



Liquid Crystalline Properties of Salicylaldimine- Based Dimers Derived From Isophthalic Acid

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ABSTRACT

The synthesis and thermotropic properties of a homologues series of salicylaldimine -based dimer liquid crystals are reported. Two 2-hydroxy-4-n-alkoxybenzaldehyde groups are connected to a central part consisting of 2-Methyl-4-methylene-pent-2-enedioic acid bis-(4-amino-phenyl) ester unit. The terminal alkoxy chains have been varied from 4 to 11 and 16 carbon atoms in length. All the compounds exhibit liquid crystalline phases whose behaviour depends on the length of the alkoxy terminal chains. All compounds of the series exhibit enantiotropic B-phases and the sequence B₁-B₂ on increasing terminal chain length was observed. The shorter homologues of this series show the B₁ phase, while the longer homologues exhibit B₂ phase.

Keywords: *Bent-core, enantiotropic, B₂ phase, stable.*

1. INTRODUCTION

Bent-core mesogens have been the subject of extensive investigations in the last years because they can form new mesophases with unusual properties which are different from those of calamitic mesogens. Due to their intrinsic shape the molecules can be packed in a polar fashion, which leads to a long-range correlation of the lateral dipoles. The polar packing of the bent molecules leads to ferroelectric or antiferroelectric properties [1, 2]. With respect to the bent-core molecular architectures, the traditional banana-shaped liquid crystals were generally formed by two bent-substituted rigid arms connected to a central cyclic ring (through polar or nonpolar functional groups) with a suitable bent angle and linking, where appropriate lengths of flexible chains were attached [7]. A variety of interesting phenomena, especially related to chirality and polarity, has been found in these materials, and the topic has been object of several reviews [3-7]. Based on the layer chirality and polarity, the B₂ phase has been described to be able to possess four distinct types of structures; two homochiral SmC_SPF and SmC_APA and two racemic SmC_SPA and SmC_APF [2]. Antiferroelectric state is generally ground state. More popularly observed B₂ structure is synclitic antiferroelectric (SmC_SPA), while anticlinic antiferroelectric (SmC_APA) order is less frequently observed. However, despite this intensive activity in basic research, very few studies refer to possible applications of bent-core liquid crystals. This is due to several factors such as the chemical instability of many of these materials and the difficulty of obtaining well aligned cells. In addition, there is still a certain lack of knowledge in some important aspects of the physics

of several mesophases. The B phases are typically formed from molecules with a rigid bent-core and flexible alkyl or alkoxy chains on each end of the molecule. There are eight known major bent-core mesophases, of which the B₂ (SmCP) phase is the most heavily investigated due to its ferroelectric and antiferroelectric switching properties [1, 8]. Depending on the polar direction and molecular tilted direction in neighbouring layers of the SmCP phase, ferroelectric (F) and antiferroelectric (A) states possessed identical/ inverse polarizations and synclitic (S)/anticlinic (A) arrangements with alike/opposite molecular tilted aspects between layer to layer, respectively. It is found that the banana mesophase are very sensitive to the substituents connected to different positions of the aromatic rings keeping constant the molecular architecture. The situation is more complicated if the linking groups are changed for esters or vinylcarboxylate groups. More and more banana shaped compounds with ester connecting groups were published [9]. Systematic work was carried out on investigating the influence of the carboxyl function on the mesomorphic properties in five aromatic ring bananas building up symmetrical and asymmetrical structures [10]. Synthesis of bent-core compounds with different chemical architecture is of topical interest for understanding the relationship between the chemical structure and mesophase behaviour. Most of the BC compounds exhibiting mesophases that have been reported in the literature are symmetrical about the central unit and are derived from 1, 3-dihydroxybenzene [3, 11–15], 2, 7-dihydroxynaphthalene [16, 17] and benzene-1, 3-dicarboxylic acid [18]. Introduction of lateral substituents on the arms of BC molecules for modifying the mesomorphic properties has been carried out [9, 19–23] on a number of different systems. It is also well known that by increasing

the number of aromatic rings along the bent-core, the thermal stabilities as well as the thermal ranges of the mesophases are increased. The phase sequence as a function of carbon atoms on ascending a homologous series is well understood [11, 12, and 15].

In this paper, we report the mesomorphic properties of homologous series of symmetrical compounds with isophthalic acid as the central core of the bent-core molecule. In these compounds the terminal chain of both the arms is varied.

2. EXPERIMENTAL

2.1. Materials

Isophthalic acid, 4-nitrophenol, 2, 4 dihydroxy benzaldehyde, 1-bromoalkane, Dicyclohexylcarbodiimide, 4-(N, N-dimethyl) aminopyridine, palladium on activated carbon (10% Pd/C), were purchased from Aldrich Chemical co. All other solvents and reagents were purchased commercially and used without purification. Tetrahydrofuran obtained were purified and dried as per the standard procedures.

2.2. Measurements

IR spectra were recorded on a Perkin-Elmer Spectrum 1000 FT-IR spectrometer. NMR spectra were recorded using Bruker AMX-400 (400 MHz). The identification of the mesophases and determination of phase transition temperatures were achieved with the help of polarizing optical microscope (Leica DMLP) provided with a heating stage (Mettler FP90). The sample placed between a clean untreated glass slide and a cover slip was used for this particular study. The mesophase assignment was based on the observation of birefringence and fluidity when examined under POM. To confirm the transition temperatures and to determine their associated enthalpies, a differential scanning calorimeter (Perkin Elmer DSC7) calibrated using pure Indium was employed. The peaks observed in DSC traces (obtained at a rate of $10^{\circ}\text{C}/\text{min.}$) due to phase transition was reproducible and peak temperatures were consistent with those deduced from the optical experiments.

2.3. Synthesis

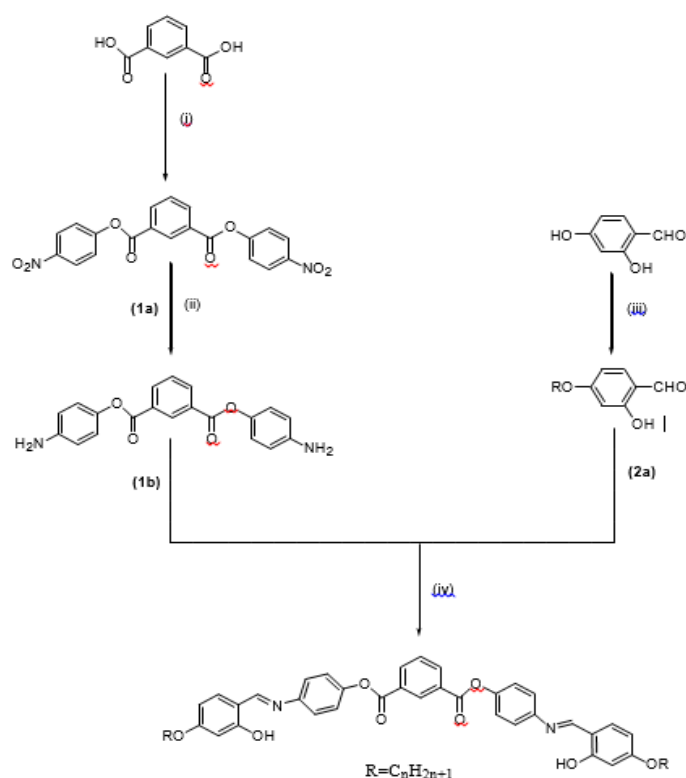
The target banana compounds were purified by column chromatography and recrystallization choosing appropriate mixture of solvents; while the intermediates were purified by column chromatographic technique. Chromatography was performed using either silica gel (100-200,230-400 mesh). Thin layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (merck, kieselgel,60F254). Infrared spectra were recorded on a Perkin-Elmer Spectrum 1000 FTIR spectrometer; the spectral positions (absorption maxima) are given in wave numbers (cm^{-1}). NMR spectra were recorded using Bruker AMX 400(400 MHz) spectrometer. For ^1H NMR spectra, the chemical shifts are reported in parts per million relative to SiMe_4 (TMS) as an internal standard and coupling constants are presented in Hertz. Elemental

analysis was performed using a Eurovector model EA 3000 CHNS elemental analyzer.

The intermediate (1b) were synthesized in two steps. Firstly, The esterification of isophthalic acid with 4-nitrophenol, dicyclohexylcarbodiimide, N, N-dimethylaminopyridine and tetrahydrofuran as the solvent to obtain compound (1a). Reduction of this compound by 10% Pd/C using tetrahydrofuran as the solvent gives the intermediate (1b). Both intermediates were performed according to literature procedures [24].

Isophthalic acid bis-{4-[(4-butyloxy-2-hydroxy-benzylidene)-amino]-phenyl} ester

Compound 1b (0.5mol, 1 equiv.), compound 2a (1mol, 2 equiv.), absolute ethanol (15ml) and a few drops of glacial acetic acid were refluxed for 2 h. The product was filtered and recrystallised from ethanol.



Series A-n**D-4**

Yield: 47%: a yellow solid [found C, 72.78; H, 5.35; N, 4.6.C₄₂H₄₀N₂O₈ requires C,71.98; H,5.75; N, 4.00]; IR (KBr pellet): 3219, 2938, 1759, 1764, 1619, 1267, 839, 714 cm⁻¹.¹H NMR (CDCl₃,200MHz) δ: 8.91 (d, J=8.8Hz, 4H, Ar), 8.42 (s, 2H, 2X CH=N), 8.39 (d, J=9.2Hz, 2H, Ar), 7.51 (d, J=8.5Hz, 4H, Ar), 7.37 (d, J=8.2Hz, 2H, Ar), 7.24 (m,2H, Ar), 6.27 (t, 4H, Ar), 4.01 (t, 4H, 2X Ar-OCH₂), 1.80-1.42 (m, 8H, 4XCH₂), 0.90 (t, 6H, 2XCH₃).

D-5

Yield: 45%: a yellow solid [found C, 73.01; H, 5.69; N, 3.24.C₄₄H₄₄N₂O₈ requires C,72.51; H, 6.09; N, 3.84]; IR (KBr pellet): 3219, 2938, 1759, 1764, 1619, 1267, 839,714 cm⁻¹.¹H NMR (CDCl₃,200MHz) δ: 8.91 (d, J=8.8Hz, 4H, Ar), 8.42 (s, 2H, 2X CH=N), 8.39 (d, J=9.2Hz, 2H, Ar), 7.51 (d, 4H, Ar), 7.37 (d, J=8.0Hz, 2H, Ar), 7.24 (m, 2H, Ar), 6.28 (t, 4H, Ar), 4.01(t, 4H, 2X Ar-OCH₂), 1.81-1.42 (m,12H, 6XCH₂), 0.89 (t, 6H, 2XCH₃).

D-6

Yield: 52%: a yellow solid [found C, 73.7; H, 5.79; N, 3.50.C₄₆H₄₈N₂O₈ requires C,73.00; H, 6.39; N, 3.70]; IR (KBr pellet): 3219, 2938, 1759, 1764, 1609, 1267, 839,724 cm⁻¹.¹H NMR (CDCl₃,200MHz) δ: 8.90 (d, J=8.8Hz, 4H, Ar), 8.42 (s, 2H, 2X CH=N), 8.39 (d, J=9.2Hz, 2H, Ar), 7.51 (d, J=8.8Hz, 4H, Ar), 7.34 (d, J=8Hz, 2H, Ar), 7.24 (m, 2H, Ar), 6.35-6.27 (m, 4H, Ar), 4.01 (t, 4H, 2X Ar-OCH₂), 1.80-1.42 (m,16H, 8XCH₂), 0.88 (t, 6H, 2XCH₃).

D-7

Yield: 55%: a yellow solid [found C, 74.05; H, 6.88; N, 3.27.C₄₈ H₅₂N₂O₈ requires C,73.45; H, 6.68; N, 3.57]; IR (KBr pellet): 3219, 2937, 1759, 1764, 1609, 1269, 839,724 cm⁻¹.¹H NMR (CDCl₃,200MHz) δ: 8.93 (d, J=8.8Hz, 4H, Ar), 8.42 (s, 2H, 2X CH=N), 8.40 (d, J=9.2Hz, 2H, Ar), 7.49 (d, J=8.4Hz, 4H, Ar), 7.34 (d, J=8.0Hz, 2H, Ar), 7.24 (m, 2H, Ar), 6.36-6.27 (m, 4H, Ar), 4.01 (t, 4H, 2X Ar-OCH₂), 1.80-1.42 (m,20H, 10XCH₂), 0.88 (t, 6H, 2XCH₃).

D-8

Yield: 60%: a yellow solid [found C, 74.57; H, 6.34; N, 4.05.C₅₀H₅₆N₂O₈ requires C, 73.87;H, 6.94; N,3.45]; IR (KBr pellet): 3219, 2937, 1759, 1764, 1609, 1269, 839, 727 cm⁻¹.¹H NMR (CDCl₃,200MHz) δ: 8.91 (d, J=8.4Hz, 4H, Ar), 8.40 (s, 2H, 2XCH=N) 8.38 (d, J=9.0Hz, 2H, Ar), 7.51(d, J=8.4Hz, 4H, Ar), 7.34(d, J=8Hz, 2H, Ar), 7.23(2H, Ar), 6.37 (t, 4H, Ar), 4.01(t, 4H, 2X Ar-OCH₂), 1.80-1.41(m, 24H, 12XCH₂),0.88 (t, 6H, 2XCH₃).

D-9

Yield: 60%: a yellow solid [found C, 74.46; H, 6.69; N, 4.03.C₅₂H₆₀N₂O₈ requires C, 26; H, 7.19; N,3.33]; IR(KBr pellet): 3212, 2937, 1759, 1764, 1609, 1269, 836,727 cm⁻¹.¹H NMR (CDCl₃,200MHz) δ: 8.92 (d, J=8.0Hz, 4H, Ar), 8.42 (s, 2H, 2X CH=N), 8.39 (d, J=9.0Hz, 2H, Ar), 7.50 (d, J=8.8Hz, 4H, Ar), 7.34 (d, J=8.8Hz, 2H, Ar), 7.22 (m, 2H, Ar), 6.34-6.27 (m, 4H, Ar), 4.02(t, 4H, 2X Ar-OCH₂), 1.80-1.42 (m, 28H, 14XCH₂), 0.89 (t, 6H, 2XCH₃).

D-10

Yield: 60%: a yellow solid [found C, 74.33;H,7.72; N,3.22.C₅₄ H₆₄ N₂ O₈ requires C,74.63; H, 7.42; N, 3.22]; IR (KBr pellet): 3212, 2941, 1759, 1764, 1609, 1269, 836, 727 cm⁻¹.¹H NMR (CDCl₃,200MHz) δ: 8.91 (d, J=8.8Hz, 4H, Ar), 8.42 (s, 2H, 2X CH=N), 8.38 (d, J=9.2Hz, 2H, Ar), 7.50 (d, J=8.8Hz, 4H, Ar), 7.34 (d, J=8Hz, 2H, Ar), 7.29 (m, 2H, Ar), 6.36 (d, 4H, Ar), 4.01(t, 4H, 2X Ar-OCH₂), 1.80-1.42 (m,32H,16XCH₂), 0.88 (t,6H, 2XCH₃).

D-11

Yield: 65%: a yellow solid [found C, 75.77; H, 8.14; N, 3.32. $C_{56}H_{68}N_2O_8$ requires C, 74.97; H, 7.64; N, 3.12]; IR (KBr pellet): 3212, 2941, 1759, 1764, 1609, 1269, 836, 727 cm^{-1} . 1H NMR ($CDCl_3$, 200MHz) δ : 8.91 (d, J=8.8Hz, 4H, Ar), 8.42 (s, 2H, 2XCH=N), 8.38 (d, J=9.2Hz, 2H, Ar), 7.50 (d, J=8.8Hz, 4H, Ar), 7.38 (d, J=8Hz, 2H, Ar), 7.24 (m, 2H, Ar), 6.36-6.30 (m, 4H, Ar), 4.01 (t, 4H, 2X Ar-OCH₂), 1.80-1.42 (m, 36H, 18XCH₂), 0.88 (t, 6H, 2XCH₃).

D-16

Yield: 71%: a yellow solid [found C, 77.31; H, 9.15; N, 2.52. $C_{66}H_{88}N_2O_8$ requires C, 76.41; H, 8.55; N, 2.70]; IR (KBr pellet): 3212, 2951, 1759, 1765, 1609, 1269, 839, 723 cm^{-1} . 1H NMR ($CDCl_3$, 200MHz) δ : 8.91 (d, J=8.4Hz, 4H, Ar), 8.42 (s, 2H, 2X CH=N), 8.38 (d, J=9.0Hz, 2H, Ar), 7.50 (d, J=8.8Hz, 4H, Ar), 7.34 (d, J=8Hz, 2H, Ar), 7.24 (m, 2H, Ar), 6.36-6.30 (m, 4H, Ar), 4.02 (t, 4H, 2X Ar-OCH₂), 1.80-1.42 (m, 56H, 28XCH₂), 0.89 (t, 6H, 2XCH₃).

3. RESULTS AND DISCUSSION

The liquid crystalline behaviour of the compounds was preliminarily investigated with the help of POM and DSC. Transition temperatures and associated enthalpies obtained from DSC thermograms are shown in Table.1. A study of large number of compounds has indicated that the occurrence of B₁ and B₂ phases is dependent on terminal chain length.

However the nature of the mesophase has varied from lower to higher homologues. The transition temperatures are higher for salicylaldimines due to the presence of intramolecular H-bonding between H-atom of hydroxyl group and N- atom of imine functionality. All the compounds were found to be mesomorphic and the obtained enthalpy values of about 19 to 24 J g⁻¹ for mesophase to isotropic phase transition are in agreement with the values reported for banana-shaped compounds.

Table 1. Transition temperatures ($^{\circ}C$) and enthalpies of transitions ($KJ mol^{-1}$) for the compounds

Compound	n	Cr	Heating Cooling	B ₁	Heating Cooling	B ₂	Heating Cooling	I
A4	4	•	164.0[33.9] 179.3[32.6]	•	221.4[21.9] 224.8[22.4]		-	•
A5	5	•	157.2[39.0] 162.3[36.8]	•	218.6[20.5] 217.6[21.0]		-	•
A6	6	•	141.5[29.0] 153.9[30.1]	•	220.3[19.2] 219.0[18.1]		-	•
A7	7	•	149.2[28.8] 158.2[32.0]	•	214.8[23.7] 215.0[23.1]		-	•
A8	8	•	120.1[31.0] 127.3[30.9]	•	213.8[19.2] 214.5[18.5]		-	•
A9	9	•	118.4[27.5] 125.8[29.0]	•	213.9[15.7] 213.1[17.6]		-	•
A10	10	•	116.5[33.6] 123.7[30.4]		-	•	209.5[22.9] 210.0[23.4]	•
A11	11	•	113.4[28.7] 121.0[29.7]		-	•	211.7[21.8] 209.3[21.5]	•
A16*	16		99.7[32.5] 101.4[32.9]					

*This compound exhibit Cr-Cr transition.

All the compounds except A-16 exhibit enantiotropic liquid crystalline phases, its type depending on the length of the terminal alkoxy chain. The longer homologues A-10 and A-11 exhibit B₂ mesophase, but A-16 does not show any phase. It exhibit only crystal to crystal

transition. An example of the B₂ textures observed for A-10 is given in fig.1. The bent cores A-6 and A-7 show an identical mesophase over 219 $^{\circ}C$ and 215 $^{\circ}C$ temperature range respectively.



Fig.1. Photomicrograph of the texture observed on cooling from the isotropic state for A-10 at 210°C.

For the short tailed members, the B₁ phase was observed on cooling from the isotropic state by the formation of small battonets. Fig.2 show the texture seen under the polarized microscope for the compound A-8 at 214.5°C. The textural patterns matches with textures obtained for the B₁ phase of the lower homologues of the parent series of banana compounds.



Fig.2. Photomicrograph of the texture observed on cooling from the isotropic state for A-8 at 214.5°C.

4. CONCLUSION

All nine salicylaldimine-based compounds that have been synthesized exhibit stable liquid crystalline phases. As in most banana-shaped liquid crystals, a phenyl or biphenyl central part promotes the formation of B-phases. In our studies B₁ phase was observed for the lower homologues and the higher homologues exhibit B₂ phase.

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