 75.28 H, 8.84 N, 5.85; O, 10.03 found C, 75.79 H, 8.85 N 5.80, O, 10.07. Yield: 82%.



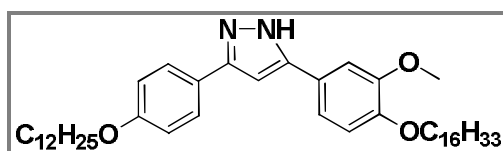
3-(4-(dodecyloxy)phenyl)-5-(4-(hexyloxy)-3-methoxyphenyl)-1H-pyrazole (4e): FT-IR (cm^{-1}): 3454, 3250, 2917, 1738, 1613, 1583, 1304, 1251. ^1H NMR (DMSO, 400 MHz) δ : 0.88(t, $-\text{CH}_3$, 6H), 1.35(m, $-\text{CH}_2$, 20, H), 1.44 (m, $-\text{CH}_2$, 4H), 1.80 (m, $-\text{CH}_2$, 4H), 3.94 (s, $-\text{OCH}_3$, 3H), 4.01(t, $-\text{OCH}_2$, 2H), 4.07(t, $-\text{OCH}_2$, 2H), 6.65 (d, 1H), 6.94 (m, ArH, 3H), 7.44 (d, $J=8$ Hz, ArH, 2H), 7.77 (d, $J=8.8$ Hz, ArH, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 14.20, 14.70, 22.70, 25.90, 29.23, 29.56, 31.87, 56.12, 64.89, 68.72, 98.36, 108.50, 111.12, 114.93, 114.98, 119.28, 119.87, 122.90, 128.20, 130.20, 150.40, 150.67, 159.40, 162.04, 169.35. LCMS: 535.56 $[\text{M}+\text{H}]^+$. Elemental Analysis (%): Calcd for $\text{C}_{34}\text{H}_{50}\text{N}_2\text{O}_3$, C, 76.36; H, 9.42; N, 5.24; O, 8.98. found C, 75.79; H, 9.55; N, 6.20; O, 8.79. Yield: 78%.



5-(4-(dodecyloxy)-3-methoxyphenyl)-3-(4-(dodecyloxy)phenyl)-1H-pyrazole (4h): FT-IR (cm^{-1}): 3454, 3150, 2917, 1738, 1613, 1583, 1304, 1251. ^1H NMR (DMSO, 400 MHz) δ : 0.88(t, $-\text{CH}_3$, 6H), 1.35(m, $-\text{CH}_2$, 30H), 1.44 (m, $-\text{CH}_2$, 6H), 1.80 (m, $-\text{CH}_2$, 4H), 3.94 (s, $-\text{OCH}_3$, 3H), 4.01(t, $-\text{OCH}_2$, 2H), 4.07(t, $-\text{OCH}_2$, 2H), 6.65 (d, 1H), 6.94 (m, ArH, 3H), 7.44 (d, $J=8$ Hz, ArH, 2H), 7.77 (d, $J=8.8$ Hz, ArH, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 14.20, 14.70, 22.70, 25.90, 29.23, 29.56, 31.87, 56.12, 64.89, 68.72, 98.36, 108.50, 111.12, 114.93, 114.98, 119.28, 119.87, 122.90, 128.20, 130.20, 150.40, 150.67, 159.40, 162.04, 169.35. LCMS: 619.56 $[\text{M}+\text{H}]^+$. Elemental Analysis (%): Calcd for $\text{C}_{40}\text{H}_{62}\text{N}_2\text{O}_3$, C, 77.62; H, 10.10; N, 4.53; O, 7.76. found C, 78.79; H, 10.55; N, 4.20; O, 7.79. Yield: 76%.



3-(4-(dodecyloxy)phenyl)-5-(4-(hexadecyloxy)-3-methoxyphenyl)-1H-pyrazole (4j): FT-IR (cm^{-1}): 3454, 3150, 2917, 1738, 1613, 1583, 1304, 1251. ^1H NMR (DMSO, 400 MHz) δ : 0.88(t, $-\text{CH}_3$, 6H), 1.35(m, $-\text{CH}_2$, 34H), 1.44 (m, $-\text{CH}_2$, 10H), 1.80 (m, $-\text{CH}_2$, 4H), 3.94 (s, $-\text{OCH}_3$, 3H), 4.01(t, $-\text{OCH}_2$, 2H), 4.07(t, $-\text{OCH}_2$, 2H), 6.65 (d, 1H), 6.94 (m, ArH, 3H), 7.44 (d, $J=8$ Hz, ArH, 2H), 7.77 (d, $J=8.8$ Hz, ArH, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 14.20, 14.70, 22.70, 25.90, 29.23, 29.56, 31.87, 56.12, 64.89, 68.72, 98.36, 108.50, 111.12, 114.93, 114.98, 119.28, 119.87, 122.90, 128.20, 130.20, 150.40, 150.67, 159.40, 162.04, 169.35. LCMS: 675.56 $[\text{M}+\text{H}]^+$. Elemental Analysis (%): Calcd for $\text{C}_{44}\text{H}_{70}\text{N}_2\text{O}_3$, C, 78.29; H, 10.45; N, 4.15; O, 7.11. found C, 78.79; H, 9.55; N, 4.20; O, 7.80. Yield: 76%.



RESULTS AND DISCUSSION

Thermal behavior: In an effort to understand the molecular structure-liquid crystal property relationship, the chain length in final pyrazole compounds one terminal alkoxy tails (C_1 to C_7 , C_{10} , C_{12} , C_{14} and C_{16}) have been varied keeping the other terminal fixed by C_{12} . The transition temperature and the phase sequence of the compounds synthesized in this investigation are presented in [table 1](#). The mesomorphic behaviour of all the synthesized compounds has been evaluated mainly by

polarizing optical microscopy. However, for some representative compounds, the phase transition temperatures have been confirmed by DSC studies. Both the series was exhibit nematic and/or smectic phases. The molecular structure of the series has a rigid pyrazole ring at the core. **Figure 1** represents the following phases. **Figure 1(a)** show the photomicro-graph of the Sm phase (at 69.2°C) for decyl derivative **4g**, **figure 1(b)** shows the texture of N phase (55.4°C) for dodecyl derivative **4h**, **figure 1 (c)** shows the texture of N phase (81.0°C) for pentyl derivative **4d**, **figure 1(d)** shows the texture of N phase (67.3°C) for hexadecyl derivative **4j**. The POM observations revealed that except for the ethyl homologue all the synthesized unsymmetrical 3,5-disubstituted-1*H*-pyrazole derivatives were nantiotropic liquid crystals. Non-mesomorphic behavior of the ethyl homologue derivatives is attributed to their high crystallizing tendency due to their relatively short alkoxy terminal chains. Hence, the corresponding homologous molecules are unable to resist exposed thermal vibrations, which results in the sudden breaking of the crystal structure and converts the substance sharply into the isotropic liquid state from the solid state without exhibition of a liquid crystalline mesophase. Hence, they melt sharply without showing any liquid crystal property.

A plot of the transition temperature versus the number of carbon atoms present in n-alkyl terminal chain consists of three transition curves, solid isotropic/mesomorphic transition curve, smectic nematic curve and nematic-isotropic curve was plotted for pyrazole series as shown in **Figure 2**. The solid isotropic or mesomorphic transition curve rises and falls as the series is ascended in a zigzag manner and it is also observed that isotropic curve has descended gradually in the series, thus exhibiting enhanced liquid crystalline nature. Present investigation showed predominantly smectogenic and partly nematic with a middle ordered melting type. Liquid crystalline transitions vary in both the series with different magnitudes of phase lengths including smectic and nematic phase lengths.

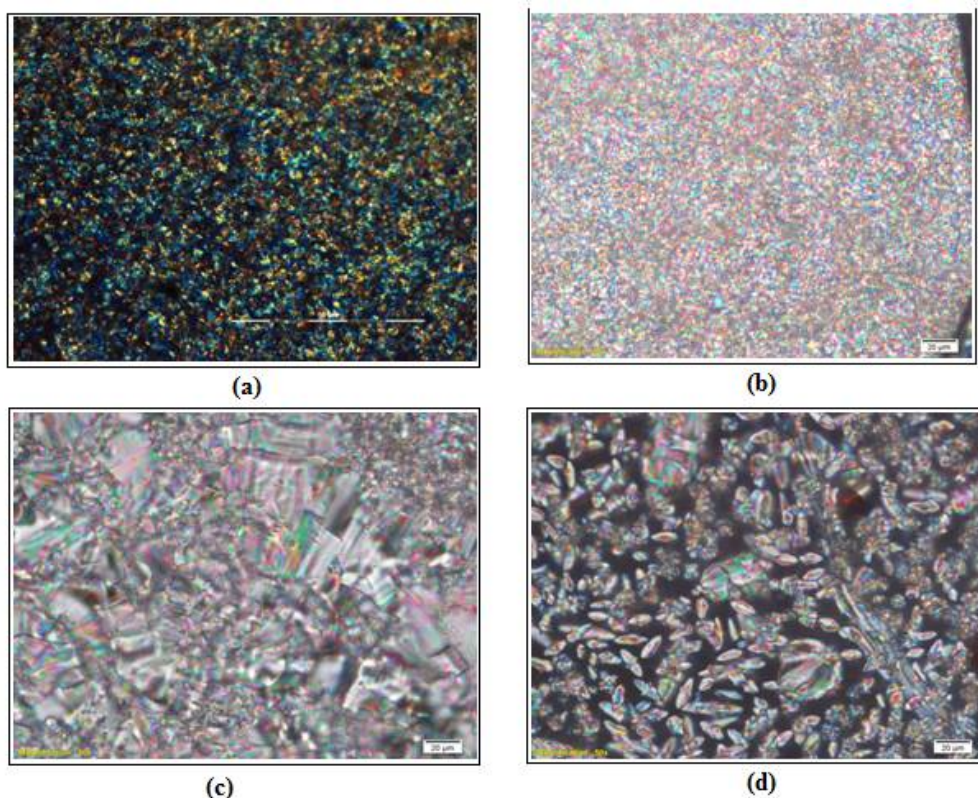
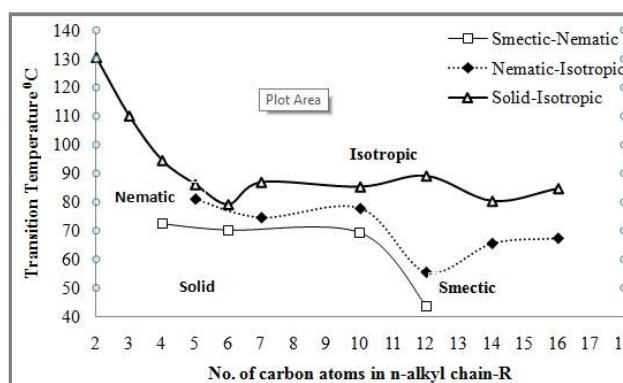


Figure.1 Characteristic optical textures of (a) the Sm phase observed for the compound 3g at 58.9°C, (b) the N phase observed for the compound 4h at 56.4°C, (c) the N phase observed for the compound 4d at 83°C, and (d) the N phase seen for the compound 4j at 68.3°C

Table 1. Transition temperatures of pyrazoles in °C

S. No	R=C _n H _{2n+1}	Smectic	Nematic	Isotropic
4a	2	--	--	130.5
4b	3	--	--	110.0
4c	4	72.4	--	94.4
4d	5	--	81.0	86.0
4e	6	70.2	--	79.0
4f	7	--	74.5	86.8
4g	10	69.2	77.7	85.2
4h	12	43.4	55.4	89.0
4i	14	--	65.5	80.2
4j	16	--	67.3	84.6

**Figure 2.** Plot of transition temperature against the number of carbon atoms in the n-alkoxy chains.

The exhibition of mesogenic properties from the propyl to the hexadecyl homologues is attributed to the suitable magnitudes of anisotropic intermolecular forces of attraction caused by the favorable molecular polarity and polarizability, aromatic, electronic-electronic interactions, length-to-breadth ratio and the ratio of the polarity to polarizability as a consequence of the resultant molecular rigidity and flexibility [25-27].

Variations in the mesomorphic properties in both the series are attributed to the variation in the central group or by varying the terminal alkoxy groups, keeping the other one fixed. As the chain length progresses liquid crystalline property also enhanced. Compounds exhibited the smectic and nematic phase in some compounds but predominantly nematogenic which can be attributed due to the presence of rigid pyrazole core at the central owing to their ability to impart lateral and/or longitudinal dipoles combined with changes in the molecular shape as most of the heteroatoms (N, O and S) are more polarizable than carbon and by increased conjugation through the molecule. This favors the molecular planarity and anisotropy of electronic polarizability and consequently promoting liquid crystal behavior. Further, the presence of heterocycle moiety increased the liquid crystalline nature and dramatically decreased the melting point of the compounds by extended conjugation through the molecule in mesophase formation.

APPLICATION

The hydrothermal method of pyrazole derivatives has advantages such as good product yield, eco-friendly, benign reaction conditions and easy isolation of products.

CONCLUSION

In conclusion a solvent free, clean and efficient method has been developed for the synthesis of 5-(4-(dodecyloxy)-3-methoxyphenyl)-3-(4-(dodecyloxy)phenyl)-1*H*-pyrazole in moderate to good yields to study their mesomorphic behavior by polarizing optical microscope and DSC. To understand the structure-property relationships, alkoxy tails have been varied keeping the other terminal fixed. Our investigation revealed that except for ethyl homologue all other compounds exhibited mesomorphic state. Middle and higher homologues exhibited smectic and nematic phase. Overall, variations in the mesomorphic properties for the synthesised series is attributed to varying features due to central group, linking group, molecular shape and rigidity.

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