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Research Article

THE BANANA-SHAPED SALEN-TYPE LIQUID CRYSTAL COMPOUND DERIVED FROM 4, 4' DIAMINO SULFONE: SYNTHESIS AND CHARACTERISATION

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ABSTRACT: 4, 4' diamino sulfone derivetives have been synthesised and characterized. Antimicrobial activity has been determined in *s.aureus, b.subtilis, p.vulgaris, p.aeruginosa and c.albicans.* Results have shown most of the synthesized compounds were found to be good antibacterial and antifungal agents due to aromaticity and conjugation of molecules.

INTRODUCTION

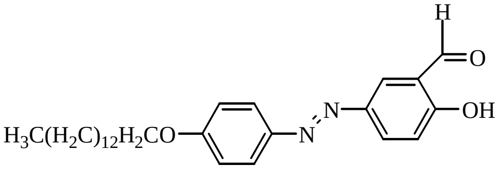
Conventional thermotropic liquid crystals (LCs) are formed by anisometric molecules (mesogens) that are either rod-shaped (calamitic LCs)[1] or disc-shaped (discotic LCs) [2]. By employing these two anisometric moieties many conventional low molar mass (monomers) as well as high molar mass (polymers) liquid crystalline systems have been designed and synthesized. The thermal behaviour of such monomeric and polymeric LCs are mostly well understood. LCs with rod-like molecules exhibit nematic (N) and/or smectic (Sm) mesophases whereas LCs with flat disc-shaped molecules organizes to give N and/or columnar (Col) mesophases [3]. Over the past ten years or so there has been resurgence in the molecular design, synthesis and characterization of a new class of LCs in which the anisotropic shape of the molecules is distorted away from the classical rod or disc-shape [4]. Such materials have been termed as "non-conventional LCs", some examples of which are oligomeric LCs, bent-core molecules, polycatenars, dendrimers, etc. Of all the non-classical molecular architectures known to support liquid crystalline behaviour, the bent-core molecules [5] have been attracting a great deal of attention as they exhibit liquid crystalline property though their molecular geometry significantly deviates from the classical rod or disc-shape. In fact these molecule are known since the days of Vorlander who himself along with Apel [6, 7] reported the first synthesis of such molecules. These molecules can be broadly classified into two categories: (i) V-shaped, and (ii) banana-shaped. Attaching two mesogenic segments covalently to a benzene ring at 1,2-positions forms bent-core V-shaped molecules [5a] where as bent-core banana-shaped materials are formed when two mesogenic segments are covalently connected to either a benzene ring at 1,3-positions or to the terminals of an odd-alkylene spacer [5b]. However it is now well established that the mesomorphic behaviour of these two classes of bent-core molecules are different which is attributed to the bending angle between the mesogenic segments (arms) attached to central benzene nucleus. As we shall see later in detail, bent-core V-shaped molecules are known to exhibit mesophases, which are similar to those shown by classical calamitic LCs whereas banana-shaped mesogens exhibit new smectic phases including two-dimensional ones, which are not comparable or miscible with the phases formed by the calamitics. In this article we focus our attention on bent-core V-shaped molecules only.

Bent-core V-shaped compounds are also known as fused twins [4e] or U-shaped molecules [5b]. However, in this article we shall adopt the term bent-core V-shaped mesogens. As mentioned above, Vorlander and Apel [7] were the first to report bent-core V-shaped molecules namely, 1,2-phenylene bis[4-(ethoxyphenylazoxy)benzoate which were recently shown to exhibit a nematic phase [8]. Later, in 1991 Kuboshita *et al.* [9] reported the synthesis and characterization of 1,2-phenylene bis[4-(4-alkoxy benzylidene amino)benzoates and their 3- and 4-methyl variants. These three series of compounds were found to display nematic (N), smectic A (SmA), and smectic B (SmB) phases. In 1993 Matsuzaki and Matsunaga reported different series of bent-core V-shaped molecules namely, 4-*tert*-butyl-/ phenyl 1,2-phenylene bis[4-(4-alkoxybenzy-lideneamino)benzoate, 1,2-phenylene bis[4-(4-alkoxypheny-liminomethyl) benzoates and their 3- and 4-methyl variants and 2,3-naphthylene bis[4-(4-alkoxyphenyl-iminomethyl)benzoates and bis[4-(4-alkoxybenzylideneamino)benzoates. The compounds were also found to exhibit the N, SmA and SmB phases. For the SmA phase formed by these compounds, a partial-bilayer structure was suggested based on the X-ray diffraction studies. Interestingly, Kato *et al.* [11] described the nematic behaviour of bent-core molecules formed as a result of hydrogen bonding between phthalic acid and stilbazole. Recently, Prasad from our laboratory has reported a number of azobenzene based bent-core V-shaped molecules, which were found to exhibit the N, SmA and crysal E phases [12]. More recently, Rao and Paul have described synthesis and characterization of several bent-core molecules [13]. Among these, a bent-core V-shaped tetradentate ligand that is relevant to this article has been prepared by condensing 1,2-phenylenediamine with 2-hydroxy-5-(4-*n*-dodecyl)phenylazobenzaldehyde and was found to exhibit mesomorphic behaviour.

In addition to these, there have been some interesting reports on the new forms of such bent-core structures in which two mesogenic segments are connected to a benzene ring at 1,2-positions through alkylene spacers that have been called bent-core V-shaped dimers. Attard and Douglass [5a] reported the early examples such bent-core V-shaped dimeric LCs, the benzene-1,2-di-(4-carboxybenzyliedene-4-*n*-alkylanilines) in which the central benzene ring is connected to two Schiff's base mesogenic segments at 1,2-positions through alkylene spacers. Among the four series of compounds described, the members of the two homologues series comprising of odd-parity alkylene spacers were found to show the N and SmA phases as a function of terminal chain length. Whereas materials having an odd-parity alkylene spacers were found to be purely smectogenic. Xray studies revealed the bilayer structure for the smectic phases exhibited by these compounds. Recently, Yoshizawa and Yamaguchi [14] have described the synthesis and characterization of a bent-core V-shaped dimeric molecule formed by connecting two phenylpyrimidine segments to catechol through C_6 alkylene spacer. This compound was found to exhibit smectic-like layer ordering in the nematic phase, and unusual enthalpy change were observed in the nematic phase on heating from the monotropic smectic C (SmC) phase.

Thus it is evident from the literature that azoxybenzene [7, 8] or Schiff's base [9, 10], stilbazole [11], or azobenzene [12] mesogenic segments have been connected covalently at 1, 2-positions of benzene ring to obtain bent-core V-shaped mesogens. In order to understand the underlying structure-property relation further, different cores have to be incorporated. To the best of our knowledge the salicylaldimine [*N*-(2-hydroxy-4-alkoxybenzylidene) aniline] moiety, which is well known for its thermal stability, has not been employed to realize such bent-core V-shaped mesogens. As a first step, we intend to realize a series of structurally closely related banana-shaped compounds, in which the azomethine (imine) (along with hydroxy group) and ester linkages are interchanged. Herein we report the synthesis and characterization of a homologues series of symmetrical five-ring banana-shaped compounds **1-7**, the molecular structures of which are shown in Scheme 1.

Synthesis of 2-hydroxy-5- (4'-n-tetradecyloxy) phenylazobenzaldehyde (14n$_2$)

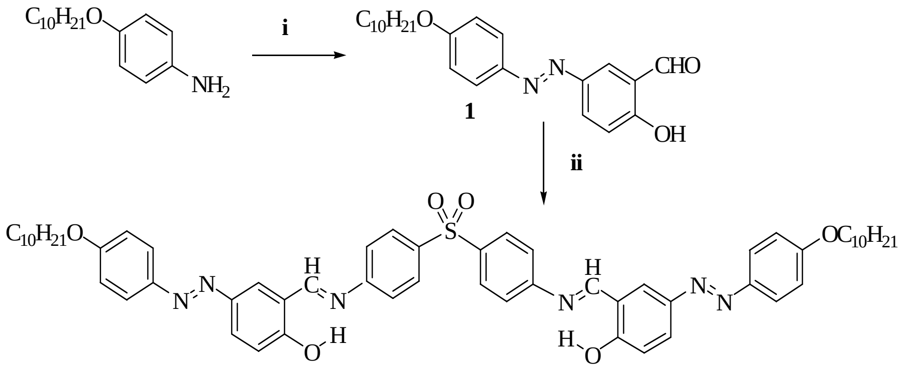


To a solution of 30ml of water containing hydrochloric acid (6.85 ml, 4.4M, 0.03mol) 4-n-tetradecyloxyaniline (0.01mol) was added slowly to form a clear solution. To the resulting solution, which was stirred and cooled to 0°C, an aqueous cold solution of $NaNO_2$ (0.76g, 0.011 mol) was added drop wise maintaining the temperature of the reaction mixture at 0-5°C, to yield the diazonium chloride. It was subsequently coupled with salicylaldehyde (1.22 g, 0.01mol), which was dissolved in 11.5 ml of aqueous 2 N NaOH (0.92 g, 0.023mol) solution. The reaction mixture was stirred for 1h at 0-5°C and then allowed to warm slowly to room temperature with stirring for over 1 hour. The resulting yellow precipitate was filtered, washed with water several times. The crude product was dissolved in CH_2Cl_2 dried over Na_2SO_4. After removal of the solvent under reduced pressure the sample was recrystallised from ethanol to give a single spot on thin layer chromatography.

Yield: 90%. m.pt=124.7°C. IR (KBr pellet, data in cm^{-1}): 3100 (ν_{OH}),, 2955, 2919 (ν_{aCH}, methyl or methylene), 2849,2873 (ν_{sCH}, methyl or methylene), 1673 ($\nu_{C=O}$), 1506 ($\nu_{C=C}$); 1287 (ν_{O-C}). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, 3H, J = 6.3 Hz, CH_3), 1.26-1.44 (m, 28H, $(CH_2)_4$), 4.00 (t, 2H, J = 6.3 Hz, CH_2O), 6.41 (d, 1H,J=2.3Hz,Ar), 6.52 (dd, 1H, J = 2.0 and J = 8.6 Hz, Ar), 7.41 (d, 1H, J = 8.6 Hz, Ar), 9.69 (s, 1H, CHO) and 11.48 ((s, 1H, OH)

Synthesis of N,N'-bis-[2-hydroxy-5-(4'-n-decyloxy)phenylazobenzylidene]-4,4'-diamino diphenylsulfone (DDSO10)

Orange solid; Yield 82%; m.pt 296 °C; IR (KBr): νmax 3436(ν_{OH}), 2922 (ν_{aCH}, methyl or methylene), 2851(ν_{sCH}, methyl or methylene), 1617 ($\nu_{C=N}$), 1582 ($\nu_{C=C}$); 1501 ($_{N=N}$), 1351(ν_{SO2}) and 1246(ν_{O-C}); ^{1}H NMR (400MHz, $CDCl_3$) δ 13.85 (s, OH, 2H, H), 8.77(s, CH=N, 2H, H), 8.03 (d, 8.8 Hz, 4H, H), 7.89-7.91 (m, 4H, H), 7.31 (d, 8.8 Hz, 4H, H), 7.28 (d, 8.4 Hz, H), 7.16 (d, 8.4 Hz, H) 7.03 (d, 8.8 Hz, 2H, H), 4.09 (t, 6.6 Hz, 4H, H), 1.25 to 1.80 (m, 32H, H), 0.88 (t, 6.5 Hz, 6H, H); Anal. calcd. for $C_{58}H_{68}N_6O_6S$: C, 71.28; H, 7.01; N, 8.60; O, 9.82; found C, 71.75; H, 7.93; N, 8.51;O, 9.01



Scheme 1 : Reagents and conditions: **i.** HCl, $NaNO_2$, H_2O, 0-5^{0}C, NaOH, H_2O and salicylaldehyde; **ii.** 4,4'-diaminodiphenylsulfone,abs EtoH, cat AcOH, reflux,3h.

DDSO11

Orange solid; Yield 82%; m.pt 285 °C; IR (KBr) νmax : 3436(ν_{OH}), 2922 (ν_{aCH}, methyl or methylene), 2851(ν_{sCH}, methyl or methylene), 1617 ($\nu_{C=N}$), 1582 ($\nu_{C=C}$); 1501 ($_{N=N}$), 1351(ν_{SO2}) and 1246(ν_{O-C}). ^{1}H NMR (400MHz, $CDCl_3$) δ13.85 (s, OH, 2H,H), 8.77(s, CH=N, 2H, H), 8.03 (d, 8.8 Hz, 4H, H), 7.89-7.91 (m, 4H, H), 7.31 (d, 8.8 Hz, 4H, H), 7.28 (d, 8.4 Hz, H), 7.16 (d, 8.4 Hz, H) 7.03 (d, 8.8 Hz, 2H, H), 4.09 (t, 6.6 Hz, 4H, H), 1.25 - 1.80 (m, 36H, H), 0.88 (t, 6.5 Hz, 6H, H).Anal. calcd. for $C_{60}H_{72}N_6O_6S$: C, 71.68; H, 7.22; N, 9.55;O, 9.82; found C, 71.73; H, 7.59; N, 9.41;O, 9.41.

DDSO12

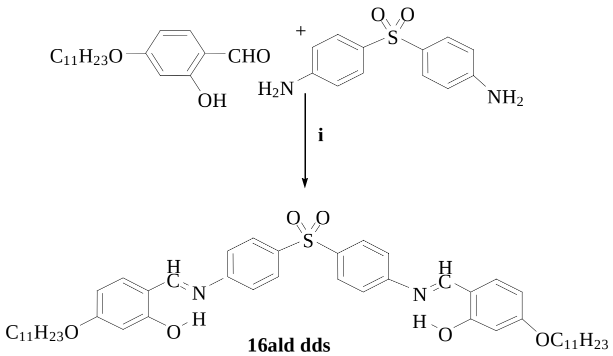
Orange solid; Yield 82%; m.pt 273°C; IR (KBr) νmax: 3436(ν_{OH}), 2922 (ν_{aCH}, methyl or methylene), 2851(ν_{sCH}, methyl or methylene), 1617 ($\nu_{C=N}$), 1582 ($\nu_{C=C}$); 1501 ($_{N=N}$), 1351(ν_{SO2}) and 1246(ν_{O-C}). ^{1}H NMR (400MHz, $CDCl_3$) δ13.85 (s, OH, 2H, H), 8.77(s, CH=N, 2H, H), 8.03 (d, 8.8 Hz, 4H, H), 7.89-7.91 (m, 4H, H), 7.31 (d, 8.8 Hz, 4H, H), 7.28 (d, 8.4 Hz, H), 7.16 (d, 8.4 Hz, H) 7.03 (d, 8.8 Hz, 2H, H), 4.09 (t, 6.6 Hz, 4H, H), 1.25 - 1.80 (m, 36H, H), 0.88 (t, 6.5 Hz, 6H, H).Anal. calcd. for $C_{62}H_{76}N_6O_6S$: C, 72.06; H, 7.41; N, 8.13; O, 9.29; found C, 72.44; H, 7.92; N, 8.53; O, 9.93

DDSO14

Orange solid; Yield 82%; m.pt 269 °C; IR (KBr) νmax: 3436(ν_{OH}), 2922 (ν_{aCH}, methyl or methylene), 2851(ν_{sCH}, methyl or methylene), 1617 ($\nu_{C=N}$), 1582 ($\nu_{C=C}$); 1501 ($_{N=N}$), 1351(ν_{SO2}) and 1246(ν_{O-C}). ^{1}H NMR (400MHz, $CDCl_3$) δ13.85 (s, OH, 2H, H), 8.77(s, CH=N, 2H, H), 8.03 (d, 8.8 Hz, 4H, H), 7.89-7.91 (m, 4H, H), 7.31 (d, 8.8 Hz, 4H, H), 7.28 (d, 8.4 Hz, H), 7.16 (d, 8.4 Hz, H) 7.03 (d, 8.8 Hz, 2H, H), 4.09 (t, 6.6 Hz, 4H, H), 1.25 - 1.80 (m, 36H, H), 0.88 (t, 6.5 Hz, 6H, H).Anal. calcd. for $C_{64}H_{80}N_6O_6S$: C, 72.76; H, 7.77; N, 7.71; O, 8.81; found C, 73.36; H, 8.54; N, 7.12; O, 8.34;

Synthesis of *N,N'*-bis-[2-hydroxy-5-(4'-n-undecyloxy)benzylidene]-4,4'-diamino diphenyl sulfone (11ald dds)

Yellow solid**;** Yeild 83%; IR (KBr) νmax: 2922 (ν_{aCH}, methyl or methylene), 2851(ν_{sCH}, methyl or methylene), 1627 ($\nu_{C=N}$), 1587 ($\nu_{C=C}$), 1342(ν_{SO2}) and 1254 (ν_{O-C}); ^{1}H NMR (400MHz, $CDCl_3$) 13.52 (s, OH, 2H, H), 8.50(s, CH=N, 2H, H), 7.99 (d, 8.5 Hz, 4H, H), 7.93 (d, 8.4 Hz, 4H, H), 7.72 (d, 8.6 Hz, 2H, H), 6.67(d, 2.3,8.7 Hz, 2H, H), 6.50 (d, 2.1 Hz, 4H, H), 3.98 (t, 6.5 Hz, 4H, H), 1.20 to 1.80 (m, 36H, H), 0.80 (t, 7.3 Hz, 6H, H); Anal. calcd. For $C_{48}H_{64}N_2O_6S$: C, 72.33; H, 8.09; N, 3.51; O, 12.04; found C, 72.76; H, 8.65; N, 3.98; O, 12.43;



16ald dds

Scheme 2.: Reagents and conditions:
i. abs EtoH, cat AcOH, heat,3h.

16aldds

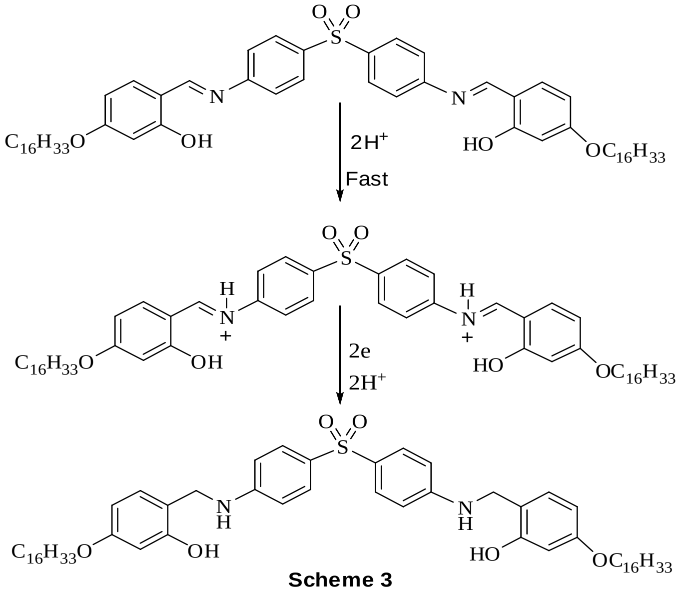
Yellow solid**;** Yeild 83%; IR (KBr) νmax: 2922 (ν_{aCH}, methyl or methylene), 2851(ν_{sCH}, methyl or methylene), 1627 (ν⍰$_{C=N}$), 1587 ($\nu_{C=C}$), 1342(ν_{SO2}) and 1254 ($\nu_{O\text{-}C}$); ^{1}H NMR (400 MHz, $CDCl_3$) 13.52 (s, OH, 2H,H), 8.50(s, CH=N, 2H, H), 7.99 (d, 8.5 Hz, 4H, H), 7.93 (d, 8.4 Hz, 4H, H), 7.72 (d, 8.6 Hz, 2H, H), 6.67 (d, 2.3,8.7 Hz, 2H, H), 6.50 (d, 2.1 Hz, 4H, H), 3.98 (t, 6.5 Hz, 4H, H), 1.20 to 1.80 (m, 36H, H), 0.80 (t, 7.3 Hz, 6H, H); Anal. calcd. for $C_{58}H_{84}N_2O_6S$: C, 74.32; H, 9.03; N, 2.99; O, 10.24; found C, 73.82; H, 9.65; N, 3.51; O, 10.65;

18aldds

Yellow solid**;** Yeild 83%; IR (KBr) νmax: 2922 (ν_{aCH}, methyl or methylene), 2851 (ν_{sCH}, methyl or methylene), 1627 ($\nu_{C=N}$), 1587 ($\nu_{C=C}$), 1342(ν_{SO2}) and 1254 ($\nu_{O\text{-}C}$); ^{1}H NMR (400MHz, $CDCl_3$) 13.52 (s, OH, 2H,H), 8.50(s, CH=N, 2H, H), 7.99 (d, 8.5 Hz, 4H, H), 7.93 (d, 8.4 Hz, 4H, H), 7.72 (d, 8.6 Hz, 2H, H), 6.67 (d, 2.3,8.7 Hz, 2H, H), 6.50 (d, 2.1 Hz, 4H, H), 3.98 (t, 6.5 Hz, 4H, H), 1.20 to 1.80 (m, 36H, H), 0.80 (t, 7.3 Hz, 6H, H); Anal. calcd. for $C_{62}H_{92}N_2O_6S$: C, 74.96; H, 9.33; N, 2.82; O, 9.66;found C, 75.01; H, 9.83; N, 3.33; O, 9.98;

Cyclic voltammetry study

11ald dds exhibits in fact only one irreversible reduction peak with the range of Ep=-0.99 to = -1.33 V at υ=0.1 V /s and c = 0.003M. Variation of the scan rate up to 500 V causes no substantial modification of the voltammetric behaviour. The current function, Ip/√υ is independent of the scan rate. It confirms the diffusion contolled nature of the electro chemical reduction of 11ald dds. In the presence of acetic acid pre-peak appeared which is more positive than the main reduction potential. The appearance of a pre-peak in the voltammetric reduction of 11ald dds in the presence of acetic acid may also relate to its basic properties. In the presence of acetic acid protonation of the imine may take place to give an iminium ion, the reduction potential of which is expected to be more positive than that of the starting imines. The observed pre-peak may be attributed to the reduction of the iminium ion. The addition of 1 equivalent Bu_4NOH (tetra butyl ammonium hydroxide) shifts the original peaks towards more negative potential side. This peak is to be attributed to the reduction of the monodissociated conjugated base. Addition of a further equivalent of base eliminates this peak. This reduction of the doubly dissociated dianion is beyond the cathodic discharge. So that in the presence of 2 equivalents of Bu_4NOH no peaks were observed. The electrode reduction scheme of 11alddds is given in scheme 3. While increasing alkyl chain length there is not much effect on reduction potential. Cyclic voltammetric peak parameters for the reduction of 16ald dds on platinum electrode containing 1X10^{-3} (M) and 0.1M TBAB are given in figure 1.



Scheme 3

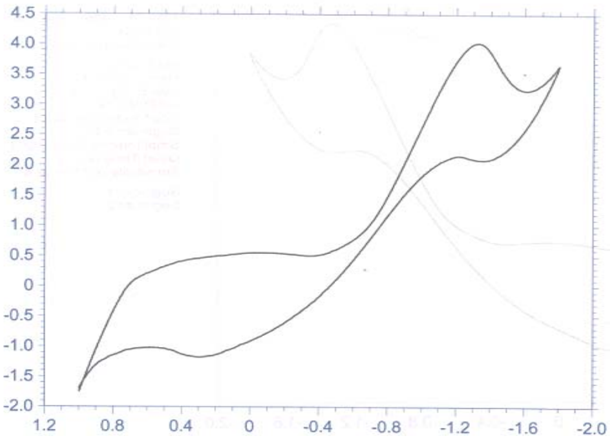


Fig. 1: Electrochemical reduction of 11ald dds at ν=0,C=$1X10^{-3}$

Reductions potential for all compounds of these types are given in table 1.

Table 1: Values of peak potential (-Ep, V) and peak current (Ip, μA)

Compound	Ip(μA)	-Ep(V)
11ald dds	4.63	0.99
16ald dds	4.33	1.23
18ald dds	4.35	1.19

Fig. 2: Antimicrobial activity of synthesized compounds(1,2 and 3) against S.aureus

Fig. 3: Anticrobial activity of synthesized compounds (4,5, and 7) against S.aureus

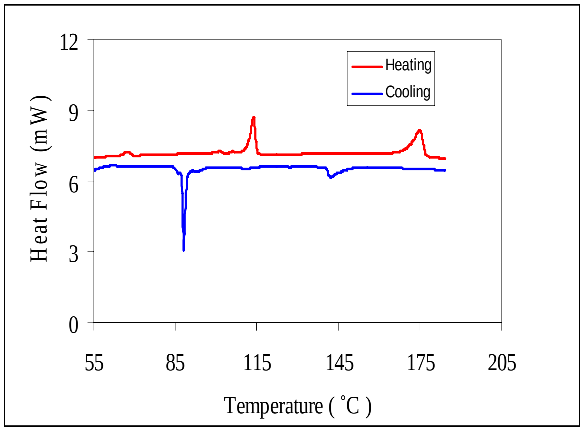


Fig. 4: DSC traces obtained for the first heating and cooling cycles of 16ald dds at a rate of 5 °C /min^{-1}.

Mesomorphic property

DDSOn series are not showing mesomorphic property either heating or cooling cycle. The 16ald dds exhibits one enantiotropic phase transitions as detected by differential scanning calorimetry at 113.73°C (24.7 J/g) and 175.00 °C (2810.3 J/g) in heating cycle and 145.88 °C (29.23 J/g), 92.94°C (51.43 J/g) in cooling cycle is presented in figure 4. However polarizing optical microscopy studies exhibits two transitions at 105°C and 164.5°C. 11aldds and 18ald dds also exhibits one enantiotropic phase transition and the observed characteristic textures of the sample sandwiched between glass plate and cover slip whose thickness may be more than 25 µm. On cooling the sample from the isotropic phase to room temperature several distinct characteristics in the optical textures of the sample were observed. The sample exhibited an unusual viscous grainy texture and presented in figure 5. However, there was no particular change in textures from the Isotropic to grainy texture transition temperature, polarizer is slightly rotated clockwise, then a right upper region becomes dark and a left lower domain becomes bright. If the polarizer is rotated counter clockwise, bright and dark regions are interchanged. This gave grainy texture. As a representative case here we have given details of 16aldds.

Texture observations by thermal microscopy

Optical property was observed in several bent-core materials [185c,d], being characteristic of spontaneous resolution of chiral domains. The brightness of the domains interchanges when one of the polarizers is uncrossed toward the opposite direction, indicating a chiral nature of these grainy textures.

Biological study

The antimicrobial activity of synthesized compounds namely DDSOn and 16ald dds-n are given in the table 2. It shows most of the synthesized compounds were found to be good antibacterial and antifungal agents due to aromaticity and conjugation of molecules The activity of synthesized compounds compared with standard was shown in figure 2 and figure 3.

Fig. 5: Photomicrographs of the optical textures of M phase mesophases obtained just below the isotropic liquid phase of 16aldds

Table 2: Antimicrobial activity of compounds against *S.aureus, B.subtilis, P.vulgaris, P.aeruginosa and C.albicans* (Zone of inhibition in mm)

Compound	*S.aureus*	*B.subtilis*	*P.vulgaris*	*P.aeruginosa*	*C.albicans*
11ald dds	11	8	11	13	12
16ald dds	13	11	13	13	10
18ald dds	11	12	12	11	12
DDSO11	13	12	12	13	11
DDSO12	R	R	8	R	9
DDSO14	R	R	7	R	9
DDSO16	R	R	7	R	9
Standard	30	26	26	36	15

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