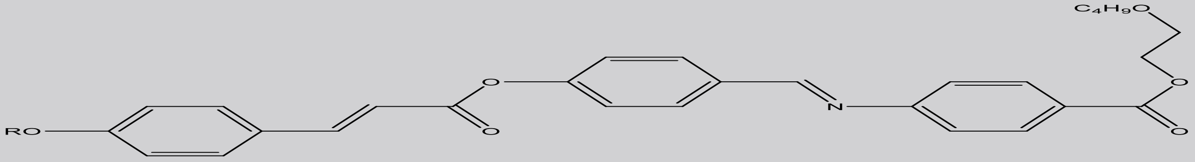
Journal of Complementary Medicine Research, ISSN: 2146-8397 Vol. 14, No. 1, 2023 (pp. 169-185)

RESEARCH ARTICLE WWW.JOCMR.COM

Mesogenic Homologous Series of Alkoxy Cinnamaldehyde with aminobutoxy Terminal Tail

[a]Neel. B. Shah, [a]Ashwin Barasiya, [b]H N Patel,[c]Tarun M. Patel
[a]Department of Chemistry, Surendranagar University,[b]Shree Maneklal M. Patel Institute of Sciences & Research Sector 15/23, Kadi Sarva Vishwavidhyalaya, Gandhinagar, India . [c] Sir P. T Sciences College Department of Chemistry, Modasa,
***Author for correspondence: hemant_2patel@yahoo.co.in**

ABSTRACT



where, R = - C_nH_{2n+1}, n = 1 to 8,10,12,14,16

Terminal butoxy ethyl functional groups present in a molecule have their own significance because of their polarity. It has been known that terminally ethyl substituted compounds shows more steady mesophases than do non-substituted mesogenic compounds. Any ethylterminal functionalgroup, which increases the molecular polarizability, without significantly increasing the molecular breadth, increases the thermal stability of the resulting phase transition. Newsynthesized mesogenic homologous series of alkoxy cinnamaldehyde with aminobutoxy ester terminal tail: [2-butoxyethyl -4-3-4 -alkoxy phenyl) acryloyl) oxy) benziledene) amino) benzoate]has been synthesized by condensing an appropriate 4-*n*-alkoxycinnamaldehydewith butoxyethyl 4-aminobenzoate. The synthesized compounds were characterized by combination of elemental analysis and standard different spectroscopic methods like IR, NMR and DSCThe Phase transition were showed using a optical polarizing microscope. Thin films derivatives were obtained by sandwiching them between a glass slide and cover slip.

Twelve members ofthe series were synthesized. All the members Exhibit mesomorphism. Methoxy to tetradecyloxyderiivativeis nematogenic. Butoxy to *n*- tetradecyloxy derivatives exhibit enantiotropicsmectic Aas well as nematicmesophases. Only hexadecyloxy derivatives exhibit Smectic A phase. The mesomorphic properties of the present series were compared with different structurally related mesogenic homologous series to evaluate the effect of aminobutoxy ethyl tail and alkoxycinnamoyloxy central linkage as well as Schiff's base unit on phase transition.

Introduction:

Liquidcrystallinematerialshavemanycriticalpractical applications in technical areas, specific as in-plane switching, light-emitting diode, in plane switching mode liquid crystal display, as well as biomaterials due to their interesting optical and L.C. properties [1-4]. The molecular architecture of liquid crystalline [L.C.]compounds highly affects the phase behavior stability, where the change in molecular shape provides a significant proper change in their mesomorphic characteristics and phase behavior. [5,6]. Most thermo- tropic liquid crystals have rod-like molecular shape holding a rigid core containing two ormore phenyl rings linked to groups that increase polarizability of the whole molecule and flexible terminal alkyl chains [-R]. Schiff's base (-CH = N-), is used as a linking group in many liquid crystalline[L.C.] materials since the discovery of 4-methoxybenzylidene-4′-butylaniline (MBBA), which exhibits a room temperature nematic phase [7]. However, it provides a stepped core molecular structure yet maintains the molecular linearity by providing higher stability and allowing the formation of mesophase behavior. [8]. Lateral substitution plays a vital role in the mesogenic characteristics as it broadens the molecule. Introducing a lateral group in a rigid core could inhibit close packing of the liquid crystalline molecule and reduces the melting temperature [9-16].

Key words: Aminobutoxy ethyl tail, cinnamoyloxy central linkage, enantiotropic, phase transition.

DOI: 10.5455/jcmr.2023.14.01.32

In the present study, to obtain further understanding of the effect of alkoxy chain [-OR] length and the butoxy ethyl(-$C_2H_4OC_4H_9$) terminal substitution on mesogenic properties, a new series of liquid crystalline[L.C.] compounds having Schiff's base with cinnamoyl and ester with central linkages have been prepared and compared with shape related liquid crystalline compound.

Preparation of [2-butoxyethyl -4-3-4 -alkoxy phenyl) acryloyl) oxy) benziledene) amino) benzoate] [Final]

[1] 4-*n*-Alkoxybenzaldehydes:

4-*n*-Alkoxybenzaldehydeswere synthesized by alkylation of 4-hydroxybenzaldehyde using the conventional method of Vyas and Shah [17].0.1 Mole 4-Hydroxybenzaldehyde, 0.15 moleof anhydrous K_2CO_3and0.15 mole of corresponding 1-bromoalkane were added to 60 ml dry acetone. The mixture was refluxed on water bath for 6 to 8 hours. In the case of higher member, the refluxing period was extended up to 10 to 12 hours. Completion of the reaction was checked by TLC (70% Ethylacetate-hexane). The whole mass was added to cold water this separated was extracted with ethers. Ether extract washed with 5% solution of $NaOH_{(aq)}$ (25ml x 3), water (25mlx3), brine and was then dried over anhydrous Na_2SO_4. Reaction mass was purified by column chromatography using silica (60-120 mesh size) and 10% ethylacetate-hexane as eluent furnished the product. Yield: 58-65%.

[2]*trans*-4-*n*-Alkoxycinnamic acids:

trans-4-*n*-Alkoxycinnamic acids were prepared by the method of Gray and Jones [18]. 0.02 Mole of appropriate 4-*n*-alkoxybenzaldehyde, 0.04 moleof malonic acid, pyridine and piperidine were mixed and heated at 100^{c}Con a steam bath for three to four hours. In the case of higher members refluxing period was extended to six to eight hours. The mass was poured into cold aqueous 1:1 HCl, stirred it for sometime, filtered and washed with water. The insoluble mass separated was crystallized several times from acetic acid till constant transition temperatures were obtained. Yield: 85 to 90%.

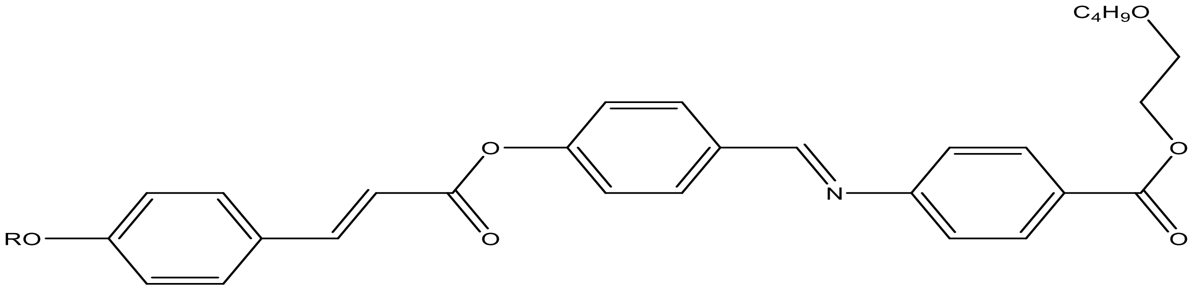
[3]*trans*-4-*n*-Alkoxycinnamoyloxybenzaldehydes [A]:

0.1 Mole of *trans*-4-*n*-Alkoxycinnamic acids , 0.1 mole of 4- hydroxyl benzaldehyde0.1 mole of DCC [19] and 0.1 mole of DMAP were dissolved in dryTHF and stirred at room temperature for over night. The insoluble solid was removed through filtration.The crude product was repeatedly crystallized from the ethanol. All the compounds of the present series were synthesized with the same method. Yield in general is 60-65%. The elemental analysis of all the compounds was found to be satisfactory and all are listed in table **1.** The IR (figure**1** and **2**) and ^{1}H NMR (figure **4** and **5**) spectral data of representative compounds were found to be consistent with the proposed structure.

[4]Butoxy ethyl 4-aminobenzoate (B) was synthesized as per the method describedbelow [20]. Dry hydrochloric acid gas was passed in mole) butoxy ethanol till it wassaturated (approximately for about3 hours). To this saturated solution 12g (0.088mole) 4-aminobenzoic acid was added and the mixturewas refluxed for about 8 to 10hours. The hot solution wasthen poured intoexcess of ice-cold water *and* sodium carbonate wasadded tothe solutionuntil it was neutral tolitmus. The precipitatedester wasfiltered and dried. The product crystallized fromaqueous methanolM.P. 52 ^{0}C (75-80%)The synthetic route to compounds of series **I** is illustrated in the scheme **2.**

[5] [2-butoxyethyl -4-3-4 -alkoxy phenyl) acryloyl) oxy) benziledene) amino) benzoate] [Final]

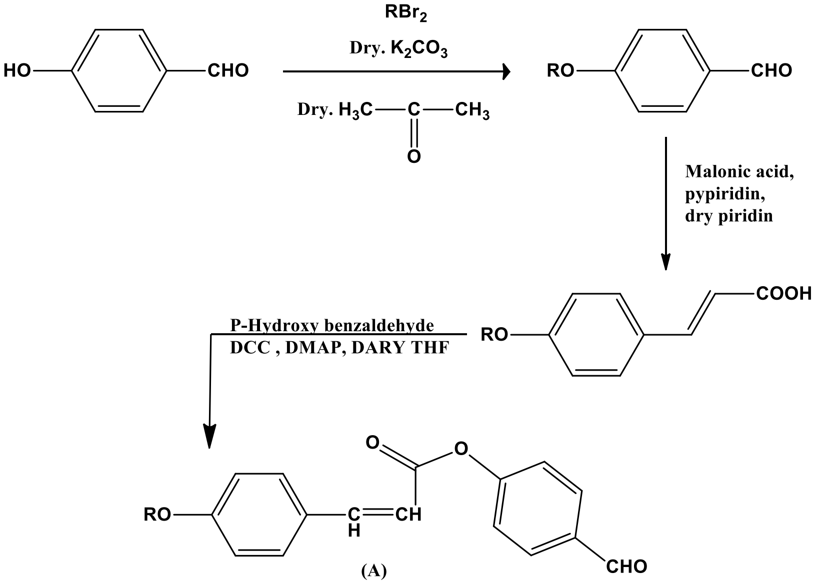
The corresponding 0.1 Mole of *trans*-4-*n*-Alkoxycinnamoyloxy benzaldehydes**[A]** was dissolved in ethanol. The solution was added drop wise to the round bottom flask containing 0.1 mole of Butoxy ethyl 4-aminobenzoate**[B]**, which was previously dissolved in ethanol and few drops of acetic acid. After mixing them the content of the flask heated under reflux for four-five hours .The crude product was repeatedly crystallized from the ethanol. All the compounds of the present series were synthesized with the same method. Yield in general is 80-85%. The transition temperatures agree well with the reported value [21].



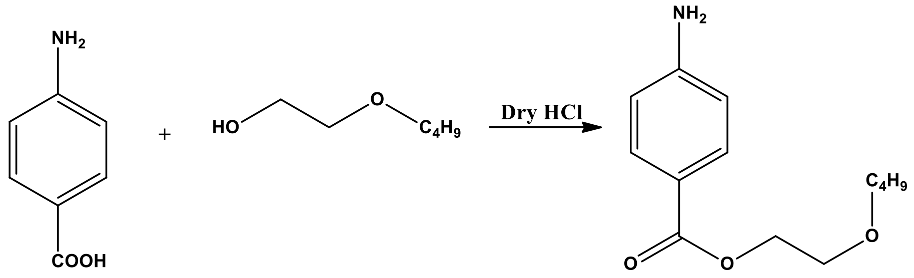
where, R = - C_nH_{2n+1}, *n* = 1 to 8,10,12,14,16

Synthetic Route :

STEP : 1



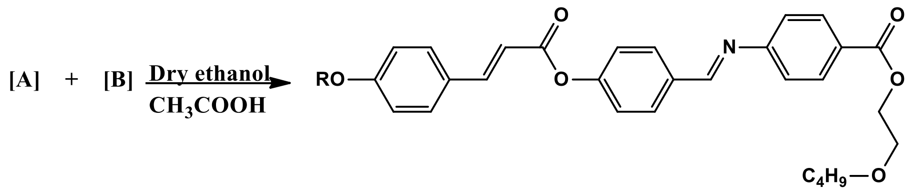
STEP : 2



B

R=C_nH_{2n+1}	Cr	SmA		N		I	
1	●			197	●	280	●
2	●			199	●	272	●
3	●			203	●	264	●
4	●	171	●	207	●	256	●
5	●	156	●	211	●	248	●
6	●	140	●	219	●	239	●
7	●	124	●	191	●	215	●
8	●	106	●	163	●	196	●
10	●	91	●	134	●	171	●
12	●	86	●	99	●	147	●
14	●	68	●	87	●	142	●
16	●	62	●			130	●

STEP : 3

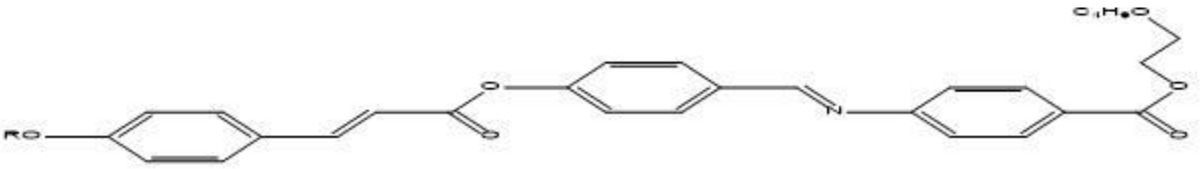


where, R = - C_nH_{2n+1}, n = 1 to 8,10,12,14,16

Table 1: Transition temperatures (°C) of the series I compound

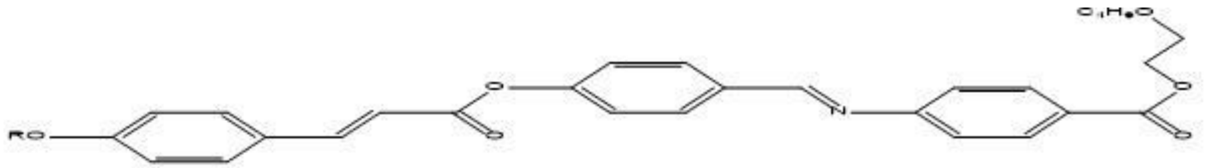
.
Cr=crystalline solid; SmA=smectic A phase; N=nematic phase; I=isotropic, liquid phase; •=phase exists

Table-2 :Elemental analysis for series compounds



Compound No.	**R= -C_nH_{2n+1} n=**	**Formula**	**% Required (% found)**
			CHN

1	**1**	$C30H_{31}O_6N$	71.85 (71.81)	6.13(6.18)	2.79 (2.75)
2	**2**	$C_{31}H_{33}O_6N$	72.23 (72.21)	6.64 (6.67)	2.71 (2.78)
3	**3**	$C_{32}H_{35}O_6N$	72.58 (72.62)	6.61 (6.66)	2.64 (2.61)
4	**4**	$C_{33}H_{37}O_6N$	72.92 (72.98)	6.81 (6.79)	2.57 (2.61)
5	**5**	$C_{34}H_{39}O_6N$	73.24 (73.25)	7.01 (6.99)	2.51 (2.53)
6	**6**	$C_{35}H_{41}O_6N$	73.55 (73.56)	7.81 (7.88)	2.45 (2.44)
7	**7**	$C_{36}H_{43}O_6N$	73.84 (73.85)	7.35 (7.32)	2.29 (2.31)
8	**8**	$C_{37}H_{45}O_6N$	74.12 (74.15)	7.51 (7.48)	2.33 (2.32)
9	**10**	$C_{39}H_{49}O_6N$	74.46 (74.51)	7.81 (7.83)	2.23 (2.25)
10	**12**	$C_{41}H_{53}O_6N$	75.11 (75.13)	8.09 (8.07)	2.13 (2.15)
11	**14**	$C_{43}H_{57}O_6N$	75.54 (75.58)	8.32 (8.34)	2.04 (2.07)
12	**16**	$C_{45}H_{61}O_6N$	75.94 (75.87)	8.57 (8.54)	1.96 (1.91)



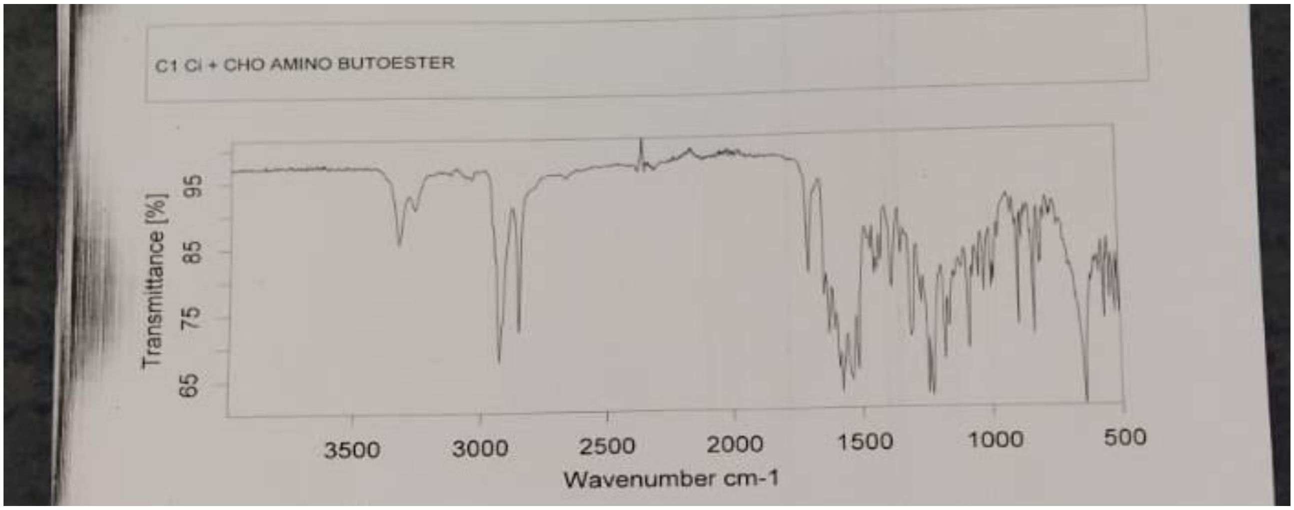
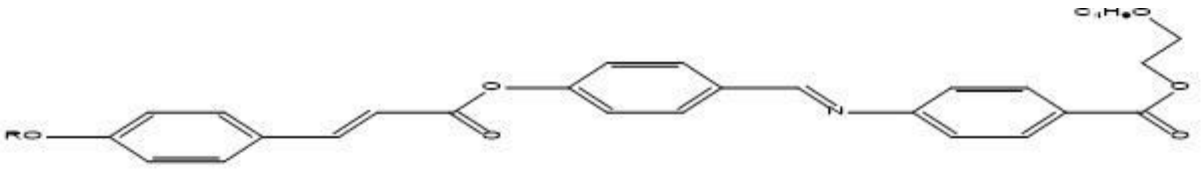


Figure 1: IR data of series **I** (*n*=**1**)

IR spectrum (KBr) v_{max}/cm^{-1}:2926, 2849, 1703 (-COO-), 1641, 1624 (-CH=CH-), 1602, 1585(-CH=N-) 1515, 1433, 1282, 1138, 827.



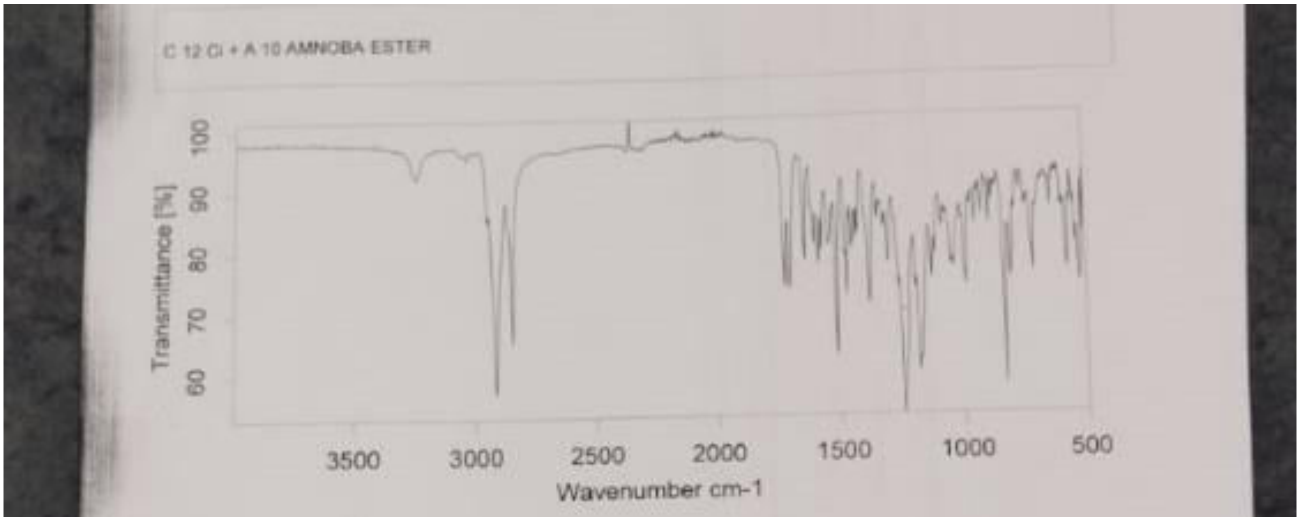
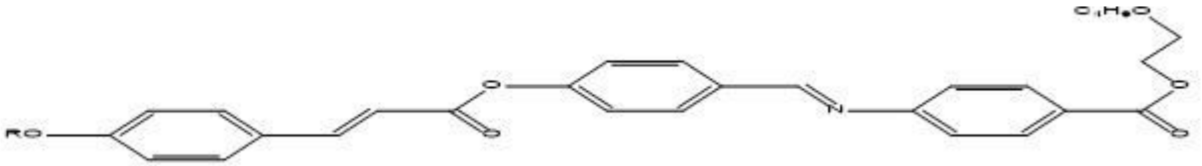


Figure 2: NMR data of series **I** (*n*=**6**)

IR spectrum (KBr) v_{max}/cm^{-1}:2913, 2850, 1723 (-COO-), 1702, 1642, 1603 (-CH=CH-), 1602, 1584 (-CH=N-), 1435, 1280, 1136,



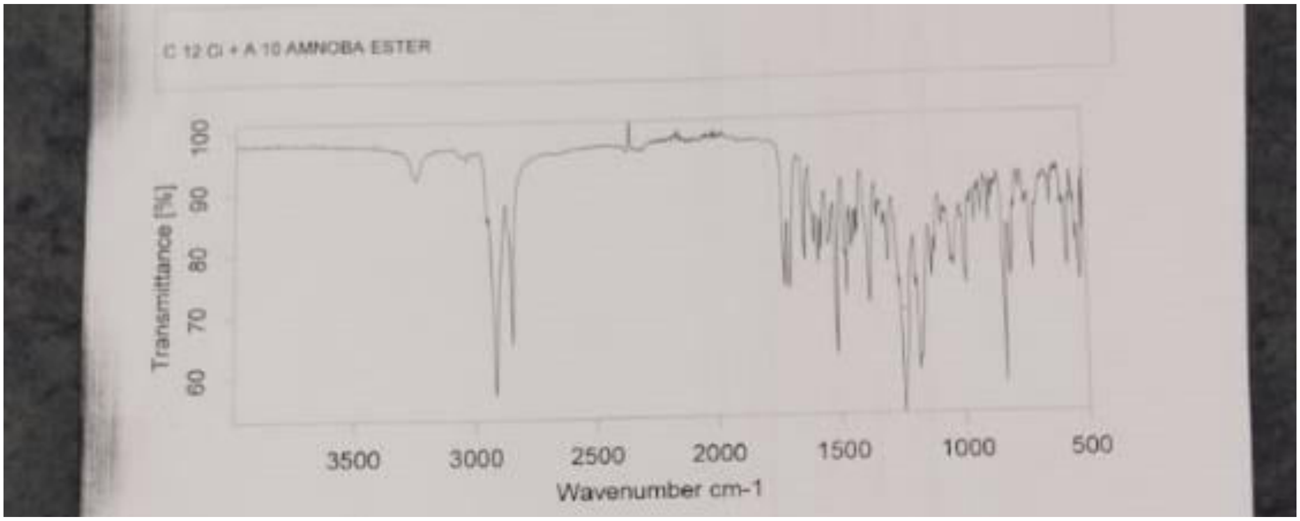


Figure 3: NMR data of series **I** (*n*=**12**)

IR spectrum (KBr) ν_{max}/cm^{-1}:2911, 2848, 1725 (-COO-), 1702, 1641, 1604 (-CH=CH-), 1602, 1582 (-CH=N-), 1436, 1281, 1133

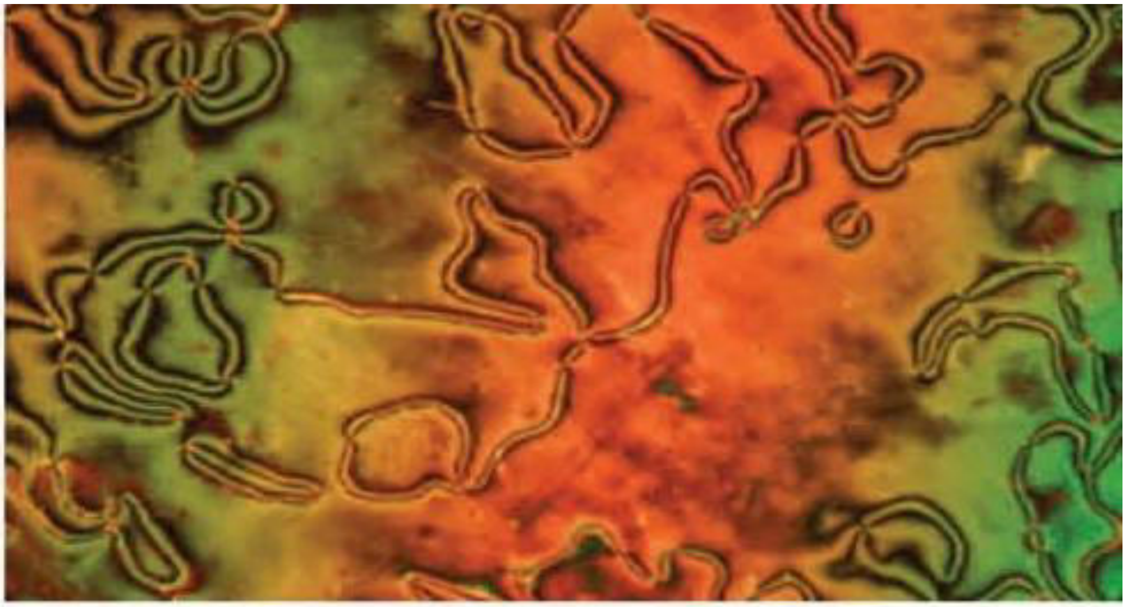
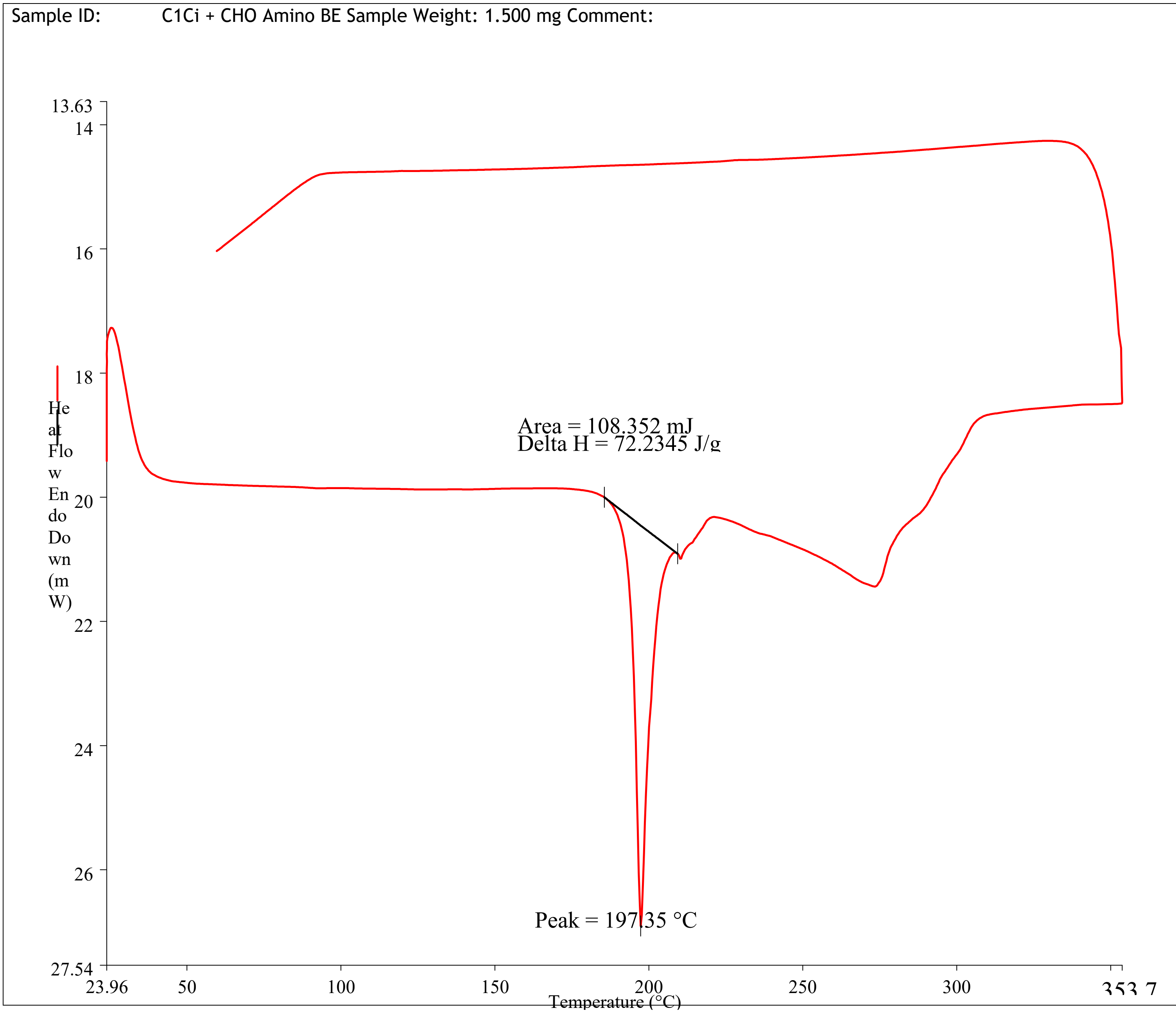


Figure4.(on line) Schlierennematicphaseat225°Cof compound *n=6* on heating.

Filename: D:\Bhargav\KBIPE...\C1Ci + CHO Amino BE.d6d Operator ID:

Figure5.(on line) Smectic A phaseat112°Cof compound *n=6* on heating.

Calorimetric studies



Sample ID: C1Ci + CHO Amino BE Sample Weight: 1.500 mg Comment:

Figure6.DSC thermograph of n=1

Filename: D:\Bhargav\KBIPER\C12Ci+CHO AminoBE.d6d
Operator ID:

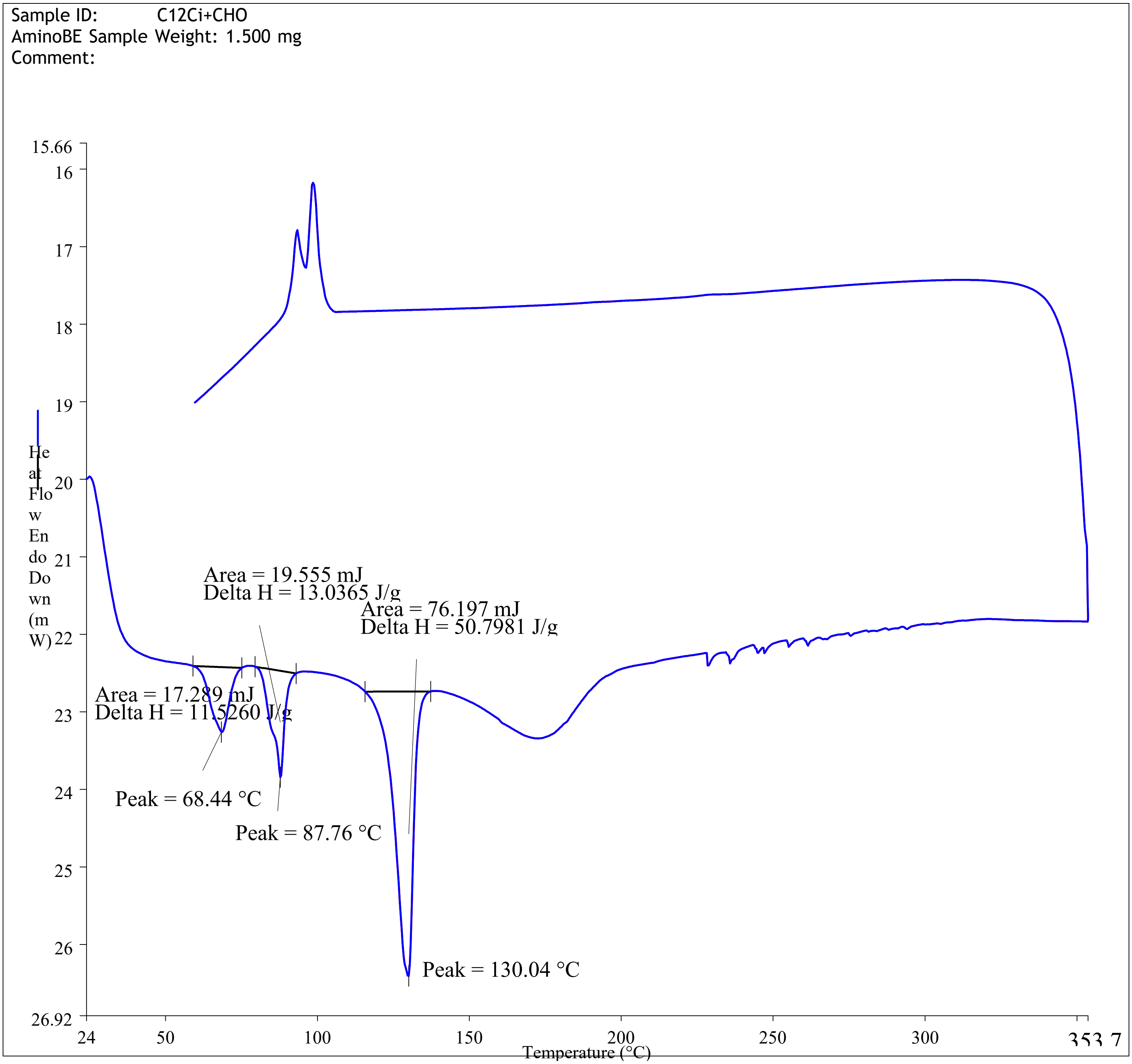
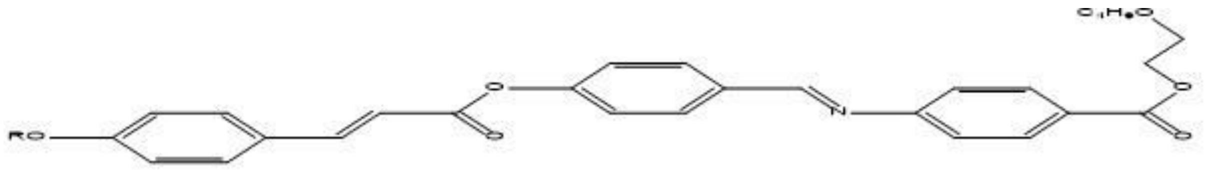


Figure7.DSC thermograph of n=12



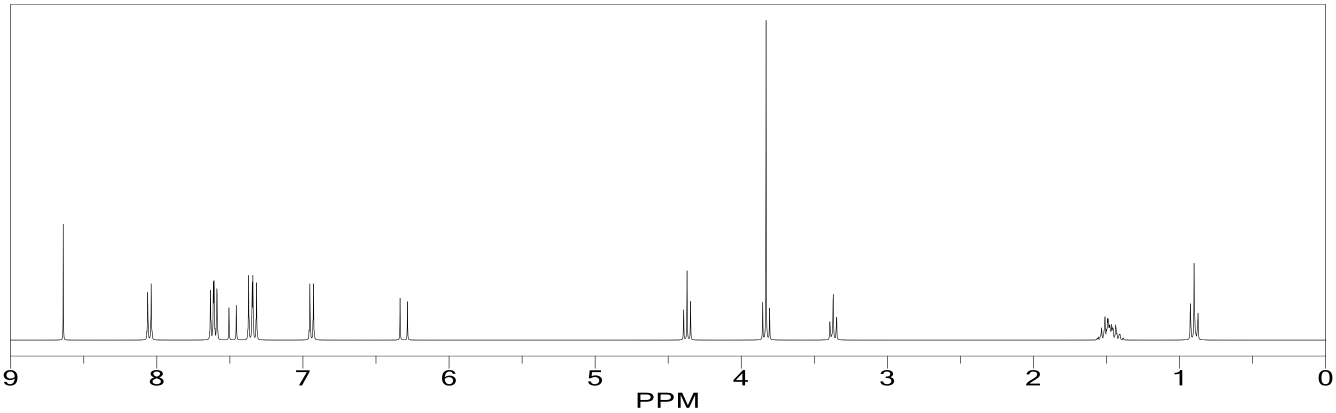
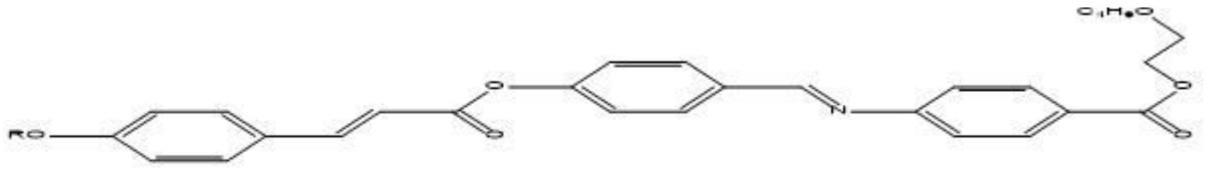


Figure 8: NMR data of series **I** (*n*=**1**)

[2-butoxyethyl -4-3-4 -methoxy phenyl) acryloyl) oxy) benziledene) amino) benzoate]

¹H NMR spectrum*(400 MHz)*:**δ**3.84 (t, 3H, -CH_3), 0.90 (t, 3H, -CH_3),1.44-1.51(m,4H, 2 x-CH_2-), 3.37-3.83(m,4H,-CH_2-O-CH_2) 4.37 (t, 2H of -$COOCH_2$), 6.31(d,1H, Ar-CH=),6.94(d, J=8.7Hz 2H,ArH),7.33-7.36(m,4H,ArH),7.48(d, 1H,=CH-COO), 7.60-7.62(m,4H,ArH),8.05(d,J=8.5Hz,2H,ArH), 8.64(s,1H,CH=N)



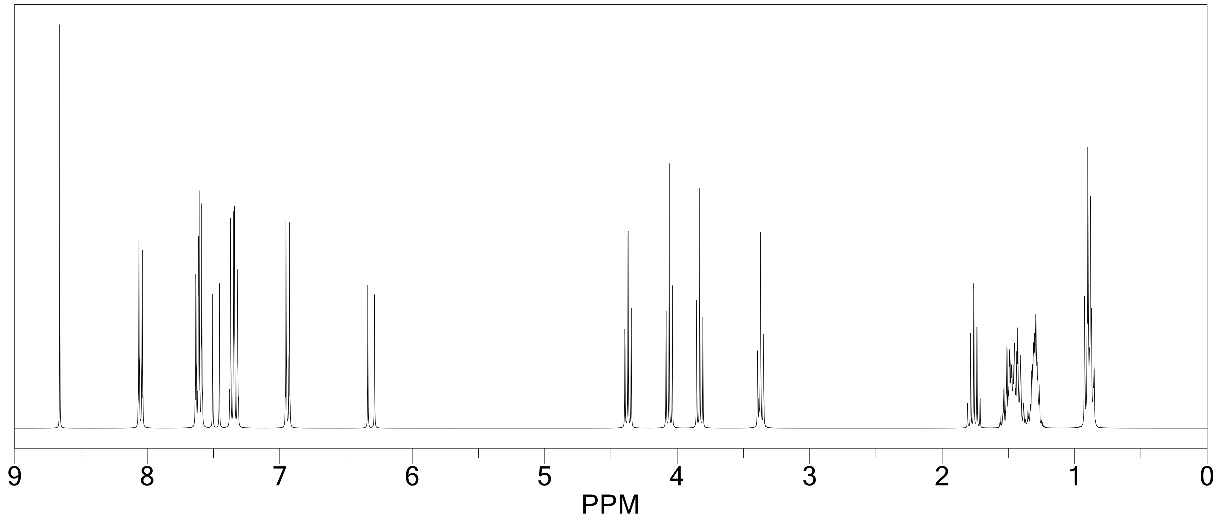
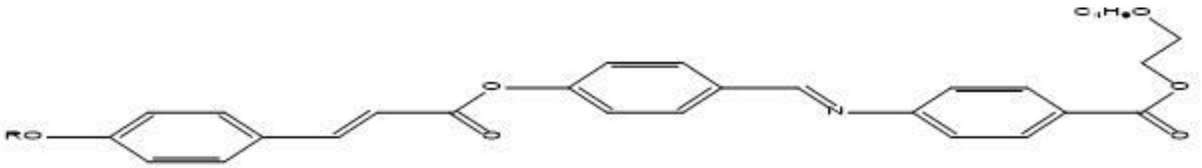


Figure 9: NMR data of series **I** (*n*=**6**)

[2-butoxyethyl -4-3-4 –hexyloxy phenyl) acryloyl) oxy) benziledene) amino) benzoate]

^{1}H NMR spectrum*(400 MHz)*:**δ**0.88 (t, 3H, $-CH_3$),1.29-1.76 (m, 6H, 9 x $-CH_2-$), 1.74-1.76 (quant., 2H, Ar-O-C-CH_2-), 4.06 (t, 2H of Ar-O- CH_2-), 0.90 (t, 3H, $-CH_3$),1.45-1.51(m,4H, 2 x-CH_2-), 3.37-3.83(m,4H,-CH_2-O-CH_2) 4.37 (t, 2H of -$COOCH_2$), 6.31(d,1H, Ar–CH=),6.94(d, J=8.7Hz 2H,ArH),7.33-7.36(m,4H,ArH),7.48(d, 1H,=CH–COO), 7.60-7.62(m,4H,ArH),8.05(d,J=8.5Hz,2H,ArH), 8.64(s,1H,CH=N)



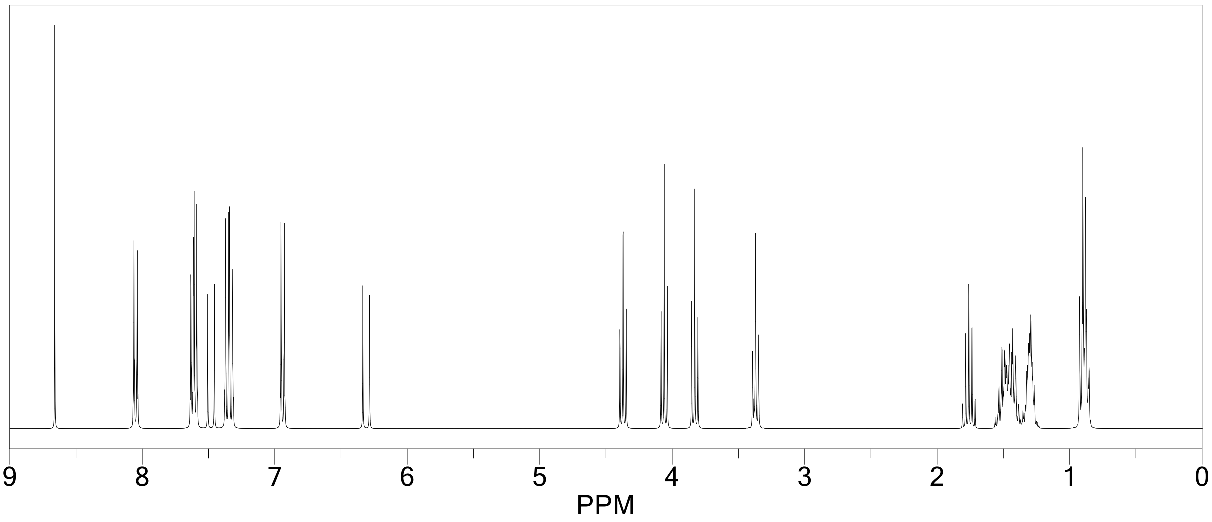


Figure 10: NMR data of series **I** (*n*=**12**)

[2-butoxyethyl -4-3-4 -dodecyloxy phenyl) acryloyl) oxy) benzildene) amino) benzoate]

***^{1}H NMR spectrum**(400 MHz)*:**δ**0.89 (t, 3H, -CH_3),1.28-1.75 (m, 18H, 9 x -CH_2-), 1.74-1.76 (quant., 2H, Ar-O-C-CH_2-), 4.05 (t, 2H of Ar-O- CH_2-),0.89 (t, 3H, -CH_3),1.44-1.50(m,4H, 2 x-CH_2-), 3.36-3.81(m,4H,-CH_2-O-CH_2) 4.36 (t, 2H of -$COOCH_2$), 6.30(d,1H, Ar-CH=),6.93(d, J=8.7Hz 2H,ArH),7.32-7.35(m,4H,ArH),7.46(d, 1H,=CH-COO), 7.59-7.62(m,4H,ArH),8.04(d,J=8.5Hz,2H,ArH), 8.63(s,1H,CH=N)

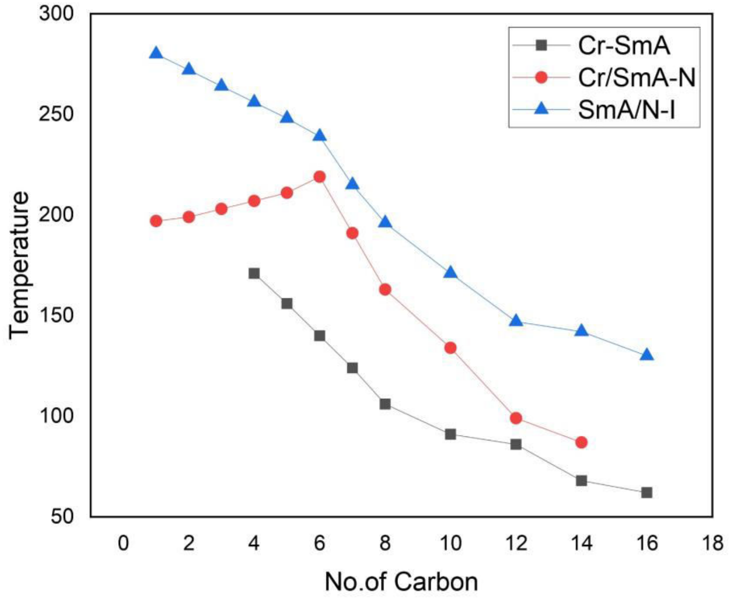


Figure 11: T.T. Graph of series **I**

RESULTSAND DISCUSSION

Series-I:

[2-butoxyethyl -4-3-4 -alkoxy phenyl) acryloyl) oxy) benziledene) amino) benzoate]

Twelve members ofthe Series-**I** were synthesized. All the members Exhibit mesomorphism. Methoxy to tetradecyloxyderiivativeis nematogenic. Butoxy to *n*-tetradecyloxy derivatives exhibit enantiotropicsmectic Aas well as nematicmesophases. Only hexadecyloxy derivatives exhibit Smectic A phase. It is clear fromtheplot oftransition temperatures against thenumber of carbon atom chainin the alkoxychain (Figure-**I**) that thenematic-isotropictransitiontemperatures exhibit the usual alterations associated withnewseries of phasetransitionthecontainingalkylchain madeup ofodd and evennumberofcarbon atoms. Hence, thetransition points lie on twofalling curves.

POM studies

ThePolarizing optical microscopic study concluded that the mesophase exhibited by compounds of theseries as a primary investigation found consistent with the previous results. Microphotograph texture of Schlieren nematic mesophase (Series **I**; *n*=6) at 170 ºC on cooling (Figure **4**.)

Table-**4**summarizesthermalstability, mesophase temperature range and comparative geometry of the present Series-Xand thestructurallyrelated Series I[22],**A** [23], **B** [24] and **C** [23].

Table **4** also indicates that the smectic A mesophase thermal stability of series $\mathbf{X}_{12}$is higher by 4°C than that of series $\mathbf{I}_{12}$, whereas the smectic A mesophase temperature range is higher by 10°C than that of series $\mathbf{I}_{12}$. As discussed earlier, the lower smectic A mesophase thermal stability is probably attributed to the increase in the length of the molecule of series $\mathbf{X}_{12}$has broken alkoxy chain (-$C_2H_4OC_4H_9$) at the terminusbecause of the extra two methylene groups which adversely affects the smectic A mesophase thermal stability as compared to series $\mathbf{I}_{12}$.

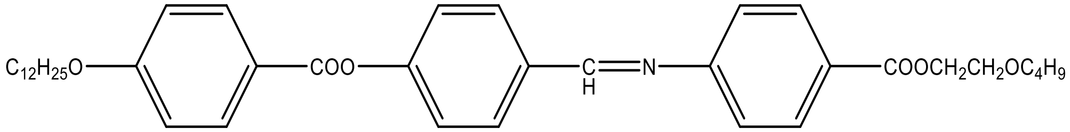
Table **4** also indicates that the smectic A mesophase thermal stability of series $\mathbf{X}_{12}$is lower by 6.5°C than that of series **A**, whereas the smectic A mesophase temperature range is lower by 11°C than that of series **A**. In addition, one should remember that the temperature range of the mesophase is determined partly by the Cr-SmA transition temperatures, and due to the very low Cr–SmA transition temperatures of series $\mathbf{X}_{12}$ as compared to series **A**, the smectic A mesophase temperature range is also lower for series $\mathbf{X}_{12}$.Table **4** also indicates that the smectic mesophase range of series **B** is higher by 56° C. It can also be noticed that the smectic transition temperatures of series **B** are higher by 64° C, respectively, than those of Series-**X**. The molecules of series **B** and Series-**X** differ only at the terminus. series **B** has a chloro terminal group, whereas Series-**X** has an butoxy ethyl terminal group. The presence of polar terminal chloro group increases the overall polarizability of series **B** compared to Series **X**. which is responsible for the higher transition temperature and greater mesophase thermal range of **seriesB**.

Table **4**shows that the smectic mesophase range of series **C** is lower by 24° C. It can also be noticed that the smectic transition temperatures of series **C** are lower by 77° C, respectively, than those of Series-**X** to the molecular structure of both these compounds shows that the both the compounds differ in the number of benzene ring and central linkage. Series **X** have longer and more polarizable in comparison with series **C** due to the presence of additional azomethine central linkage and benzene moiety, which is responsible for the greater mesophase length and higher thermal stabilities of series **X**.Gray [25] has explained that the increase in the length of the molecules, as a result of its polarizability, increases theintramolecularcohesive forces which would beresponsible forinduction of nematicmesophaseandthehighersmecticthermal stabilities ofthe present series-**X**.

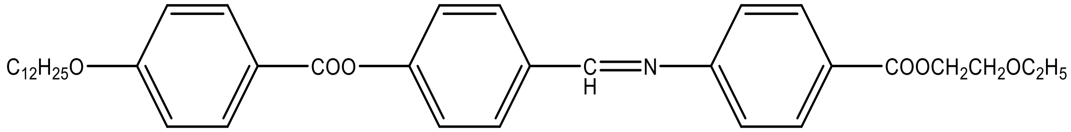
Table:4 Comparative study of the phase transition temperatures, smetic A mesophase range and comparative molecular structures of compoundsX, and**I, A** to **C**

Compound	**Cr-SmA**	**SmA-Iso**	**Mesophase range/°C**	**Commencement of smectic A phase**
I	82	137	55	C_2
A	92.5	158	65.5	C_2
B	142	211	69	C_3
C	62	70	08	C_5
X	86	147	61	C4

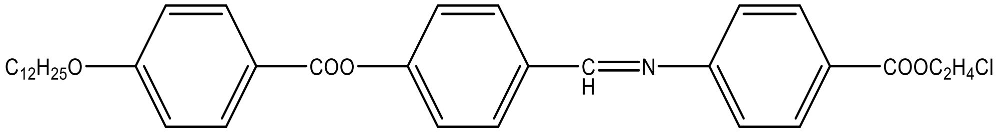
Series-X



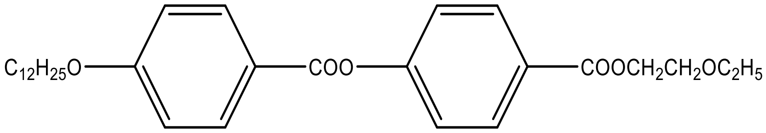
Series- I



Series- A



Series- B



Series- C

CONCLUSION

Broken alkoxyterminal butoxy ethyl(-$C_2H_4OC_4H_9$) chain withthree phenyl rings having ester andazomethine [-CH=N-] central linkages exhibit nematic and smectic Amesophases. Thestudy indicated that broken alkoxy terminal chain affected more adversely onmesophase thermal stabilities as compared to branched chain terminus.

References:

[1] WeiP,WangYP,XiaYM,etal.Synthesisandproperties of novel photocrosslinkable aromatic-aliphatic liquid crystal copolyesters based on poly(ethylene glycol)andcinnamicacid.LiqCryst.2019;46(2):176-184.

[2] Dmochowska E, Bombalska A, Kula P. Synthesis and mesomorphic properties of four ring, rod-like fluorene derivatives- the influence of the lateral substitutionon mesomorphic properties of 2,7-bis(4-alkylphenyl)- fluorenes. LiqCryst. 2020;47(1):17-27.

[3] ZhuG,WangF,LiuWJ,etal.Synthesisofphotosensi-

tivepolyimideforliquidcrystalalignmentunder non-polarised UV ageing lamp irradiation and a study on the possible mechanism of alignment. LiqCryst. 2020;47(4):489–499.

[4] Yu HL, Zhu G, Wang YH. Preparation of polyimide alignment films with high photosensitivity and low solid content. LiqCryst. 2021;48(4):598–606.

[5] Dave JS, Bhatt HS. Synthesis of liquid crystals with lateral methyl group and study of their mesomorphic properties. Molecular Crystals and Liquid Crystals. 2012;562(1):1–9.

[6] Quan-Y-Y,WangD,He-Q-Q,etal.V-shapedSchiff's base liquid crystals based on resorcinol: synthesis and characterisation. LiqCryst. 2020;47(5):737–749.

[7] Kelker H, Scheurle B. A Liquid-crystalline(Nematic) Phase with a Particularly Low Solidification Point. AngewChemInt Ed. 1969;8(11):884–885.

[8] Date RW, Imrie CT, Luckhurst GR, et al. Smectogenic dimeric liquid crystals. The preparation and properties of the α,ω-bis(4- N -alkylanilinebenzylidine-4′-oxy) alkanes. Liquid Crystals. 1992;12(2):203–238.

[9] Prajapati AK, Thakkar V, Bonde N. New mesogenic homologous series of schiff base cinnamatescompris- ing naphthalene moiety. . Molecular Crystals and Liquid Crystals. 2003;393(1):41–48.

[10] Ahmed HA, Saad G. Mesophase behaviour of laterally di-fluoro-substituted four-ring compounds. LiqCryst. 2015;42(12):1765–1772.

[11] Durgapal SD, Soni R, Soman SS, et al. Synthesis and mesomorphic properties of coumarin derivatives with chalconeandiminelinkages.JMolLiq.2019. DOI:10.1016/j.molliq.2019.111920

[12] AhmedHA,HagarM,El-SayedHE,etal.Schiff'sbase/ ester liquid crystals with different lateral substituents: mesophasebehaviour and DFT calculationsLiq.Cryst. 2019;46(7):1–11.

[13] HagarM,AhmedHA,SaadGR.Mesophasestabilityof newSchiffbaseesterliquidcrystalswithdifferentpolar substituents. . Liquid Crystals. 2018;45(9):1324–1332.

[14] Naoum MM, Mohammady SZ, Ahmed HA. Lateral protrusion and mesophase behaviour in pure andmixed states of model compounds of the type 4-(4′- substituted phenylazo)-2-(or 3-)methyl phenyl-4'- alkoxy benzoates. LiqCryst. 2010;37(10):1245–1257.

[15] Al-Hamdani UJ, Abbo HS, Al-Jaber AA, et al. New azo-benzothiazole based liquid crystals: synthesis and study of the effect of lateral substituents on their liquid crystalline behaviour. . Liquid Crystals. 2020;47(14-15):2257–2267.

[16] Hagar M, Ahmed HA, Aouad MR. Mesomorphic and DFT diversity of Schiff base derivatives bearing pro-trudedmethoxygroups..LiquidCrystals.2020;47(14- 15):2222–2233

[17] Vyas, G. N., Shah, N. M., Org. Syn. Coll. Vol. IV, (Revised-edition of annual volume 30-39, John Wiley and Sons Inc., New York, p. 836 (1963).

[18] Gray, G. W. and Jones, J. B., J. Chem. Soc., 1467 (1954).

[19] Hassen, A. and Alexanian, V., Tetra. Lett., 4475 (1978).

[20] Vogel A.I. Textbook of Practical Organic Chemistry, (Longman Group UK Ltd. 1989) p. 701.

[21] Dave, J. S. and Patel, P. R., Mol. Cryst., **2**,115 (1966).

[22] Chitra A Padh, European Journal of Molecular & Clinical Medicine ISSN 2515-8260 Volume 9 Issue 9, 2022.

[23]A.K. Prajapati, H.C. Sharma and N.K. Chudgar, Mol. Cryst. Liq. Cryst. 364 813 (2001). [24]A.K. Prajapati, N.L. Bonde, H. Patel. Phase Transitions, 78, 507 (2004)

[25] Gray, G. W., Molecular Structure and the Properties of Liquid Crystals, Academic press, London, (1962).