

Synthesis of 1,2-Bis[n-Alkyloxy) Benzal Hydrazones from Thiocarbohydrazide and 4-(Alkyloxy) Benzaldehyde and their Liquid Crystalline Properties

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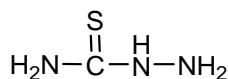
Abstract

1,2-bis[(n-Alkyloxy)benzal hydrazones were synthesized by the condensation reaction between thiocarbohydrazide and 4-(alkyloxy) benzaldehydes. All the synthesized compounds have been characterized by ¹H-NMR and IR spectra. The thermal behavior of the synthesized hydrazones was examined under polarizing microscope fitted with a hot and cold stage to observe the liquid crystalline properties .The liquid crystalline property was also examined by differential scanning calorimetry (DSC).

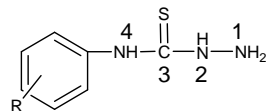
Keywords: Thiocarbohydrazide, hydrazone, Polarizing microscope, Differential scanning calorimetry (DSC).

Introduction

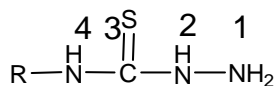
Thiosemicarbazides, thiosemicarbazone and thiocarbohydrazones derivatives have occupied a unique position in heterocyclic chemistry due to their anti-tubercular, antibacterial and biological activity.^[1] Thiosemicarbazide and their derivatives have been marked as biologically and pharmacologically active product. The substituted thiosemicarbazides also possess different activities like anti-bacterial^[2], anti-tubercular^[3], anti-fungal^[4]. An unexpected by product (thiocarbohydrazide) with good yield formed during the synthesis of 4-arylsubstituted thiosemicarbazide from substituted aniline.



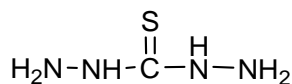
Thiosemicarbazide



4-Aryl substituted thiosemicarbazide



Alkyl substituted thiosemicarbazide

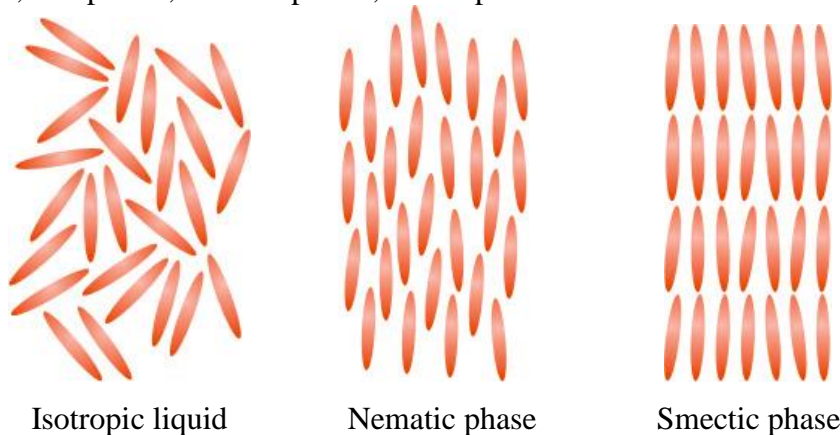


Thiocarbohydrazide

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Thiocarbohydrazide reacts with 4-(alkyloxy) benzaldehyde to produce 1,2-bis(n-alkyloxy) banzalhydrazones having a rigid part and a flexible part. So, these types of compounds are expected to show liquid crystalline property.

Liquid crystals are compounds that exhibits features of both the solid and the fluid phase. Liquid crystals have the ordering properties of solids but they flow like liquids. Liquid crystals can be classified into thermotropic, lyotropic and metallotropic Liquid crystal. Thermotropic liquid crystal shows different type of phases such as nematic phase, smectic phase ,chiral phase ,blue phase , discotic phase ,bowlic phase .^{[5][6]}



In above figure, isotropic liquid is oriented arbitrarily, but LC nematic and smectic phase are oriented orderly but flows like liquid .

Liquid crystals have found use in different areas of science and engineering as well as device technology e.g. liquid crystal displays, liquid crystal tunable filters , liquid crystal thermometers.^[7] A special characteristic of liquid crystal materials is that it changes color when stretched or stressed. Thus, liquid crystal sheets are often used in industry to look for hot spots, map heat flow, measure stress distribution patterns, and so on. Liquid crystal in fluid form is used to detect electrically generated hot spots for failure analysis in the semiconductor industry.^[8] Polymer Dispersed Liquid Crystal (PDLC) sheets and rolls are available as adhesive backed Smart film which can be applied to windows and electrically switched between transparent and opaque to provide privacy .

A new and promising application using liquid crystals is the liquid crystal semiconductor. Liquid crystals are organic molecules similar to polymers. In polymers containing conjugated systems (alternating single and double bond) the creation of a higher and lower pi-bond leads to the creation of a band gap similar to semiconductors. The use of such a liquid crystal in a device similar to the Grätzel cell can lead to new types of solar cells.

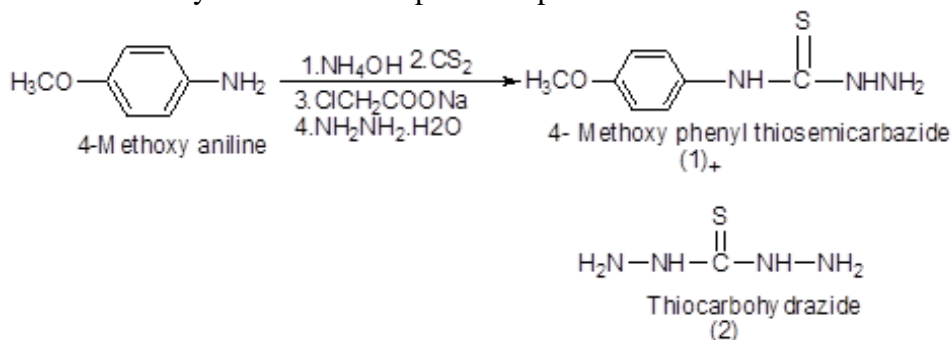
Literature survey on the diverse structure of liquid crystalline compounds has led to assume that thiosemicarbazones having long chain hydrocarbon should show properties of liquid crystal.

Synthesis

Synthesis of 4-(4'-methoxy phenyl)thiosemicarbazide

An ethanol solution of 4-methoxyaniline (1.20g, 9.756 mmol) was treated with ammonium hydroxide (4 mL, 25% solution) and carbon disulfide (3 cm³, 20 mmol). The resultant mixture was stirred for half an hour and left at room temperature for one hour. Sodium chloroacetate (1.13 g (9.756 mmol)) was added to this solution. Then hydrazine hydrate (8 mL) was finally added, immediate precipitation took place.

Precipitate collected from the reaction mixture by filtration. This precipitate was a by product compound (2) characterized by IR and ¹NMR spectroscopic method. The filtrate was kept overnight to yield a solid which on washing with methanol afforded the pure compound (1) characterized by IR and ¹NMR spectroscopic method.



Two products were obtained from the above reaction. The yield of product (1) is 9% , melting point 154°C ,the product was found pure on TLC examination (Pet ether : Ethylacetate = 1:2) ; R_f 0.52.

IR (KBr) Spectrum (ν_{max} , cm^{-1}) of compound (1)

3206.79 and 3168.22 (m, ν_{NH} for NH_2); 3374.31 (s, ν_{NH} for NH ,N-4); 3320.60(s, ν_{NH} for NH ,N-2) ; 3013.90 (w, ν_{CH} aromatic); 2964 (w, ν_{CH} aliphatic); 1638 (sh, $\nu_{C=C}$ aromatic); 1528.55 and 1511.29 (m, δ_{NH}); 1244.14 (w, ν_{C-N}); 1287.54 (s, $\nu_{C=S}$); 832.32 (s,para substituted benzene ring).

1H -NMR (DMSO- d_6 , 400 MHz) of compound (1)

δ (ppm): 9.498 (s, 1H,NH); 8.949 (s, 1H,NH); 6.862 (d, $J_o=10$ Hz, 2H, aromatic); 7.432 (d, $J_o= 10$ Hz, 2H, aromatic); 4.713 (br, 2H, NH_2); 3.738 (s, 3H).

The yield of product (2) is 79% , melting point 170°C ,the product was found pure on TLC examination (Pet ether : Ethylacetate = 1:3) ; R_f 0.35 .

IR (KBr) Spectrum (ν_{max},cm^{-1}) of compound (2)

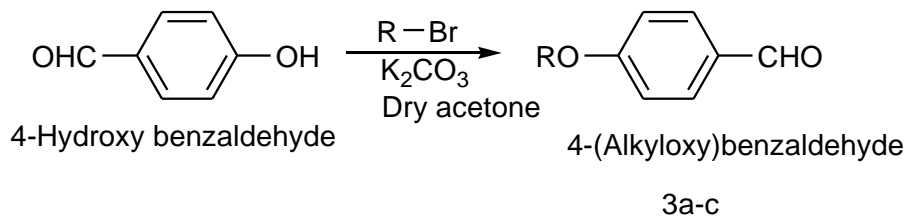
3307.10,3274.31 and 3208.72 (m, ν_{NH} for NH and NH_2); 1653,1512 and 1490 (m, ν_{NH}); 1247.03 (w, ν_{C-N}); 1287.54 (s, $\nu_{C=S}$).

1H -NMR (DMSO- d_6 , 400 MHz) of compound (2)

δ (ppm): 8.662 (br, 2H, NH); 4.477 (br, 4H, NH_2).

Synthesis of 4-alkyloxy benzaldehyde :

4-Hydroxybenzaldehyde (0.05 mol) was treated with anhydrous K_2CO_3 (0.075 mol) and n-alkyl bromide (0.05 mol) in acetone (35-50 mL). The reaction mixture was refluxed for 8-12 hours on water bath. After cooling to room temperature the reaction mixture was filtered to remove the solids. Solvent was evaporated by rotary vacuum evaporator from the filtrate to afford an oil containing some unreacted 4-hydroxy benzaldehyde. This oil was redissolved in CH_2Cl_2 and extracted the solution with 5% aqueous solution of NaOH several times for the removal of the residual unreacted 4-hydroxy benzaldehyde which eventually afforded the expected compound in the pure form.



R= C₆H₁₃ (a), C₈H₁₇(b), C₁₀H₂₁(c).

Table-1: Physical data of synthesized compounds

Compound	% of yield	Boiling point(b.p.)/Melting point(m.p.) (°C)	Color	Solubility	R _f (pet-ether :ethylacetate=3:1)
3a	73	100-101(b.p.)	Golden	CHCl ₃	0.82
3b	59	140-142(b.p.)	Golden	CHCl ₃	0.92
3c	63	172-173(b.p.)	Golden	CHCl ₃	0.88

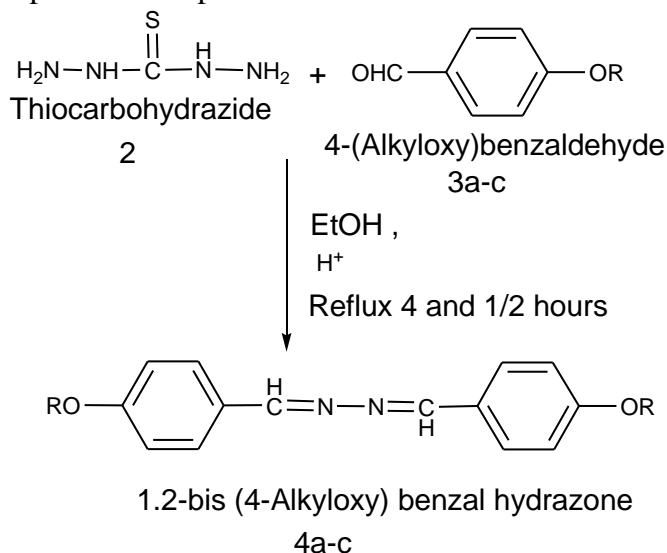
Table-2: IR (KBr) and ¹H-NMR spectral data of synthesized compounds

Compound	IR (KBr) Spectrum (ν _{max} , cm ⁻¹)	¹ H-NMR (CDCl ₃ , 400 MHz)
3a	2851.88 and 2734.21 (w, ν _{CH} aliphatic, CH ₃); 2931.93 (s, ν _{CH} aliphatic, CH ₂); 3013.90 (w, ν _{CH} aromatic); 1699.36 (sh, ν _{C=O} aldehyde); 1601.95 (s, ν _{C=C} aromatic); 1258.61(s, ν _{C-O}); 1311.65 and 1022.32 (m, ν _{CH} in- and oop of aliphatic C-H); 832.32 (s, para disubstituted benzene ring)	9.875 (s, 1H); 6.991 (d, J= 8.8, Hz, 2H); 7.824 (d, J= 8.4 Hz, 2H); 4.039 (m, 2H, OCH ₂); 1.795 (m, 2H, CH ₂); 1.463 (m, 2H, CH ₂); 1.368 (m, 4H, CH ₂); 0.919 (t, 3H, CH ₃).
3b	2851.88 and 2734.21 (w, ν _{CH} aliphatic, CH ₃); 2931.93 (s, ν _{CH} aliphatic, CH ₂); 3013.90 (w, ν _{CH} aromatic); 1699.36 (sh, ν _{C=O} aldehyde); 1601.95 (s, ν _{C=C} aromatic); 1258.61(s, ν _{C-O}); 1311.65 and 1022.32 (m, ν _{CH} in- and oop of aliphatic C-H); 832.32 (s, para	9.859 (s, 1H); 6.978 (d, J= 8.8, Hz, 2H); 7.810 (d, J= 8.8 Hz, 2H); 4.023 (m, 2H, OCH ₂); 1.801 (m, 2H, CH ₂); 1.765 (m, 2H, CH ₂); 1.445 (m, 4H, CH ₂); 1.356 (m, 8H, CH ₂); 0.909 (t, 3H,

	disubstituted benzene ring) .	CH ₃).
3c	2848.02 and 2734.31 (w, ν_{CH} aliphatic, CH ₃); 2926.14 (s, ν_{CH} aliphatic, CH ₂); 3013.90 (w, ν_{CH} aromatic); 1695.50 (sh, $\nu_{\text{C=O}}$ aldehyde); 1603.88 (s, $\nu_{\text{C=C}}$ aromatic); 1259.57(s, $\nu_{\text{C-O}}$); 1311.65 and 1027.14 (m, ν_{CH} in- and oop of aliphatic C-H); 833.28 (s, para disubstituted benzene ring) .	9.891 (s, 1H); 7.003 (d, J= 8.4, Hz, 2H); 7.838 (d, J= 8.4 Hz, 2H); 4.052 (m, 2H, OCH ₂); 1.829 (m, 2H, CH ₂); 1.462 (m, 2H, CH ₂); 1.295 (m, 12H, CH ₂); 0.909 (t, 3H, CH ₃).

Synthesis of 1.2-Bis 4-(alkyloxy) bezal hydrazone from thiocarbohydraide and n-alkyloxybenzaldehydes:

To a solution of thiocarbohydraide (0.01 mol) in ethanol containing two drop of Conc. HCl, n-(akyloxy) benzaldehyde (0.01 mol) was added and the mixture refluxed for four and half hour on an oil bath. On cooling a precipitate came out of the reaction mixture. It was filtered to give a crude product. This crude product was recrystallized from ethanol to yield the expected compound in the pure form.



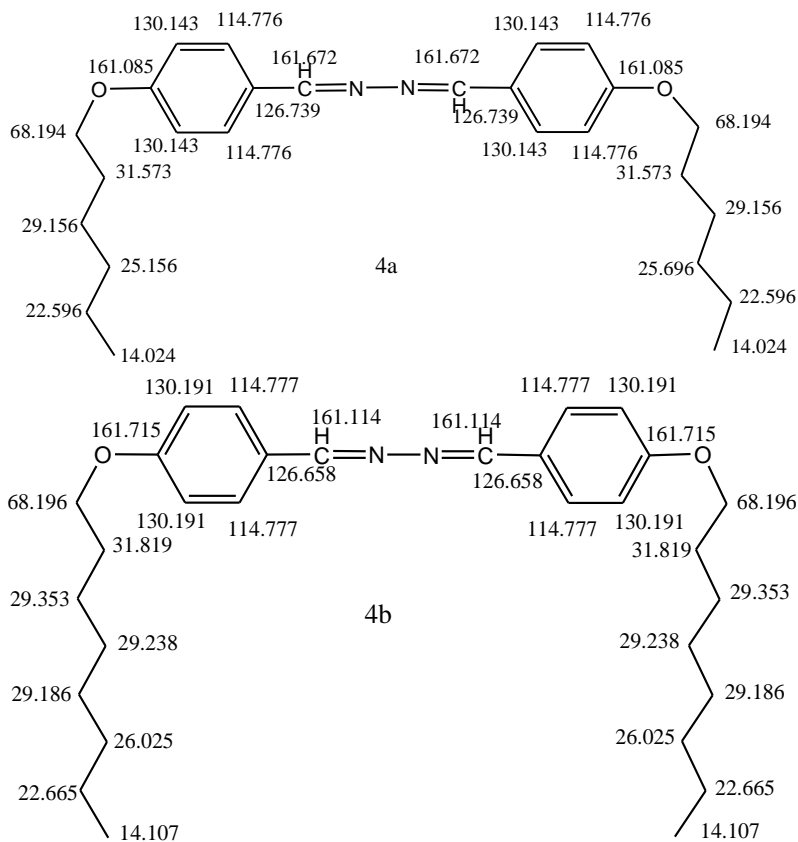
R= C₆H₁₃ (a), C₈H₁₇(b), C₁₀H₂₁(c).

Table-3: Physical data of synthesized compounds

Compound	% of yield	Melting point ($^{\circ}\text{C}$)	Color	Solubility	R_f (pet-ether :ethylacetate=3:1)
4a	75	152-153	Golden rod	CHCl_3	0.87
4b	66	131-132	Yellow	CHCl_3	0.83
4c	51	123-124	Khaki	CHCl_3	0.80

Table-4: IR (KBr) and $^1\text{H-NMR}$ spectral data of synthesized compounds

Compound	IR (KBr) Spectrum (ν_{max} , cm^{-1})	$^1\text{H-NMR}$ (CDCl_3 , 400 MHz)
4a	3012 (w, ν_{CH} aromatic); 2948.32, 2863.45(w, ν_{CH} aliphatic C-H); 1620.27, 1605.81 (m, $\nu_{\text{C}=\text{C}}$ aromatic); 1573.02 (sh, $\nu_{\text{C}=\text{N}}$); 1301 (w, $\nu_{\text{C}-\text{N}}$); 1248 (s, $\nu_{\text{C}-\text{O}}$); 1000.13 and 961.56 (w, ν_{CH} in- and out-of-plane of aliphatic C-H); 800.49 (s, para disubstituted benzene ring).	6.969 (d, $J_o = 8$, 2H, aromatic); 7.784 (d, $J_o = 8$, 2H, aromatic); 8.624 (s, 1H), 4.038 (t, 2H, OCH_2); 1.845 (m, 2H); 1.484 (m, 2H); 1.369 (m, 4H); 0.950 (t, 3H).
4b	3012 (w, ν_{CH} aromatic); 2953.14, 2940.61 and 2923.25, 2866.34, 2848.98 (w, ν_{CH} aliphatic C-H); 1620.27, 1605.81 (m, $\nu_{\text{C}=\text{C}}$ aromatic); 1573.02 (sh, $\nu_{\text{C}=\text{N}}$); 1301 (w, $\nu_{\text{C}-\text{N}}$); 1248 (s, $\nu_{\text{C}-\text{O}}$); 1000.13 and 961.56 (w, ν_{CH} in- and out-of-plane of aliphatic C-H); 800.49 (s, para disubstituted benzene ring).	6.971 (d, $J_o = 8.8$, 2H, aromatic); 7.796 (d, $J_o = 8.8$, 2H, aromatic); 8.640 (s, 1H), 4.031 (t, 2H, OCH_2); 1.807 (m, 2H); 1.471 (m, 2H,); 1.344(m, 8H); 0.917 (t, 3H).
4c	3013.90 (w, ν_{CH} aromatic); 2955.07, 2936.75 and 2923.25, 2919.39, 2873.09 (w, ν_{CH} aliphatic C-H); 1606.77 (m, $\nu_{\text{C}=\text{C}}$ aromatic); 1510.33 (sh, $\nu_{\text{C}=\text{N}}$); 1473.68 (w, $\nu_{\text{C}-\text{N}}$); 1306.83 (s, $\nu_{\text{C}-\text{O}}$); 1173.73 and 960.59(w, ν_{CH} in- and out-of-plane of aliphatic C-H); 800.04 (s, para disubstituted benzene ring).	6.979 (d, $J_o = 8$, 2H, aromatic); 7.839 (d, $J_o = 8$, 2H, aromatic); 8.640 (s, 1H), 4.031 (t, 2H, OCH_2); 1.828 (m, 2H); 1.488 (m, 2H); 1.303 (m, 12H); 0.909 (t, 3H).

^{13}C -NMR (CDCl₃, 400 MHz):**Mesogenic behavior of synthesized compounds**

The synthesized compounds were examined for their liquid crystallinity under polarizing microscope fitted with a cold and hot stage and also by differential scanning calorimetry (DSC). The transition temperatures for the compounds are presented below in tabular form.

Table: 5

Compound No.	Alkyloxy chain	Phase transition temperatures $^{\circ}\text{C}$	Liquid Crystal phase
4a	C ₆	$\text{K} \rightleftharpoons 131.81 \rightleftharpoons \text{LC} \rightleftharpoons 153.68 \rightleftharpoons \text{IL}$	LC

		116.09	147.21	
4b	C ₈	98.82 K \rightleftharpoons LC	132.07 LC \rightleftharpoons IL	LC
		54.18	121.03	
4c	C ₁₀	84.63 K \rightleftharpoons LC	124.32 LC \rightleftharpoons IL	LC
		62.86	124.26	

Complexes are abbreviated as:

K = Crystal, IL = Isotropic liquid, LC = liquid crystal phase

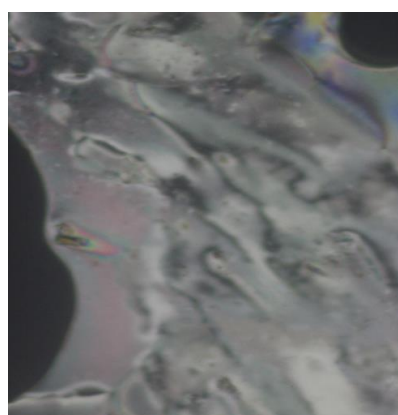
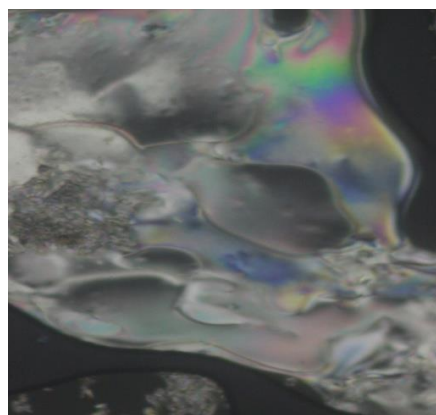
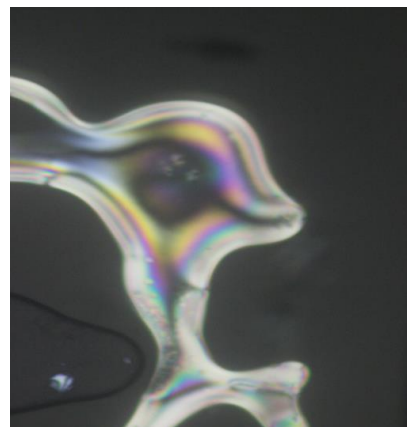
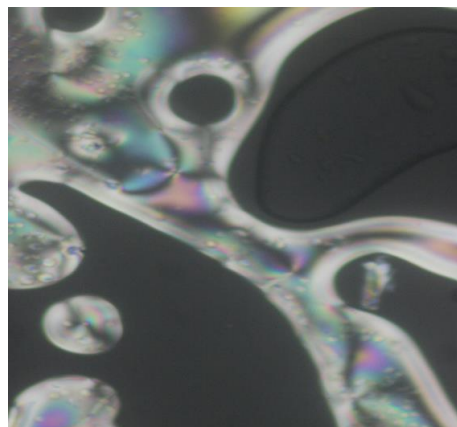


Figure 1: Optical texture for the compound (**4a**) as seen under polarizing microscope at 126°C on heating.



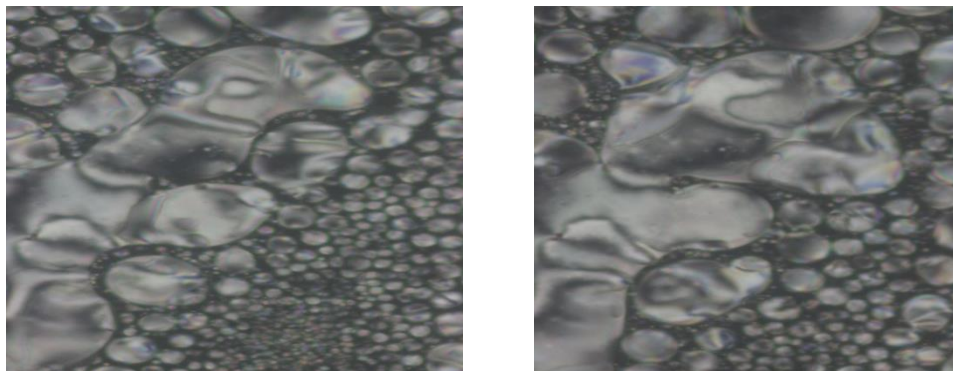


Figure 2: Optical texture for the compound (4a) as seen under polarizing microscope at 147.21°C on cooling.

DSC analysis of the synthesized compounds

DSC analysis of the compound (4a):

DSC analysis of the compound (4a) supports the microscopic observation. In heating cycle it showed exothermic peak at 131.81°C ($\Delta H = -136.58 \text{ J/g}$) and 153.68°C ($\Delta H = -3.18 \text{ J/g}$). If these data compared with the microscopic observation, the peak at 131.81°C may be assigned to crystal to LC transition while the peak at 153.68°C may be assigned to LC to IL transition. In the cooling cycle the DSC thermogram showed an endothermic peak at 147.21°C which corresponds to liquid to LC phase transition. Further cooling up to room temperature showed a peak at 116.09°C for the solidification of the compound.

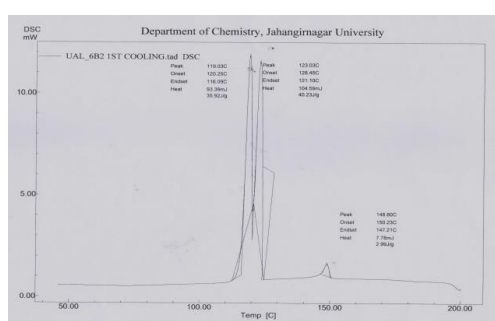
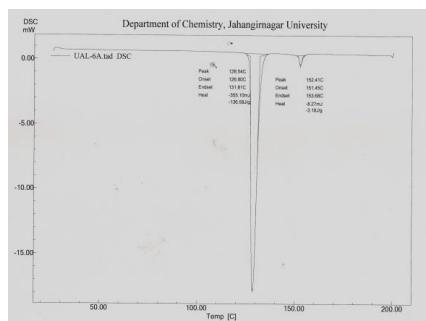


Figure 3: DSC curve (4a) during heating **Figure 4:** DSC curve (4a) during cooling

DSC analysis of the (4b) compound:

DSC analysis of the compound (4b) supports the microscopic observation. In heating cycle it showed exothermic peak at 96.82°C ($\Delta H=-60.96\text{J/g}$) and 132.07°C ($\Delta H=-85.72\text{J/g}$). If these data compared with the microscopic observation, the peak at 117.50°C may be assigned to crystal to LC transition while the peak at 132.07°C may be assigned to LC to IL transition. In the cooling cycle the DSC thermogram showed an endothermic peak at 121.03°C which corresponds to liquid to LC phase transition. Further cooling upto room temperature showed a peak at 54.18°C for the solidification of the compound.

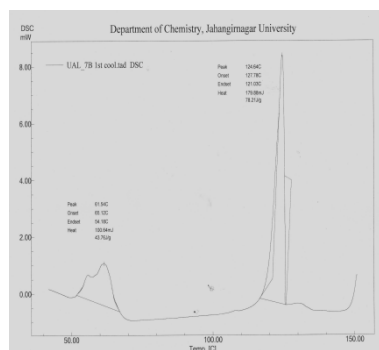
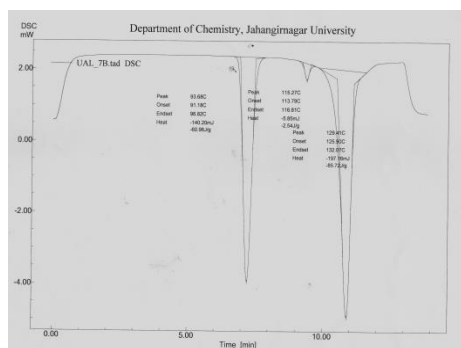


Figure 5: DSC curve (4b) during heating **Figure 6:** DSC curve (4b) during cooling

DSC analysis of the (4c) compound:

DSC analysis of the compound (4c) supports the microscopic observation. In heating cycle it showed exothermic peak at 84.63°C ($\Delta H=-72.33\text{J/g}$) and 124.32°C ($\Delta H=-82.28\text{J/g}$). If these data compared with the microscopic observation, the peak at 84.63°C may be assigned to crystal to LC transition while the peak at 124.32°C may be assigned to LC to IL transition. In the cooling cycle the DSC thermogram showed an endothermic peak at 124.26°C which corresponds to liquid to LC phase transition. Further cooling up to room temperature showed a peak at 62.8°C for the solidification of the compound.

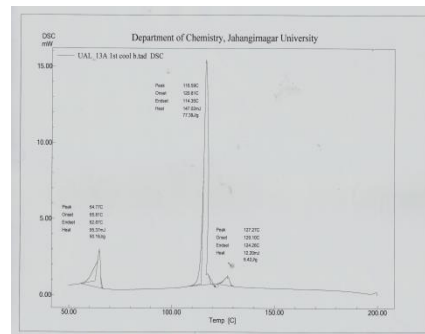
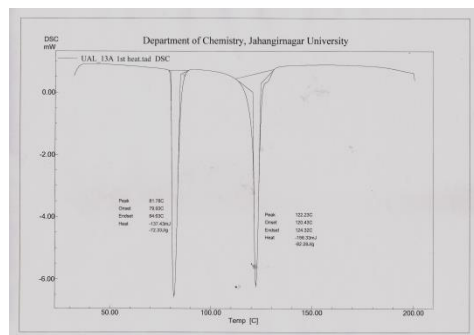


Figure 7: DSC curve(4c)during heating **Figure 8:** DSC curve(4c)during cooling

Conclusion

The synthesized compounds showed nematic liquid crystal phase.

Acknowledgement

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