

## SYNTHESIS AND CHARACTERIZATION OF NEW DISCOTIC LIQUID CRYSTALS COMPOUNDS

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### ABSTRACT

This paper consists of the synthesis of discotic liquid crystal triester derivatives of benzene namely 1,3,5-Tri[4'-n-alkoxybenzoyloxy]benzene and 1,3,5-Tri-{4-[4'-n-alkoxy-benzoyloxy] benzoyloxy} benzene. The synthesized compounds were characterized using FTIR, <sup>1</sup>H NMR and CHNS-O analysis. The liquid crystalline properties of the prepared compounds which were verified using differential scanning calorimeter (DSC) and hot-stage polarizing optical microscope (POM) were discussed. The relation between the liquid crystalline behavior with chemical constitution was discussed on the basis of the effect of terminal group (Alkoxy group).

**Keywords:** Discotic liquid crystal, triester derivatives of benzene, star shape mesogens.

### INTRODUCTION

Liquid crystal is a state of matter in which the degree of molecular order is intermediate between the perfect three dimensional, long-range positional and orientational order found in solid crystals and the absence of long-range order found in isotropic liquids, gases, and amorphous solids.

A large number of discotic mesogenic compounds have been discovered in which triphenylene, porphyrin, phthalocyanine, coronene, and other aromatic molecules are involved. In 1977, mesogenic structure, based on discotic (disc shaped) molecular structures was discovered. The first series of discotic compounds to exhibit mesophase belonged to the hexa-substituted benzene Derivatives Figure 1 synthesised by Chandrasekhar et. al.<sup>1</sup> Similarly to the Calamitic LCs, discotic<sup>2</sup> LCs possess a general structure comprising a planar (usually aromatic) central rigid core surrounded by a flexible periphery, represented mostly by pendant chains (usually four, six, or eight), as illustrated in the cartoon representation in Figure 2. As can be seen the molecular diameter (**d**) is much greater than the disc thickness (**t**), imparting the form anisotropy to the molecular structure.

The two principle discotic mesophases are Nematic and Columnar, Most of the discotic liquid crystals (DLCs) form columnar mesophases probably due to strong p-p interaction among the aromatic cores<sup>3</sup>. There are various types of columnar phases depending on the degree of order in the molecular stacking, orientation of the molecules along the columnar axis, the dynamics of the molecules within the columns, and the two-dimensional lattice symmetry of the columnar packing. Very few of the DLCs exhibit a less ordered nematic phase<sup>4</sup>.

### MATERIALS AND METHODS

#### MATERIALS

All the chemicals (reagents and solvents) were supplied from Merck, BDH, Fluka and Alfa chemicals Co. and used as received.

#### Techniques

The infrared spectra of the prepared compounds were recorded using FTIR 8300 Fourier transform infrared spectrophotometer of SHIMADZU Company as a potassium bromide (KBr) discs in the wave number range of (4000-400) cm<sup>-1</sup>. Uncorrected melting points were recorded on hot stage Gallen kamp melting point apparatus The <sup>1</sup>H NMR spectra

were recorded on Brüker ACF 300 spectrometer at 300 MHz, using deuterated chloroform or DMSO as solvent with TMS as an internal standard. Elemental analysis (CHNS-O) was carried out using EURO EA elemental analyzer instrument. Transition temperatures and enthalpies were scanned in TA instruments LINSEIS DSC PT-1000 differential scanning calorimeter with a heating rate of 10.0°C/min in air and it was calibrated with indium (156.6°C, 28.45 J/g). The temperatures were read as the maximum of the endothermic peaks. The optical behavior observations were made using MEIJ microscope equipped with INSTEC hot stage and central processor controller mK 1000 and connected with Lumenera color video camera.

### Synthesis

The steps of the synthesis of homologous series 1,3,5-tri-[4'-n-alkoxybenzoyloxy]benzene [3<sub>a-g</sub>] are shown in the sequence of reactions depicted in Scheme 1. Where *n* designate the number of carbon atom in terminal alkoxy group substituent.

### Preparation of 4-n-Alkoxy benzoic acid

4-Hydroxybenzoic acid (5 g, 0.03 mole) was dissolved in 20 mL ethanol. (5.1 g, 0.09 mole) KOH was added with stirring, the mixture was cooled to room temperature, and then 0.036 mole of appropriate alkyl bromide was added drop wise. The solution was refluxed over night. (1.12 g, 0.02 mole) KOH dissolved in a little amount of water (~ 5mL) was added to the reaction mixture and heated for (1-3) hour the solvent was evaporated and equal volume of water was added. The solution was heated till became clear. Acidification with conc. HCl yielded white precipitate. Recrystallization from ethanol gave the desired product<sup>5</sup>.

### Preparation of 4-n-Alkoxy benzoyl chlorides

4-n-alkoxy benzoyl chlorides were prepared by reflux the corresponding *p*-n-alkoxy benzoic acid (0.03 mol) with freshly distilled thionyl chloride (15 ml) in water bath till evolution of hydrogen was gas ceased. The excess thionyl chloride was distilled off under reduce pressure using water pump. The acid chloride left behind was directly used for further reaction without purification<sup>6</sup>.

### Synthesis of 1,3,5-tri[4'-n-alkoxybenzoyloxy]benzene

(0.008 mole, 1 g) of 1,3,5-trihydroxybenzene and (0.024 mole) of 4-n-alkoxybenzoylchloride, along with 10 ml pyridine were stirred for three hours in an ice bath. The

mixture was poured onto cold water acidification with HCl and filtered. The product was washed with cold water<sup>7</sup>. Table 1 shows the melting points and % yield of the synthesized compounds. Table 2 shows the FTIR bands for synthesizes compounds.

### Preparation procedures of Tri-[4-(4'-nalkoxybenzoyloxy)benzoyloxy]benzene

The intermediate and discotic compounds (6a-g) were prepared according to scheme 2:

### Preparation of 4-[4'-n-alkoxybenzoyloxy]benzoic acid

(0.008 mole, 1.14 g) of *p*-Hydroxybenzoic acid and (0.008 mole) of 4-n-alkoxybenzoylchloride, along with 10 ml pyridine were stirred for three hours in an ice bath. The mixture was poured onto cold water acidification with HCl and filtered. The product was washed with cold water<sup>7</sup>.

### Synthesis of 1,3,5-Tri-[4-(4'-n-alkoxybenzoyloxy)benzoyloxy]benzene

(0.008 mole, 1.14 g) of Trihydroxybenzene and (0.024 mole) of 4-[4'-n-alkoxybenzoyloxy]benzoylchloride, along with 10 ml pyridine were stirred for three hours in an ice bath. The mixture was poured onto cold water acidification with HCl and filtered. The product was washed with cold water<sup>7</sup>. Table 3 shows the melting points and % yield of the synthesized compounds. Table 4 shows the FTIR bands for synthesizes compounds.

## RESULTS AND DISCUSSION

### Synthesis

The 1,3,5-tri[4'-n-alkoxybenzoyloxy]benzene (3a-g) was achieved by the reaction of 4-alkoxybenzoyl chloride with 1,3,5-trihydroxybenzene in pyridine as solvent and proton acceptor. The structures of all products were identified by using FTIR and <sup>1</sup>HNMR. The all resultant data of the spectra were in accordance with expected values. The purities of compounds were confirmed by using an elemental analysis. The elemental analysis of series (3a-g) compounds synthesized above is listed in Table 5. The observed values are in well agreement with theoretical values indicating structure of respective compounds. The spectroscopic observation of (3a) for example is given: FT-IR (KBr, cm<sup>-1</sup>) figure (3): 1736 (C = O of ester stretching), 3080 (Ar-H), 2966-2887 (ν C-H, aliphatic stretching), 1591 (ν C=C), 1261 (ν C-O). <sup>1</sup>HNMR (CDCl<sub>3</sub>, δ in ppm) figure (4): 7.72-7.51 (d-d, 12H, arom. H), 6.98 - 6.96 (s, 3H, arom.), 1.85-1.78 (q, 6H, OCH<sub>2</sub>), 0.91- 0.87 (t, 9H, OCH<sub>2</sub> CH<sub>3</sub>).

The 1,3,5-Tri-[4-(4'-n-alkoxybenzoyloxy)benzoyloxy]benzene (6a-g) was achieved by the reaction of 4-n-alkoxybenzoyloxybenzoyl chloride with 1,3,5-trihydroxybenzene in pyridine as solvent and proton acceptor.

The structures of all products were identified by using FTIR and <sup>1</sup>HNMR. The FTIR spectra of

1,3,5-Tri-[4-(4'-n-alkoxybenzoyloxy)benzoyloxy]benzene (6a-g) give the evidence for the formation of the titled compounds through, the disappearance of the hydroxyl group bands and the appearance of the ester carbonyl bands. The purities of compounds were confirmed by using an elemental analysis. The elemental analysis of series (6a-g) compounds synthesized above is listed in Table 6. The observed values are in well agreement with theoretical values indicating structure of respective compounds.

The spectroscopic observation of (6c) for example is given: FT-IR (KBr, cm<sup>-1</sup>) figure (5): 1738 (C = O of ester stretching), 3040 (Ar-H), 2948-2841 (ν C-H, aliphatic stretching), 1608 (ν C=C), 1251 (ν C-O). The <sup>1</sup>HNMR spectrum of compound (6c) (CDCl<sub>3</sub>, δ in ppm) figure (6) showed characteristic signals at δ 8.15-7.53 (d-d, 24H, arom. H), 7.2 - 6.9 (s, 3H, arom.), 4.04-3.9(t, 6H, OCH<sub>2</sub>), 2.48-2.41 (m, 12H, CH<sub>2</sub>CH<sub>2</sub>), 1.15-1.14 (t, 9H, -CH<sub>3</sub>).

### Mesomorphic Properties

The phase transitions of compounds (3a-g) series were studied using polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The phase transition temperatures observed by POM agree well with the corresponding DSC thermograms.

For the mesomorphism of the synthesized compounds all the compounds display different phase-transition temperatures related to the length of the chain.

The first compound (3a) do not reveal any liquid crystalline behavior, but simply changes from the solid crystalline state to the isotropic liquid at 130°C. Compounds (3b-g) display enantiotropic mesomorphism. The texture observed by POM on heating the solid crystal are consistent with the presence of columnar mesomorphism, with fan-shaped typical to columnar phases for compounds (3c, 3e, and 3g) and fan shaped focal conic typical to a columnar hexagonal for compound (3b, 3d, and 3f) as shown in Figure (7).

All the star-shaped mesogens exhibit liquid crystalline behaviour except for the homologues possessing the shortest alkyl spacer (*n* = 2). These compounds undergo direct isotropization on heating and crystallization on cooling, thus indicating the nonmesogenic properties. In addition, the non-

mesogenic properties can also be inferred from the DSC thermograms of these homologues which display only one endotherm and exotherm upon heating-cooling cycle. The absence of mesophase is presumably due to the short flexible spacer as the short chain may tend to hinder the peripheral units from the appropriate anisotropic arrangement in forming liquid crystalline properties<sup>8</sup>. Furthermore, shorter alkyl spacer also does not increase the polarity and polarizability of the molecules<sup>9</sup>. Therefore, phase generation is usually less apparent especially in molecule having short alkyl chain. The formation of a columnar mesophase was found to be dependent on the number of methylene units in alkoxy terminal chains attached to the rigid. The mesophase's stability was found to be poor for the first synthesized compound.

Thermal phase behavior of 1,3,5-Tri-[4-(4'-n-alkoxybenzoyloxy)benzoyloxy]benzene (6a-g) was studied using differential scanning calorimetry (DSC), polarizing optical microscopy (POM). Results of the DSC studies, which used heating and cooling rates of 10 °C/min, are show in figure (9).

Star-shaped mesogens with the alkoxy terminal groups show both nematic phase in their liquid crystalline state when viewed under a polarized optical microscope as show in figure (10).

The effects of the terminal chain length on the transition temperatures and phases behavior observed in this series are in accordance with those observed for columnar discotic mesogenes<sup>10</sup>.

### CONCLUSIONS

A new series of discotic liquid crystalline based on 1,3,5-tri hydroxybenzene derivatives with two pendant alkoxybenzoyl group and alkoxybenzoyloxy benzoyl group were designed and synthesized by varying alkoxy terminal chain length (*n*=2-8). The formation of a columnar mesophase was found to be dependent on the number of methylene unit in alkoxy terminal chains. The compounds with *n* ≥ 3, exhibited an anantiotropic columnar phase; however, compound with *n* = 1, and 2 formed a crystalline phase.

### ACKNOWLEDGEMENTS

My deep appreciation goes to my thesis advisor Dr .Nasreen R. jber for her constant help, guidance and the countless hours of attention she devoted throughout the course of this work, her priceless suggestion made this work interesting and learning for me.

**Table 1: Melting points and % yield of compounds (3a-g)**

Comp. name	Comp.No.	Yield %	m.p (°C)
1,3,5-tri[4'-ethoxybenzoyloxy]benzene	3a	81%	125-130
1,3,5-tri[4'-n-propyloxybenzoyloxy]benzene	3b	58%	112-116
1,3,5-tri[4'-n-butyloxybenzoyloxy]benzene	3c	67%	115-120
1,3,5-tri[4'-n-pentyloxybenzoyloxy]benzene	3d	73%	120-125
1,3,5-tri[4'-n-hexyloxybenzoyloxy]benzene	3e	62%	70-75
1,3,5-tri[4'-n-heptyloxybenzoyloxy]benzene	3f	50%	93-98
1,3,5-tri[4'-n-octyloxybenzoyloxy]benzene	3g	41%	89-94

**Table 2: Characteristic FTIR absorption bands of synthesizes compounds (3a-g)**

Comp.No	$\nu$ C-H arom.	$\nu$ C-H alpt.	$\nu$ C=O	$\nu$ C=C	$\nu$ C - O
3a	3080	2966&2887	1736	1591	1261
3b	3070	2965 & 2877	1733	1601	1251
3c	3070	2963 & 2871	1748	1598	1257
3d	3066	2955 & 2865	1743	1593	1255
3e	3075	2963 & 2865	1747	1602	1254
3f	3082	2975 & 2865	1748	1604	1253
3g	3045	2952 & 2865	1749	1604	1255

**Table 3: Melting points and % yield of compounds (6a-g)**

Comp. name	Comp.No.	Yield %	m.p(°C)
1,3,5-tri[4-{4'-ethoxybenzoyloxy}bezoyloxy]benzene	6a	78%	160-165
1,3,5-tri[4-{4'-n-popyloxybenzoyloxy}bezoyloxy]benzene	6b	63%	105-110
1,3,5-tri[4-{4'-n-butyloxybenzoyloxy}bezoyloxy]benzene	6c	66%	110-115
1,3,5-tri[4-{4'-n-pentyloxybenzoyloxy}bezoyloxy]benzene	6d	58%	120-130
1,3,5-tri[4-{4'-n-hexyloxybenzoyloxy}bezoyloxy]benzene	6e	71%	118-123
1,3,5-tri[4-{4'-n-heptyloxybenzoyloxy}bezoyloxy]benzene	6f	51%	105-112
1,3,5-tri[4-{4'-n-octyloxybenzoyloxy}bezoyloxy]benzene	6g	43%	130-136

**Table 4: Characteristic FTIR absorption bands of synthesizes compounds(6a-g)**

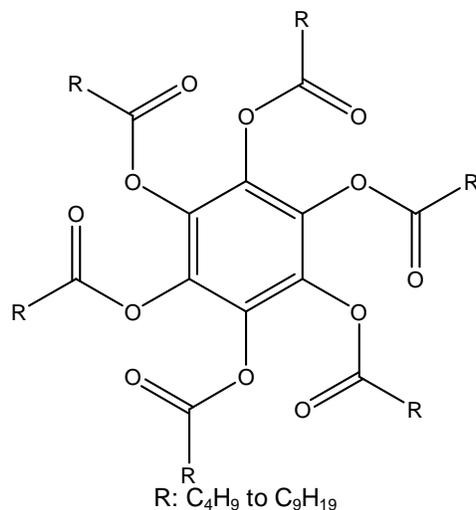
Comp.No	$\nu$ C-H aro.	$\nu$ C-H alpt.	$\nu$ C=O	$\nu$ C=C	$\nu$ C - O
6a	3075	2988&2895	1737	1604	1267
6b	3082	2939 & 2879	1735	1602	1255
6c	3040	2948 & 2841	1741	1608	1251
6d	3065	2955 & 2862	1738	1603	1251
6e	3078	2963 & 2862	1740	1605	1257
6f	3056	2995 & 2854	1736	1602	1257
6g	3067	2927 & 285665	1741	1603	1256

**Table 5: Elemental Analysis (CHNS-O) for compounds 3a-g**

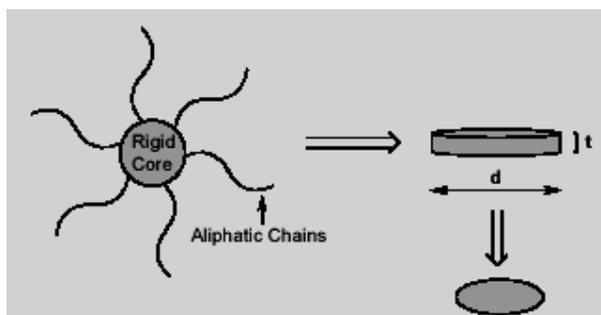
Comp. No.	Formula	%C		% H	
		Calc.	Found	Calc.	Found
3a	C <sub>33</sub> H <sub>30</sub> O <sub>9</sub>	69.47	68.99	5.26	5.21
3b	C <sub>36</sub> H <sub>36</sub> O <sub>9</sub>	70.58	69.78	5.88	5.74
3c	C <sub>39</sub> H <sub>42</sub> O <sub>9</sub>	71.55	71.53	6.42	6.40
3d	C <sub>42</sub> H <sub>48</sub> O <sub>9</sub>	72.41	72.13	6.89	6.83
3e	C <sub>45</sub> H <sub>54</sub> O <sub>9</sub>	73.17	72.98	7.31	7.30
3f	C <sub>48</sub> H <sub>60</sub> O <sub>9</sub>	73.84	74.09	7.69	7.66
3g	C <sub>51</sub> H <sub>66</sub> O <sub>9</sub>	74.45	74.56	8.02	8.03

**Table 6: Elemental Analysis (CHNS-O) for compounds 6a-g**

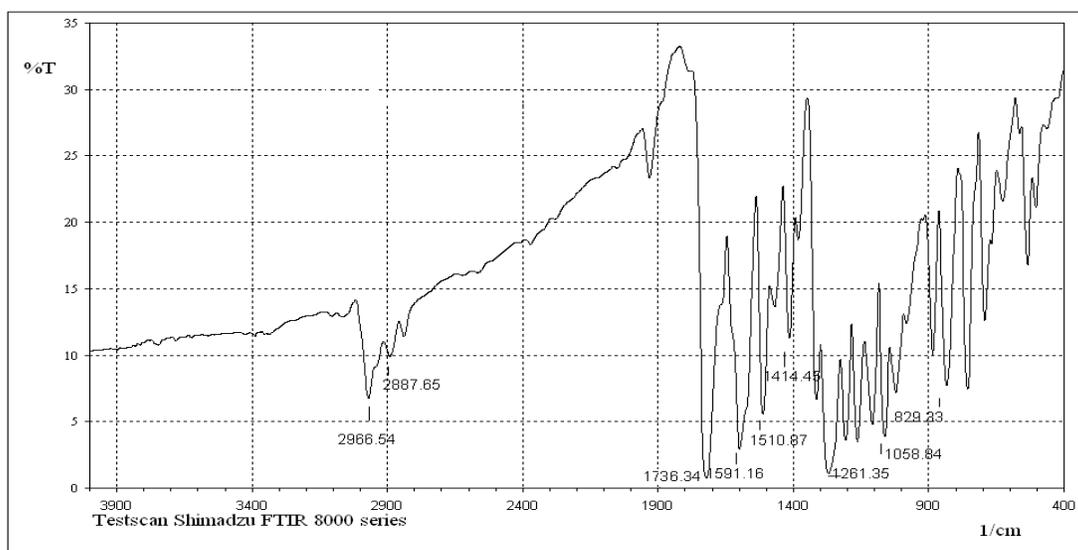
Comp. No.	Formula	%C		% H	
		Calc.	Found	Calc.	Found
6a	C <sub>54</sub> H <sub>42</sub> O <sub>15</sub>	69.67	70.01	4.55	4.58
6b	C <sub>57</sub> H <sub>48</sub> O <sub>15</sub>	70.36	70.21	4.97	4.89
6c	C <sub>60</sub> H <sub>54</sub> O <sub>15</sub>	70.99	70.97	5.36	5.28
6d	C <sub>63</sub> H <sub>60</sub> O <sub>15</sub>	71.58	71.56	5.72	5.80
6e	C <sub>66</sub> H <sub>66</sub> O <sub>15</sub>	72.12	72.36	6.05	6.09
6f	C <sub>69</sub> H <sub>72</sub> O <sub>15</sub>	72.63	72.87	6.36	6.33
6g	C <sub>72</sub> H <sub>78</sub> O <sub>15</sub>	73.09	72.98	6.64	6.62



**Fig. 1: Molecular structure of the first series of discotic LCs discovered the benzene-hexa-n-alkanoate derivatives**



**Fig. 2: Cartoon representation of the general shape of discotic LCs, were  $d \gg t$ .**



**Fig. 3: FTIR spectrum of compound 3a**

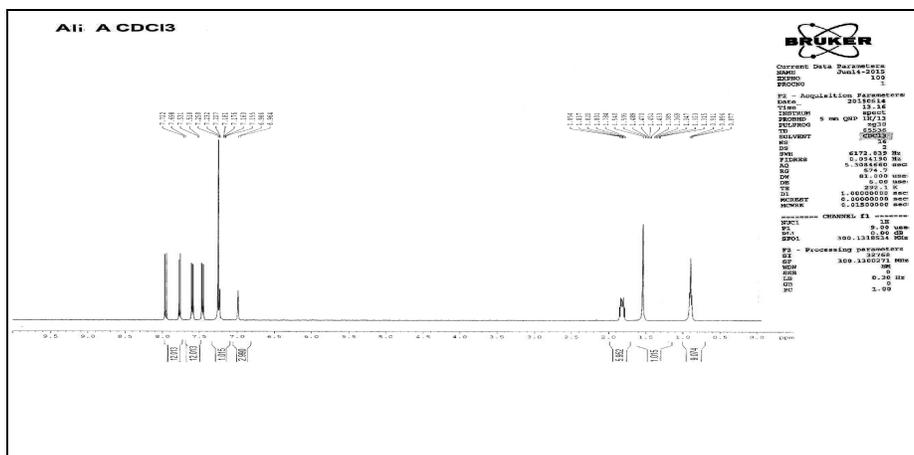


Fig. 4: <sup>1</sup>H NMR spectrum of compound 3a

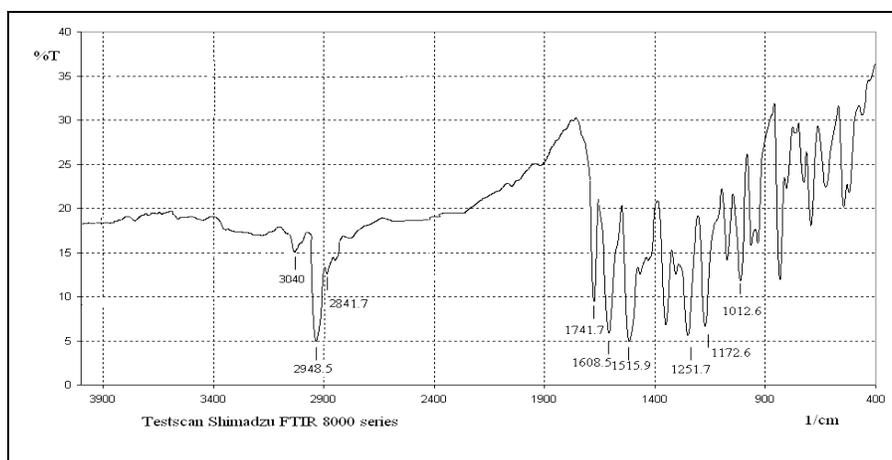


Fig. 5: FTIR spectrum of compound 6c

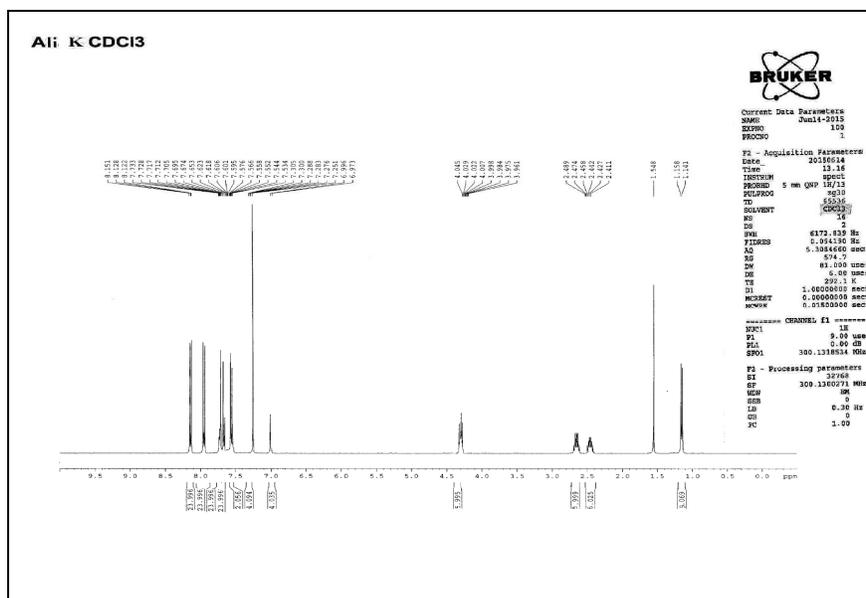


Fig. 6: <sup>1</sup>H NMR spectrum of compound 6c

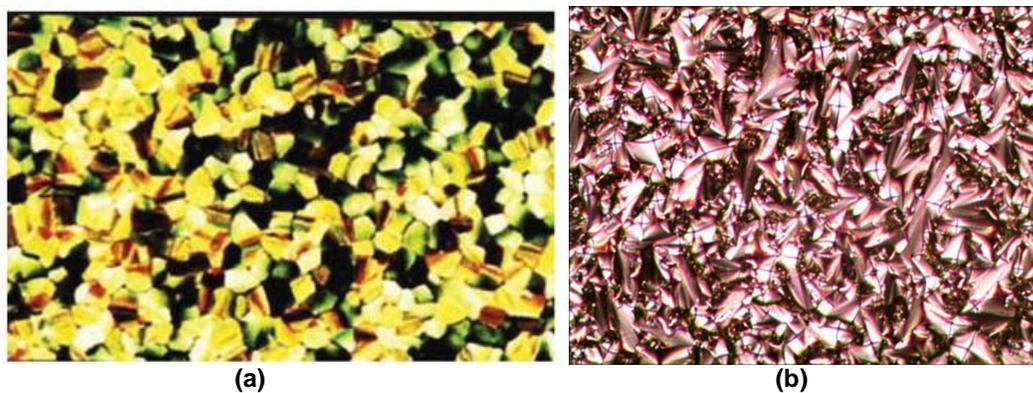


Fig. 7: Cross-polarizing Optical textures of the columnar mesophase obtained on heating and cooling (Magnification 200 $\times$ ) for compounds of series (3b-g), (a) (3e) at 79 $^{\circ}$ C, (b) (3d) at 132 $^{\circ}$ C

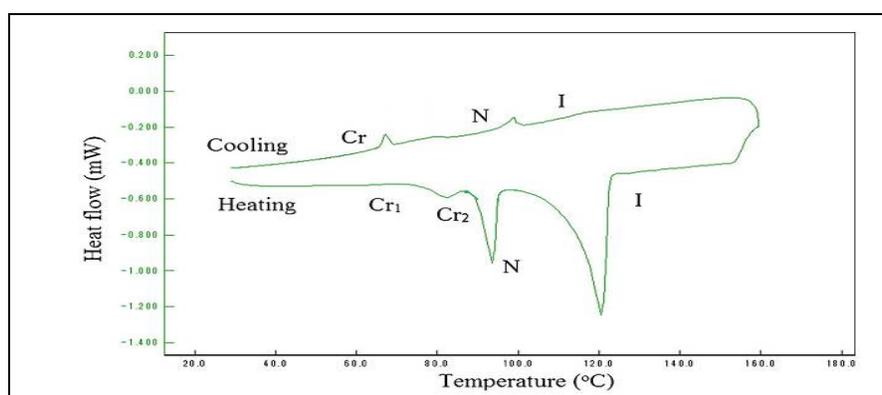


Fig. 8: DSC thermograms at 10 $^{\circ}$  C/min for compound 3f

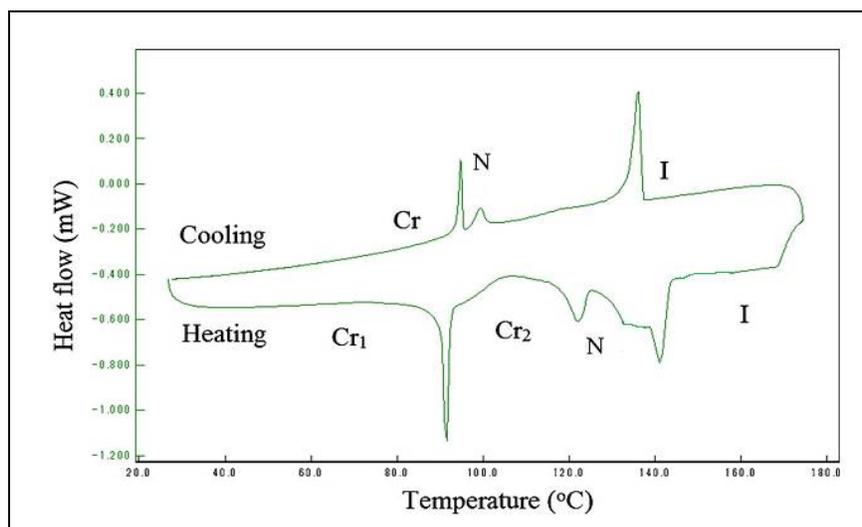


Fig. 9: DSC thermograms at 10 $^{\circ}$  C/min for compound 6d

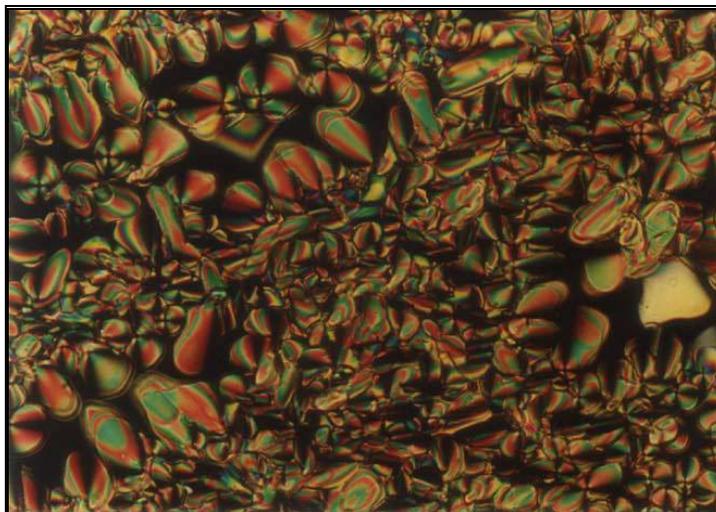
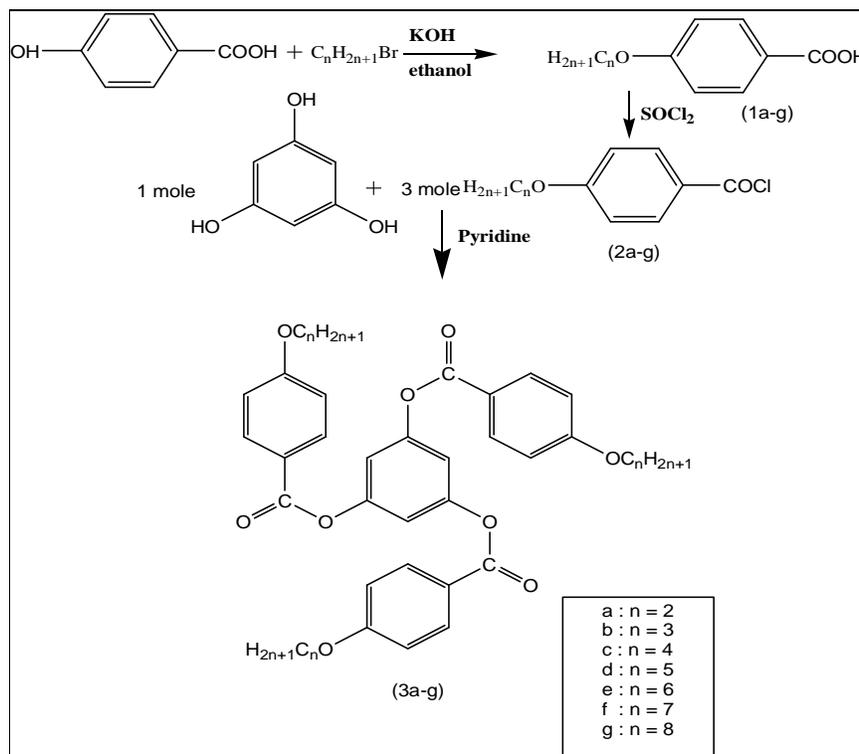


Fig. 10: Cross-polarizing Optical textures of the columnar mesophase obtained on heating and cooling (Magnification 200 $\times$ ) for compounds 6d at 123 $^{\circ}$ C.



Scheme. 1: The synthetic pathway for the discotic compounds (3a-g)

