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Synthesis of analogues of 1,3,4-Oxadiazoles under solvent free conditions and evaluation of their liquid crystal studies

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ABSTRACT

Liquid crystals have major role in many areas of science and device technology. Liquid crystals are important intermediate phases which exhibit features from both the solid and fluid state. The interest in such compounds arise from the fact that the incorporation of heteroatoms such as Nitrogen, Oxygen, Sulphur etc, can result in large changes in the corresponding liquid-crystalline phases and/or in the physical properties of the observed phases. The design of novel thermotropic liquid crystals as advanced functional materials involves selection of suitable core fragment, linking group, and terminal functionality. In this regard, new series of heterocyclic compounds with various alkoxy substituents have been synthesized in the present work. p-Hydroxy benzoic acid was the precursor compound for the synthesis of different kinds of liquid crystals in autoclave and reflux conditions for the synthesis of oxadiazoles and these were taken to next step for alkylation with different alkyl bromides($C_nH_{2n+1}Br$), where n= 4,5,6,7 to form O-alkylated heterocycles. The synthesized derivatives were characterized by Mass, IR and NMR Spectroscopy and liquid crystalline (LC's) activity was characterized by Polarising optical microscope and Differential Scanning Calorimetry (DSC).

Keywords: Heterocycles, Liquid Crystals 1,3,4-Oxadiazole.

1. INTRODUCTION

Liquid crystals are partially ordered, anisotropic fluids, thermodynamically located between the solid state and the isotropic liquid. Liquid crystalline phases represent intermediate states of soft matter, combining order and mobility at the molecular levels. These unique phases create fascinating systems, which respond to external (magnetic, electronic, chemical or mechanical) stimuli by finding a new configuration. Thus, liquid crystalline materials had great impact on recent development of mobile information technologies with numerous applications in opto electric devices. Classical rod-like liquid crystalline molecules are composed of flexible alkyl chains and anisometric units like phenyl, biphenyl, terphenyl, cyclohexyl, etc.

In this continuation work, 1,3,4 – oxadiazoles linked with the aromatic ring on the both sides with the hydroxyl group at the para-position of both sides at the aromatic rings to balance the chain length-breadth ratio. The hydroxyl groups are O-alkylated at the both sides and the chain length was increased by by taking the alkyl bromides of the increasing chain length at both the positions. Liquid crystal properties of the corresponding synthesized compounds were studied.

The synthesis of liquid crystalline compounds containing heterocyclic groups have been enormously reported due to their wide range of applications in the optical, electrical and medical fields [1–5]. Usually, 5-or 6-membered heterocycles are involved and they form part of the core in rod, bent or disc-shaped molecules.

Oxadiazole is an aromatic heterocyclic compound containing two nitrogen and one oxygen as hetero atoms. Longer threads/side chains attached to the oxadiazole at the oxygen and nitrogen atoms, instead of diamine groups, can create a possible mesogenic compound with a bend-shape. For this reason, the oxadiazole was used to build the boomerang-shaped molecules. Also a variety of mesogenic 1,2,4-oxadiazoles have been synthesized by Torgova et al and characterizing their liquid crystal properties [6]. These structures have a large dipole moment perpendicular to the molecular axis, a characteristic that influence the mesogenic properties. The electron-accepting property of the

oxadiazole ring enables substances incorporating it to be of use as electron transport layers in the development of organic light-emitting devices (OLED's)[7]. On continuation of our work on heterocyclic mesogens, we herein report the synthesis and characterization of new 1,3,4-oxadiazole derivatives in which both sides of the terminal substituent is an alkoxy group by varying the chain length.

Studies on the effect of the heterocyclic unit on liquid crystalline behaviour and on their photophysical and thermal properties are also reported. In the series of various other chemical reactions of oxidation [8,9], reduction [10-12] and substitution [13], we made an effort as a trial method for the oxidation of semicarbazone for the preparation of 1,3,4_oxadiazoles and this is surprising that we got success in the oxidation of semicarbazone.Amongst five membered aromatic heterocycles, oxadiazoles, thiadiazoles and triazoles have attracted significant interest in polymer and material science. The present communication deals with the synthesis of 1,3,4-oxadiazoles.

In dry media, reactions occur rapidly and the method avoids hazards associated with solvents especially in sealed vessels. The absence of solvent reduces reaction time as well as it improves the yield. In this context, we planned to prepare oxadiazoles under eco-friendly and environmentally benign solvent-free conditions, where in several disadvantages like long reaction time and tedious work-up could be avoided.

Chirality has become one of the most important and complex topics of liquid crystal research now a day (Collings and Hird, 1998; Goodby, 1999; Collings, 2005). The early discovery of chiral nematic phase can be dated back to end of the 1960s (Sackmann et al., 1967). Interest in chiral mesogens increased dramatically since the discovery of the first ferroelectric liquid crystal (FLC) 2- methyl butyl 4-(4-n-decloxybenzylideneamino) cinnamate (DOBAMBC) was reported by Meyer et al., in 1975.

There are numerous new mesophases which have been detected with these banana-shaped mesogens. Most of them have no analogues in LC systems formed by conventional calamitic molecules. Initially there were seven phases designated as B_1 to B_7 according to the sequence of their discovery, where B stands for bent-core, 'banana' or 'bow'. The structures and characteristic features of these phases were summarised in G Pelzl, S Diele and W Weissflog,1999 [14].The large diversity of LC phases arises due to the reduced symmetry of these molecules, leading to polar order and supramolecular chirality.

The bend in the rigid cores of such liquid crystals leads to a reduction of the rotational disorder of the molecules around their long axes. If segregation of aromatic cores and aliphatic chains is sufficiently strong, the molecular structure facilitates an organization into layers. Since the molecules are closely packed within the smectic layers and additionally, the rotation about their long axes is strongly hindered, the bent directions align parallel in each layer.

2. EXPERIMENTAL

2.1. Materials and methods

The chemical ingredients, viz…, 4-hydroxyl benzoic acid, n- bromo alkyl halides (for n=2,3,4,5,6,7,8) were procured from LOBA chemie, India. Hydrazine hydrate was purchased from Fischer scientific…, India. Sodium acetate, potassium carbonate, Diethyl ether procured from RANKEM, India. Ethanol is procured from CHANGSHU YANGUAN CHEMICAL,Silica gel (60-120 mesh size) for column chromatography was procured from LOBA chemie India. The proposed structure for the intermediate compounds and that of the final compound are confirmed by the H^1 NMR spectra obtained using an Agilent (400mhz) NMR spectrometer, Deuterated chloroform as a solvent is procured from SIGMA ALDRICH, USA and Tetra methyl Silane as internal standard. The following notations denoted the peak types in the spectra:singlet(s), doublet(d), and doublet of doublets (dd), triplet (t), quartet (q) and multiplet (m). Infrared spectra (IR) were using Perkin Elmer spectrometer. The H^1 NMR and IR spectra are used for the confirmation of the molecular structure hydrogen bonding and the purity of the sample. Mass spectra (LC-MS) were obtained using WATER LCMS spectrometer. Elemental analysis was carried out in a Fissions EA 1108 CHN instrument. Differential scanning calorimetry (DSC) thermo grams were obtained using Q 20 TA Instruments, USA. Heating rate was 1^0 C $min^{-1.}$ The LC phases were characterized by their texture studies carried out using an Olympus BH-2 Polarizing Microscope, fitted with Metler FP52 hot stage and a Metler FP% controller , samples were prepared as thin films between a glass slide and a cover slip. Column chromatography was carried out using a silica gel (60-120 mesh) as the stationary phase. Thin layer chromatography (TLC) was carried out on aluminum sheets coated in Merck Kieselgur silica gel 60, eluting with petroleum ether and ethyl acetate

2.2. Synthesis

2.2.1 General procedure for the Synthesis of ethyl 4-hydroxy benzoate

4-hydroxy benzoic acid (10g, 0.072 mol) was dissolved in a 100 ml of ethanol to the solution, added a catalytic amount of concentrated sulphuric acid (2.5 ml) as a dehydrating agent and it was refluxed for 18 hours. The reaction completion was monitored by TLC. The reaction mixture was distilled under reduced pressure and extracted with ethyl acetate. The organic layer was repeatedly washed with sodium bicarbonate to remove the unreacted acid and distilled in vacuum to form a white solid. The obtained solid was dried over calcium chloride and ethanol and recrystallized in ethanol to obtain the titled compound as white solid.

Colour-white solid, M.P-112^{0}C-116^{0}C ^{0}C

Elemental analysis; Calculated- C, 65.05; H, 6.07; O, 28.88 Observed- C-65.5,H-6.1,O-29.1

2.2.2. General procedure for the synthesis of 4-hydroxy benzohydrazides

0.036 mole of 4-hydroxy ethyl benzoate (2) in 60 ml ethanol and 1.4 equivalents of hydrazine hydrate (2.5 mol) was added and the reaction mixture was refluxed for 4-6 hours. The reation completion was monitored by TLC. The reaction mixture was cooled with crushed ice to get a pale pink precipitate and it was filtered by using whatmann filter paper and dried over calcium chloride and recrystallized with ethanol to obtain the titled compound as pale pink solid in 85% yield.

Colour-pale pink solid, yield-85%,M.P-262^{0}C-264^{0}C IR (kbr):cm^{-1} 3191 (alcohol O-H & CO stretching), 1506 (C=C vibrations),1609(C-O stretching),1328 (alcohol O-H stretching),884 (benzene1,4- disubstituted).

Elemental analysis: observed:C-55.1,H-5.01,N-18.5,O-20.9 Calculated:C, 55.26; H, 5.30; N, 18.41; O, 21.03,LC-MS m/z=152.09,153.92

2.2.3. Synthesis of 4-hydroxy benzoyl chloride

0.036 mole of 4-hydroxy benzoic acid (1) and the thionyl chloride (1.2 ml) were refluxed in a sealed tube for 12 hours using DMF as a solvent. The completion of the reaction was monitored by TLC and the reaction mixture was distilled under reduced pressure and extracted with ethyl acetate,washed with bicarbonate solution,dried in sodium sulfate and distilled in reduced pressure to get the crude 4-hydroxy benzoyl chloride (4) with 70% yield.The obtained crude was more reactive and hence used directly for further reaction.

2.2.4. Synthesis of (E)-4-hydroxy-N-(4-hydroxybenzylidene)benzohydrazide

4-hydroxy benzohydrazide (5g, 0.032mol) (3) and 4-hydroxy benzaldehyde (4g, 0.032) were refluxed in absolute alcohol (90 ml) for 4-6 hours. The reaction completion was monitored by TLC(ethyl acetate and petroleum ether,1:6) and the reaction mixture was distilled under reduced pressure, extracted with ethyl acetate and washed with 5% HCl and 20% sodium metabisulfite solution. The organic layer was again distilled under reduced pressure and recrystallized in ethanol to obtain the compound as yellow solid (5) in 75% yield.

IR (kbr) cm^{-1}:3435 υ (O-H), 3303 υ (N-H),1653 υ (C=O), 1608 υ (C=N) ^{1}H NMR (400 mhz, cdcl$_3$): δ 6.92-6.94, dd, J_1=2.8 Hz J_2=6.8 Hz,4H,arh; δ 6.97, s,1H,OH; δ 7.56-7.58, m,4H,arh; δ 7.71, s,1H,OH.

9 m/z=256.09,256.12 Elemental analysis observed; C, 65.52; H, 4.79; N, 10.99; O, 18.53.calculated; C, 65.62; H, 4.72; N, 10.93; O, 18.73.

2.2.5. Synthesis of 4- hydroxy-N'-(4-hydroxybenzoyl)benzohydrazide

The synthesized 4-hydroxy benzoyl chloride (3.5g, 0.022mol) (4) being so reactive was coupled with the 4- hydroxy benzohydrazide (2.8g, 0.022 mol). An equimolar mixture of the two reactants were dissolved in an absolute ethanol(75ml) and refluxed for 10 hours and the completeness of the reaction was monitored by TLC. The reaction mixture was cooled with crushed ice to form a pale yellow coloured precipitate and the obtained precipitate was filtered, dried and extracted with ethyl acetate or diethyl ether. The organic layer was again washed with the 5% HCl to remove the excess hydrazide and distilled over reduced pressure to obtain the hydrazone (5) as a pale yellow solid.

Colour-yellow solid, yield:75%,M.P:292^{0}C -295^{0}C , IR (kbr) 1610 cm^{-1}, C=N stretching 3316 cm^{-1} and 3274 cm^{-1}, ^{1}H NMR (400 mhz, cdcl$_3$): δ 7.01, d, *J*=8.8 Hz,4H,arh; δ 7.77-7.80, m,4H,arh; δ 9.82, s,2H,OH.m/z: 271.08 ,273.18, 274.29 Elemental Analysis: observed;C, 61.86; H, 4.54; N, 10.39; O, 23.41.calculated; C, 61.76; H, 4.44; N, 10.29; O, 23.51.

2.2.6. Synthesis of 4,4'-(1,3,4-oxadiazole-2,5-diyl)diphenol under solvent free conditions

The synthesized hydrazones (5) were subjected to thermal reaction under pressure (at 100^{0}C -120 ^{0}C) in a closed system (autoclave reactions) for cyclization to form 1,3,4-oxadiazoles. The reaction mass was cooled to release the pressure and then extracted with ethyl acetate and distilled in reduced pressure to form a

brown coloured gummy solid. The obtained crude was triturated in a mixture of DCM and Chloroform (10:1 proportion) by repeated trituration get the solid brown coloured product (6).

^{1}H NMR (400 mHz, $CDCl_3$):δ 4.94, br,2H,OH; δ 6.93-6.98, m,2H,arh; δ 7.35-7.41, m,2H,arh; δ 7.91, d, *J*=8.4 Hz,2H,arh; δ 8.02-8.05, dd, J_1=2.4 Hz J_2=8.8 Hz,2H,arh. M/z: 253.97, 255.27, 256.18 Elemental Analysis:observed; C, 65.94; H, 3.86; N, 11.22; O, 18.78 calculated; C, 66.14; H, 3.96; N, 11.02; O,18.88.

2.2.7. Alternative route for the synthesis of oxadiazoles

4-Hydroxy benzohydrazide was coupled with 4-hydroxy benzoic acid under reflux condition by using phosphorous oxychloride as a cyclizing agent. The reaction mixture was refluxed for 4 hours to form a yellow solid. The solid reaction mass was slowly quenched in ice cold water and neutralized with saturated sodium bicarbonate solution to obtain a pale yellow precipitate. The obtained precipitate was separated by filtration and washed with excess water and dried to obtain a pale yellow solid. The obtained solid was further recrystallized in ethanol to furnish the titled compound as yellow solid in 75% yield and then it is given for analysis.

^{1}H NMR (400 mHz, $CDCl_3$): δ 4.94, Br,2H,OH; δ 6.93-6.98, m,2H,arh; δ 7.35-7.41, m,2H,arh; δ 7.91, d, *J*=8.4 Hz,2H,ArH;δ 8.02-8.05, dd, J_1=2.4 Hz J_2=8.8 Hz,2H,arh. M/z: 253.97, 255.27, 256.18 Elemental Analysis:observed; C, 65.94; H, 3.86; N, 11.22; O, 18.78 calculated; C, 66.14; H, 3.96; N, 11.02; O, 18.88.

2.2.8. Synthesis of 1,3,4-oxadiazoles by chloramin-T

The synthesized compound (6) was refluxed with equivalent amount of the Chloramin-T as an oxidative cyclizing agent in ethanol for 4-6 hours. The reaction completion was monitored by TLC and the reaction mixture was distilled in reduced pressure to obtain a brown coloured semisolid. The obtained solid was then extracted with ethyl acetate and washed with water to remove the unreacted Chloramin-T and the organic layer was distilled to obtain the crude product. The obtained crude was further purified by flash column chromatography and eluted in varying polarities to obtain the required oxadiazole. The obtained product was further dried and recrystalized in ethanol to procure the extra pure oxadiazole.

^{1}H NMR (400 mHz, $CDCl_3$): δ 4.94, Br,2H,OH; δ 6.93-6.98, m,2H,arh; δ 7.35-7.41, m,2H,arh; δ 7.91, d, *J*=8.4 Hz,2H,arh; δ 8.02-8.05, dd, J_1=2.4 Hz J_2=8.8 Hz,2H,arh. M/z: 253.97, 255.27, 256.18 Elemental Analysis:observed; C, 65.94; H, 3.86; N, 11.22; O, 18.78 calculated; C, 66.14; H, 3.96; N, 11.02; O, 18.88

2.2.9. O-alkylation of synthesized Oxadiazoles

The hydroxy substituted oxdiazoles were O-alkylated with the different alkyl bromides $C_nH_{2n+1}Br$, where n=2,3,4,5,6,7,8 to form a series of O-alkylated oxadiazole derivatives. The reaction was carried out by using potassium carbonate as base and the alkyl bromides were taken in a 1:2 ratio, in DMF as a solvent. The reaction was stirred for 4-6 hours at room temperature and monitored by TLC. At the completeness of the reaction, the reaction mass was taken out and removed the DMF by adding excess water, extracted with ethyl acetate and distilled in reduced pressure. The obtained solid was recrystallized in methanol to obtain the required products and was further given for analysis for confirmation.

2.2.10. Synthesis of 2,5-bis(4-ethoxyphenyl)-1,3,4-oxadiazole

The hydroxy substituted oxdiazoles were O-alkylated with the different alkyl bromides 8(a-g) $C_nH_{2n+1}Br$, where n=2,3,4,5,6,7,8 to form a series of O-alkylated oxadiazole derivatives. The reactions were carried out by using potassium carbonate as base and the alkyl bromides were taken in a 1:2 ratio, in DMF as a solvent. The reaction was stirred for 4-6 hours at room temperature and monitored by TLC. At the completeness of the reaction, the reaction mass was taken out and removed the DMF by adding excess of water, extracted with ethyl acetate and distilled under reduced pressure. The obtained solid was recrystallized in methanol to obtain the required products and was further given for analysis for confirmation.

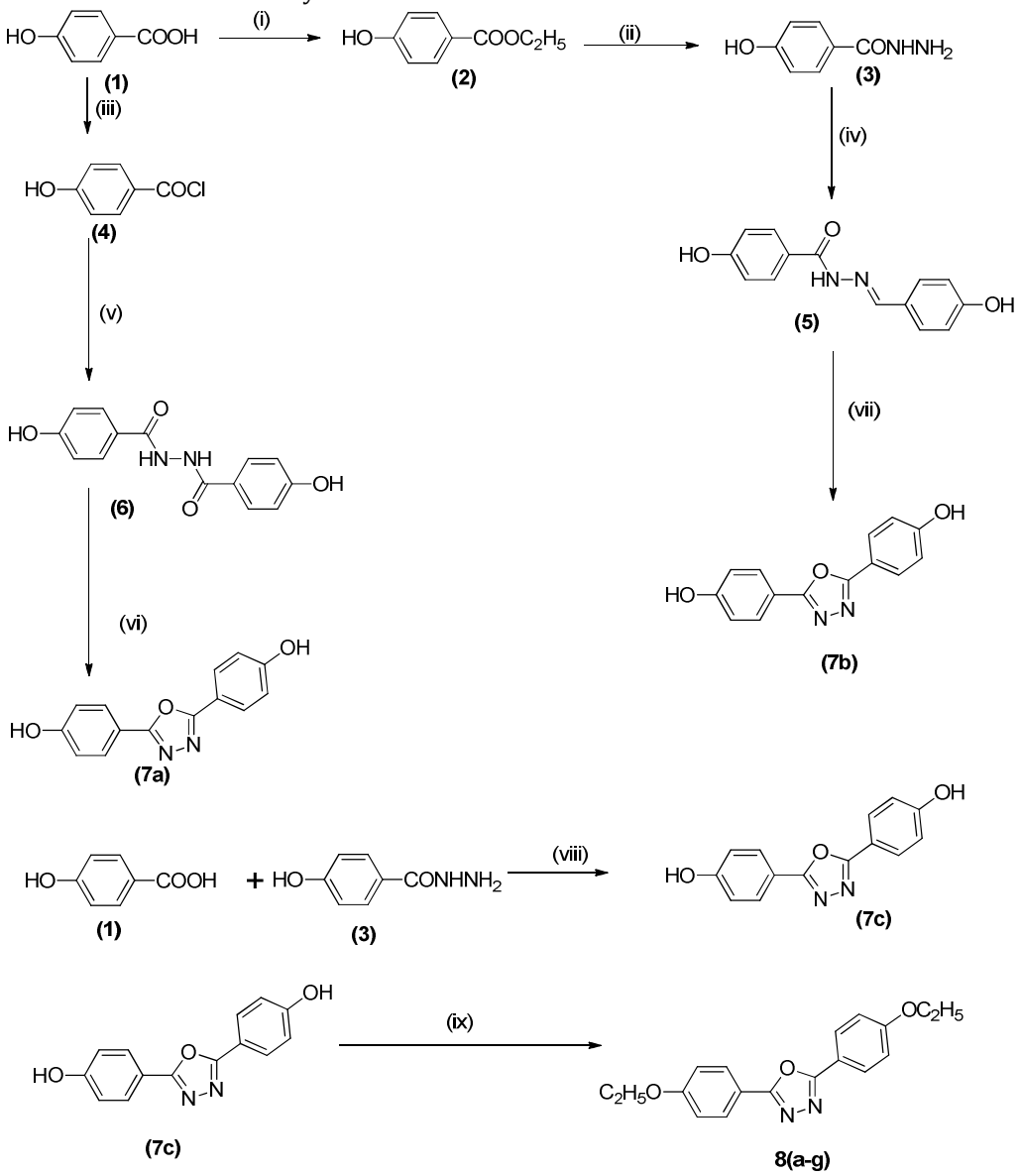
3. RESULT AND DISCUSSION

3.1. Liquid crystalline property

The thermal behaviours of all the final products 8(a-g) were investigated by Polarising Optical Microscopy (POM) and Differential Scanning Calorimetry (DSC). The compound 8f was showed the very good phase transitions at 84.96°C and 96.45°C. The compound 8g was showed the phase transitions at 90.46° and 96.70°C. The remaining compounds 8(a-e) were not exhibiting any liquid crystal behaviours and they are isotropic, there is no any phase transitions were observed.

The endothermic and exothermic peak temperatures obtained in DSC thermograms due to phase transitions were in reasonable agreement with the POM observations. The observed colour of the textures varies with the

change of temperature as it is the necessary characteristic for the cholesteric phase. It is worthy to note that all the derivatives of the oxadiazoles displayed a very wide temperature range during the heating process; however, they all decomposed before the appearance of isotropic liquid which made it impossible to further investigate the liquid crystalline behaviours upon cooling. When the terminal alkoxy chain became longer,the analogous compounds displayed both nematic and smectic A phases enantiotropically, identified respectively through the comparison of the observed textures it was found that the stability of the smectic phase increased with the elongation of the terminal alkoxy chains effect of the alkoxy chains on mesomorphic behavior is common in the calamitic mesogens.



Scheme - 1: Reaction scheme for the synthesis of 1,3,4 oxadiazole derivatives

3.2. Reaction Conditions

(i) Obsollute ethanol/conc.Sulphuric acid,reflux for 18 hours

(ii) Hydrazine Hydrate, Ethanol,reflux for 8 hours

(iii) Thionyl chloride,DMF, reflux for 18 hours

(iv) p-hydrxy benzaldehyde,ethanol,reflux for 4 hours.

(v) 4-hydroxy benzohydrazide, ethanol reflux for 8 hours

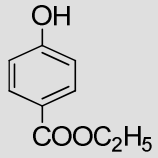
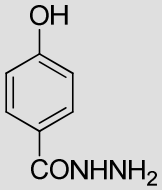
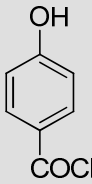
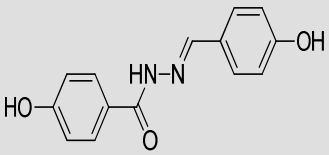
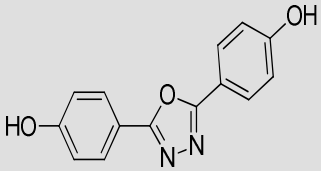
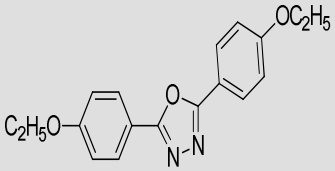
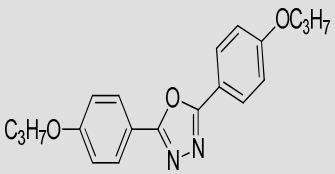
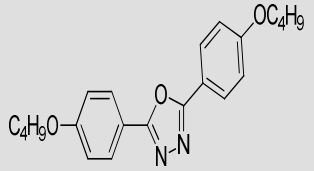
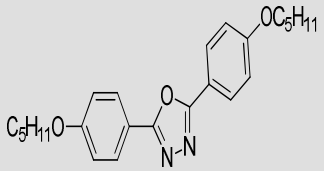
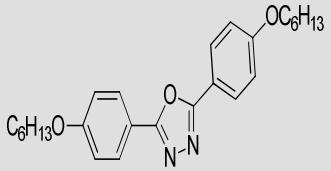
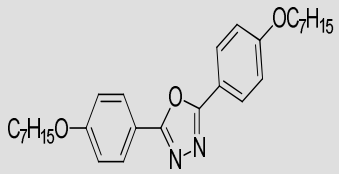
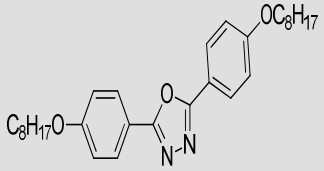
(vi) Autoclave reaction under closed vessel for 8 hours

(vii) Chloramin-T, Ethanol refux for 5 hours

(viii) $POCl_3$ Refluxed for 6 hours

(ix) Alkyl bromides C_nH_{2n+}-Br, where n= 2,3,4,5,6,7,8(2equivalents), Potassium carbonate, DMF at room temperature.

Table - 1: List of the synthesized compounds

Compound No	Structure	Yield
2		85%
3		85%
4		70%
5		75%
7		75%
7a,7b,7C		70%
8a		85%
8b		85%
8c		85%
8d		85%
8e		85%
8f		85%
8g		85%

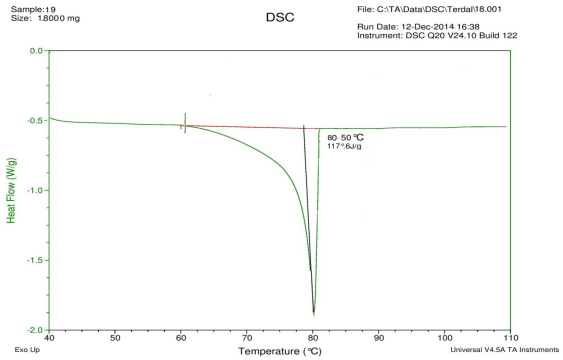


Figure – 1: DSC heating traces of compounds at 1°C/min for the compound 8c.

Table - 2: DSC Thermograms for the Synthesized Compounds

Compound	Phase Transitions	Heat flow (w/g)	J/g
8a	74.10°C	-	171.7
8b	80.50°C	-	1.176
8c	41.11°C	-0.3293	
	95.09°C	-0.3769	0.7847
	98.57°C	-0.415	
8d	40.55°C	-0.4282	0.4786

	41.97°C	-0.4496	
	94.91°C	-0.3883	1.031
	98.54°C	-0.4240	
8e	84.96°C	-0.3361	1.187
	89.75°C	-0.4122	
	96.45°C	-0.4003	0.1912
	98.59°C	-0.4078	
8f	90.46°C	-0.3112	
	96.70°C	-0.3086	0.9117
	99.61°C	-0.3555	
8g	96.08°C	-0.181	1.774
	99.47°C	-0.2475	

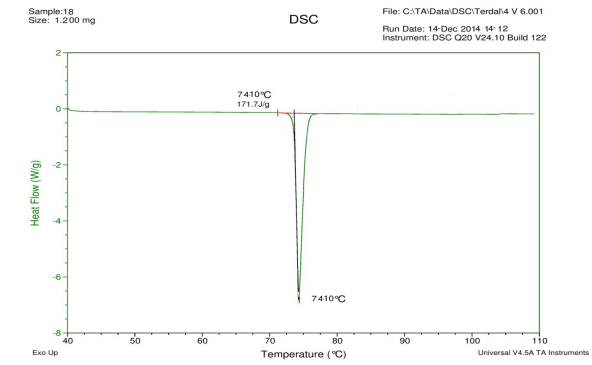


Figure - 2: DSC heating traces of compounds at 1°C/min for the compound 8d.

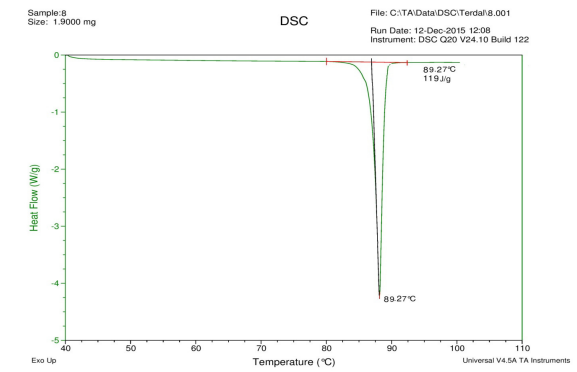


Figure - 3: DSC heating traces of compounds at 1°C/min for the compound 8e.

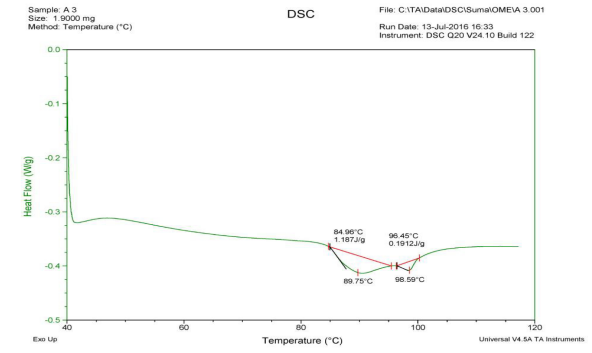


Figure - 4: DSC heating traces of compounds at 1°C/min for the compound 8f.

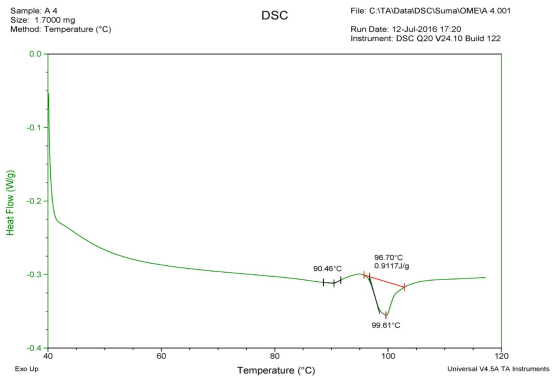


Figure - 5: DSC heating traces of compounds at 1°C/min for the compound 8g.

4. CONCLUSION

We have reported the synthesis and mesomorphism of seven new compounds derived from 1,3,4-oxadiazole fluorophore. The compounds 8(a-e) with a terminal cholesteryl segment exhibited a chiral nematic mesophase with very wide temperature range while the compounds (8f and 8g) with a terminal heptyl and octyl group displayed enantiotropic nematic and smectic A mesophases with relatively narrow temperature ranges. All the target compounds displayed a strong blue fluorescence emission with good quantum yields in chloroform solution. The relationship between the structures and properties were discussed briefly in the context of the terminal groups and the length of alkoxy chains. The results showed that the terminal groups affected the liquid crystalline behaviour greatly, but had little effect on the photoluminescent property.

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