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A switchable salicylaldimine-based achiral bent-shaped mesogen: synthesis and characterization

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The first achiral bent core banana-shaped mesogen consisting of a thermally and hydrolytically stable salicylaldimine (2-hydroxybenzylideneamine) mesogenic segment has been synthesized and evaluated for its liquid crystalline behavior. This novel compound exhibits a single switchable mesophase over 60 °C temperature range. The textural and electro-optic switching characteristics suggest that the phase could be of the antiferroelectric type.

Introduction

It is well known[1] that tilted smectic liquid crystalline phases of chiral molecules exhibit ferro-, ferri- and antiferroelectric properties resulting in the appearance of macroscopic polarization (*P*). It was generally believed for a long time that the reduced symmetry, which is responsible for these unique properties in liquid crystals, is partially a consequence of molecular chirality of the constituent molecules. However recently, the ferroelectric property has been discovered in a smectic phase formed by achiral bent core 'banana-shaped' molecules.[2] The observed behavior in these new classes of materials is attributed to the high polar nature of the molecules and their special packing (with the dipoles pointing along a common direction) within a smectic layer. This discovery initiated not only many electro-optical, structural and theoretical studies,[3–9] but also their potential application as switchable NLO-materials.[10] Consequently, the design and synthesis of a large number of new compounds having bent molecular structure focusing mainly on the structure–property evaluations[4] have been reported. These molecules now represent a new sub-group of thermotropic liquid crystals. However, these materials are associated with problems such as their chemical stability, purity and high transition (melting and clearing) temperature that are yet to be solved. Therefore there is a need for molecular engineering leading to bent cores that are stable and exhibit a wide temperature range of mesophase operating from well below and above room temperature.

All the bent core banana-shaped mesogens reported so far generally[4] comprise three important fragments, i) an angular central core which is usually a 1,3-disubstituted benzene nucleus or as in some cases an alkylene spacer ii) two linear rigid cores and iii) terminal chains. The majority of these compounds contain an imine linkage and as a consequence show poor thermal and hydrolytic stability. Therefore, the present investigations in this area need to focus on design and high-yielding synthesis of novel banana-shaped systems that have resistance to heat and moisture.

As a solution to this problem Tschierske *et al.* were the first to synthesize some bent-shaped molecules in which the imine linkage is replaced with either an ester[11*a*] or an acetylenic[11*b*] functionality which are relatively stable to heat and moisture. The banana-shaped molecules with ester linking group interestingly showed switchable mesophases while the compounds with acetylenic linking unit exhibited conventional smectic phases or were non-mesogenic with high clearing temperatures. Surprisingly none of these systems showed switchable mesophases. On the other hand, it is well documented that the salicylaldimine [*N*-(2-hydroxy-4-alkoxybenzylidene)aniline] core based liquid crystals[12] are stable to heat and moisture owing to the presence of intramolecular hydrogen bonding between the H-atom of the hydroxy group and the N-atom of the imine functionality. This prompted us to design and synthesize a banana-shaped molecule in which the central angular aromatic core is connected to a stable salicylaldimine segment. Here we report the synthesis and evaluation of mesomorphic behavior of a novel banana-shaped molecule namely, 1,3-phenylene bis[*N*-(2-hydroxy-4-*n*-decyloxybenzylidene)-4′-aminobenzoate] (**1**).

Experimental

General information

Chemicals were obtained from either Aldrich or Lancaster Company or a local source and used as such without any purification, while solvents were purified and dried following standard procedures. The synthesized compounds were purified following column chromatographic separation techniques using either silica gel or neutral aluminium oxide as a stationary phase. Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with silica gel (Merck, Kieselge10, F254). IR spectra were recorded using a Perkin–Elmer Spectrum 1000 FT-IR spectrometer. NMR spectra were recorded using a Bruker DRX-500 (500 MHz) or DPX-200 (200 MHz) spectrometer. For ^{1}H NMR spectra, the chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded on a JEOL JMS-600H spectrometer in FAB$^+$ mode using 3-nitrobenzyl alcohol as a liquid matrix. Microanalyses were obtained with the help of a Carlo Erba model 1106 elemental analyzer.

The compound was investigated for liquid crystalline behavior with the help of an optical polarizing microscope (Leitz DMRXP) in conjunction with a programmable hot stage (Mettler FP90) and by differential scanning calorimetry (Perkin Elmer DSC7). X-Ray diffraction studies were carried out using an Image Plate Detector (MAC Science, Japan) equipped with double mirror focussing optics and the sample contained in a Lindemann capillary tube.

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3-(4-Nitrobenzoyloxy)phenyl 4-nitrobenzoate (3)

Into a 100 ml two-necked round-bottomed flask equipped with an argon inlet and a septum were placed dry pyridine (AR grade, 20 ml) and resorcinol [2 g, 18.1 mmol (1 equiv.)]. The resulting solution was cooled (5–10 °C) and then a solution of 4-nitrobenzoyl chloride [10.1 g, 54.5 mmol (3 equiv.)] in dry THF (25 ml) was added dropwise over 10 min. The reaction mixture was allowed to warm up to room temperature and vigorous stirring was continued for 24 h. The reaction mixture was concentrated, the pale yellow thick mass obtained was poured into ice-cold 3 M HCl and the yellow solid separated was collected by filtration. This solid product was dissolved in CH_2Cl_2 (50 ml), washed with a 5% aqueous solution of NaOH (10 ml $\times 2$), water (10 ml $\times 2$) and dried over anhydrous Na_2SO_4. Evaporation of solvent furnished crude product that was purified by column chromatography using silica gel (60–120 mesh). Elution with a mixture of 10% EtOAc–hexanes furnished a yellow solid, which was further purified by repeated recrystallizations in a mixture of absolute ethanol–CH_2Cl_2 (9 : 1). $R_f = 0.17$ (10% EtOAc–hexanes); a yellow solid; yield: 4.3 g (quantitative); mp = 184–185 °C; IR (KBr pellet): ν_{max}/cm^{-1} 1738, 1609 and 1526; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.38 (s, 8H), 7.55 (m, 1H) and 7.25 (m, 3H); elemental analysis: calc. for $C_{20}H_{12}N_2O_8$, C 58.83, H 2.96, N 6.86. Found: C 58.68, H 3.04, N 6.65%.

3-(4-Aminobenzoyloxy)phenyl 4-aminobenzoate (2)

A mixture of 3-(4-nitrobenzoyloxy)phenyl 4-nitrobenzoate (**3**) (4 g 15.4 mmol), dry EtOAc (50 ml) and activated Pd–C (10%) (0.2 g) was hydrogenated at 15 psi pressure over a period of 6 h. The reaction mixture was filtered through a Celite bed and the filtrate was evaporated to dryness *in vacuo* furnishing pure product. $R_f = 0.53$ (EtOAc); a white solid; yield: 3.4 g (quantitative); mp = 197–197.5 °C; IR (KBr pellet): ν_{max}/cm^{-1} 3480, 1714, 1626 and 1596; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.99 (d, $J = 8.58$ Hz, 4H), 7.42 (m, 1H), 7.10 (m, 3H), 6.68 (d, $J = 8.58$ Hz, 4H) and 4.14 (s, 4H, $2 \times -NH_2$); FAB mass: *m*/*z* 348.4 $[M]^+$; elemental analysis: calc. for $C_{20}H_{16}N_2O_4$, C 68.96, H 4.63, N 8.04. Found: C 68.92, H 4.67, N 8.0%

1,3-Phenylene bis[*N*-(2-hydroxy-4-*n*-decyloxybenzylidene)-4′-aminobenzoate] (1)

A mixture of 3-(4-aminobenzoyloxy)phenyl 4-aminobenzoate (**2**) [1 g, 5 mmol (1 equiv.)], 2-hydroxy-4-*n*-decyloxybenzaldehyde [2.9 g, 10.5 mmol (2.1 equiv.)], absolute ethanol (50 ml) and a few traces of acetic acid were heated to reflux until the yellow solid compound precipitated out (15 min). The crude product obtained was collected by filtration and repeatedly washed with hot absolute ethanol. It was purified by repeated recrystallizations with a mixture of absolute ethanol–CH_2Cl_2 (9 : 1). $R_f = 0.22$ (10% EtOAc–hexanes); a yellow solid; yield: 1.8 g (40%); phase transition (°C): K 119.4 B_2 180.7 I; IR (KBr pellet): ν_{max}/cm^{-1} 2921, 2852, 1731, 1636, 1593 and 1522; ^{1}H NMR (500 MHz, $CDCl_3$): δ 13.34 (s, 2H, $2 \times$–OH), 8.57 (s, 2H, $2 \times CH{=}N$), 8.24 (d, $J = 8.5$ Hz, 4H, Ar), 7.50 (t, $J = 8.17$, 1H, Ar), 7.35 (d, $J = 8.5$, 4H, Ar), 7.30 (d, $J = 9.3$ Hz, 2H, Ar), 7.21 (m, 1H, Ar), 7.18 (dd, $J = 4.15$ Hz and $J = 2.15$ Hz, 2H, Ar), 6.52 (m, 4H, Ar), 4.01 (t, $J = 6.70$, 4H, $2 \times OCH_2$), 1.8 (m, 4H, $2 \times CH_2$), 1.6–1.23 (m, 28H, $14 \times CH_2$), 0.88 (t, $J = 6.8$ Hz, 6H, $2 \times CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, Spin Echo FT): δ 164.7 (CO), 164.65 (C), 164.45 (C), 163.46 (CH), 153.72 (C), 151.83 (C), 134.37 (CH), 132.07 (CH), 130.21 (CH), 127.11 (C), 121.60 (CH), 119.59 (CH), 116.21 (CH), 113.12 (C), 108.46 (CH), 101.90 (CH), 68.72 (CH_2), 32.23 (CH_2), 29.90 (CH_2), 29.68 (CH_2), 29.40 (CH_2), 26.31 (CH_2), 23.01 (CH_2), and 14.46 (CH_3); FAB mass: *m*/*z* 868.6 $[M^+]$; elemental analysis: calc. for $C_{54}H_{64}N_2O_8$, C 74.63, H 7.42, N 3.22. Found C 74.64, H 7.43, N 2.8%.

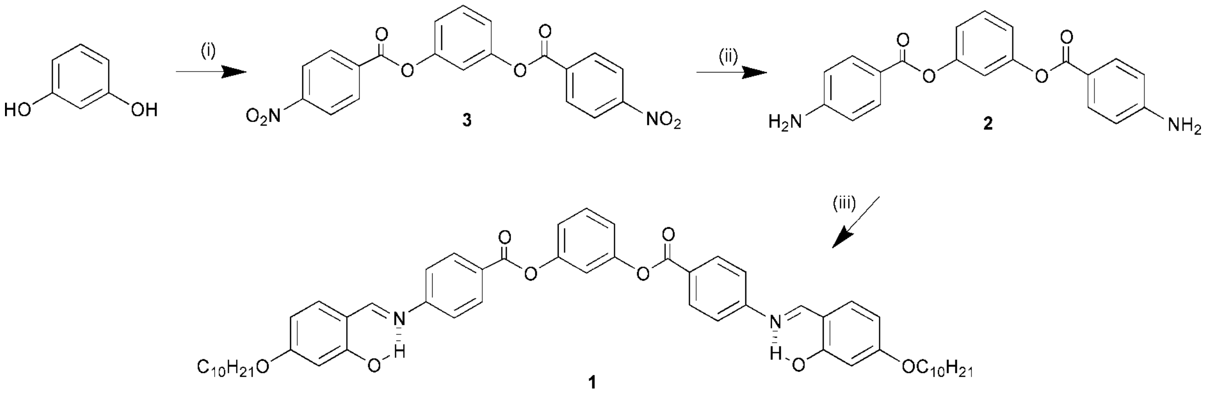
Results and discussion

Synthesis

The target banana-shaped molecule was synthesized as shown in the Scheme 1. The key intermediate, namely 3-(4-aminobenzoyloxy)phenyl 4-aminobenzoate (**2**), was obtained by the catalytic hydrogenation of 3-(4-nitrobenzoyloxy)phenyl 4-nitrobenzoate (**3**) which in turn was prepared by esterifying benzene-1,3-diol with 4-nitrobenzoyl chloride. The condensation of diamine **2** with 2-hydroxy-4-decyloxybenzaldehyde yielded the final compound **1**. The molecular structure of all the intermediates and the final product were characterized by spectral analyses (see Experimental section for details).

Thermal behavior and electro-optical switching studies

The DSC scans for compound **1** (Fig. 1) show only one mesophase which is enantiotropic. On cooling from the isotropic phase, at ~177 °C spherulitic domains exhibiting a fringe pattern superposed on a focal conic texture appear spontaneously. With further cooling new layers aggregate outside the initially formed spherulites. Some of the spherulites showed a clear Maltese cross. In fact the texture is quite similar to the one reported for the B_2 banana phase of several materials[4,13–16] It was noticed that the fringe density varied from domain to domain. Upon application of a low frequency square wave electric field (12 V μm^{-1}), two types of electro-optic switching process were observed in different domains. In some regions, the switching showed only a transient intensity change and the two field stabilized states looked identical (see Fig. 2a), indicating that the extinction direction remains the same in the two states. The switching observed in other domains was quite different: on reversing the sign of the field,



Scheme 1 Synthetic route employed for compound **1**. *Reagents and conditions*: (i) 4-nitrobenzoyl chloride, Py, rt, 24 h (quantitative); (ii) H_2/Pd–C (10%), 15 psi, EtOAc, 6 h (quantitative); (iii) 2-hydroxy-4-*n*-decyloxybenzaldehyde, abs. EtOH, AcOH (traces), 15 min, 22%.

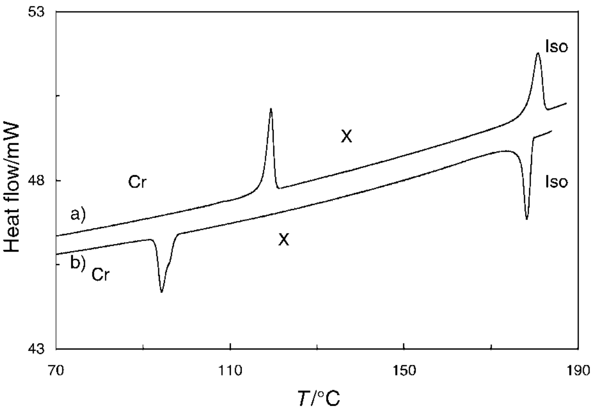
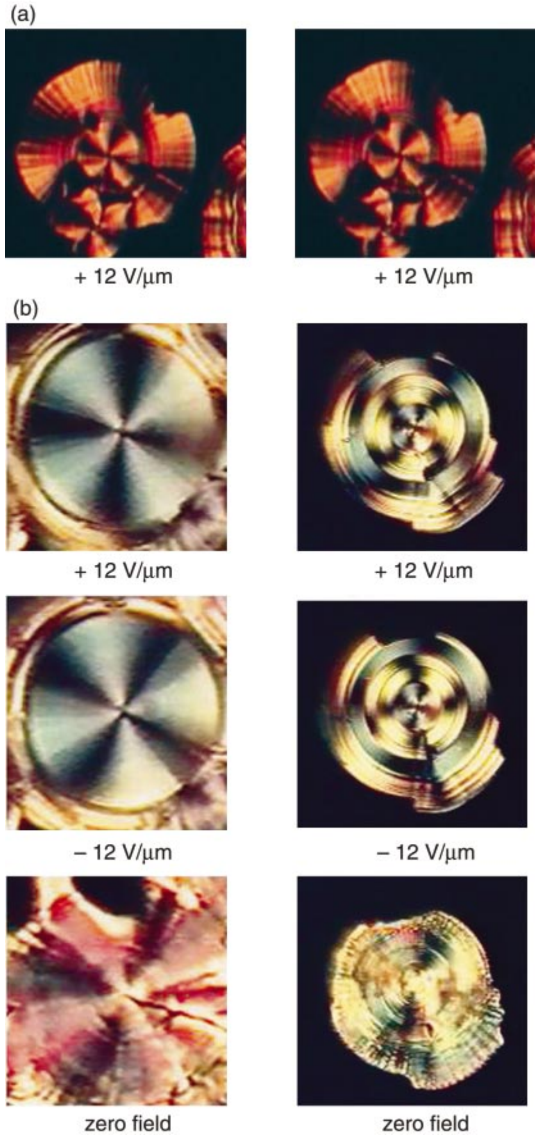


Fig. 1 DSC thermograms obtained at a rate of 5 °C min^{-1} for compound **1**: a) heating mode ; b) cooling mode. Cr = Crystal, X = mesophase and Iso = isotropic liquid.



+ 12 V/µm
+ 12 V/µm
+ 12 V/µm
+ 12 V/µm
− 12 V/µm
− 12 V/µm
zero field
zero field

Fig. 2 (a) Microphotograph taken from a racemic region of the sample in the X phase by applying a low frequency square wave electric field of 12 V µm^{-1}. (b) Microphotographs taken from the two different homochiral regions (region 1: left panels, region 2: right panels) in the X phase by applying a low frequency square-wave electric field of 12 V µm^{-1}. For comparison we also show the photographs in the no field state. Notice that reversing the polarity of the field causes a rotation of the direction of the Maltese cross in the homochiral region only. It may be noted that in the pictures shown in the right panels, the central region is racemic, while the outer ones are homochiral.

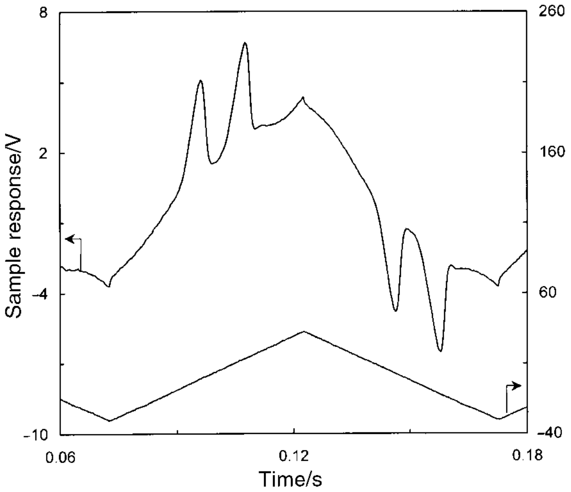


Fig. 3 The current response peaks of the sample at 154 °C on applying triangular wave field of 3.1 V µm^{-1}, 25 Hz. The observed two peaks-per-half period of the applied field indicates antiferroelectric type switching.

the Maltese crosses rotated by a significant angle (see Fig. 2b). The angle of rotation was not exactly the same in all the domains but the maximum observed was about 32°. On application of an electric field with a triangular wave form (3.1 V µm^{-1}, 25 Hz), the current passing through the sample showed two peaks per half period of the applied field (Fig. 3). The two-peak trace shows that the switching observed is of the tri-state antiferroelectric type, which is commonly observed for the banana B$_2$ phase.[16] The combined area under the two peaks is a direct measure of spontaneous polarization (P_s). The temperature dependence of P_s obtained by integrating the area under the peaks is shown in Fig. 4. The high value of P_s ($\sim$5000 µC m^{-2}) is typical for the banana-shaped compounds. P_s has weak temperature dependence far away from the isotropic transition, but on approaching it shows a precipitous drop and vanishes in the isotropic phase.

The dynamics of the polarization switching were studied by monitoring the current response of the sample to an applied square wave field (3.9 V µm^{-1}, 25 Hz). A typical time dependence of the sample output is shown in Fig. 5. Using such traces, the response time τ was estimated from the time elapsed between the appearance of the maximum of the current signal and the field reversal. The temperature dependence of τ (Fig. 6) shows an abrupt increase near the transition but has an Arrhenius type of behavior away from it. The magnitude of the activation energy that was calculated from the region with the Arrhenius behavior is 12.2 kJ mol^{-1}, a value comparable to those obtained for the banana B$_2$ phase.[15]

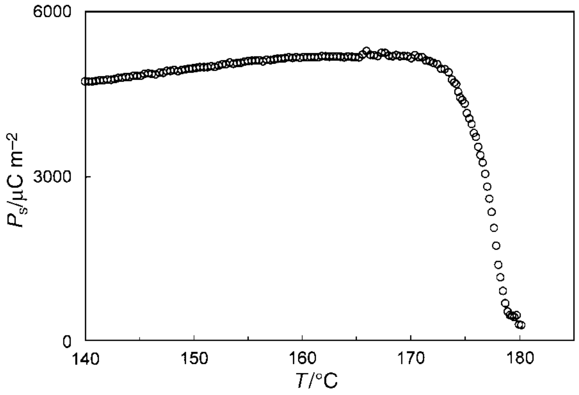


Fig. 4 Temperature variation of P_s for a fixed triangular wave field of 3.1 V µm^{-1}, 25 Hz.

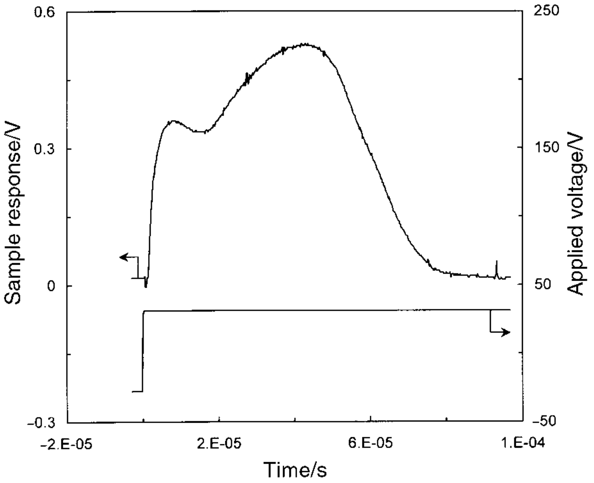


Fig. 5 Current response of the sample on application of 3.9 V µm^{-1}, 25 Hz square wave field.

X-Ray diffraction studies

X-Ray diffraction experiments were carried out on a non-oriented sample; the pattern obtained at 160 °C, along with the extracted intensity *vs.* 2θ profile is shown in Fig. 7. The diffuse character of the wide-angle peak ($\sim 20°$) indicates a liquid-like order within the smectic layer. In the small angle region two sharp reflections were seen with spacings 4.026 and 2.01 nm. The fact that the ratio of the two spacings is 2 and that the value for the first reflection is considerably smaller than the length of the molecule measured (5.46 nm) along the "bow axis" (also the director direction for the bent-core molecules) are also features commonly observed for the banana B_2 phase.

The above mentioned results bear a significant resemblance to the ones observed in the B_2 phase of banana-shaped compounds[4,16] The two types of electro-optic switching seen are supposed to correspond to those originating from the "racemic" and "homochiral" regions. In the homochiral regions, a reversal in the polarity of the field results in a rotation of the director between the two synclinic states. In contrast in the racemic regions, the two-switched states are anticlinic and therefore no rotation of Maltese cross would be observed. In view of these observations we tend to believe that the mesophase X of compound **1** is the B_2 banana phase.

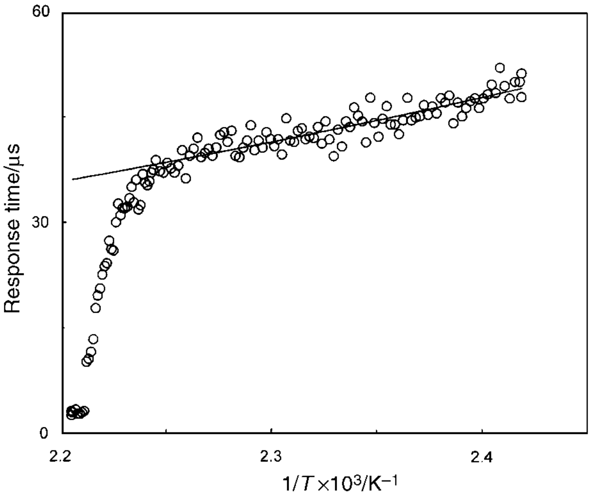


Fig. 6 Thermal variation of the response time (τ) as a function of the inverse temperature (1/T K^{-1}). The field applied was 3.9 V µm^{-1}, 25 Hz square wave. The solid line represents a fit of the data (5 °C below the isotropic transition temperature) to an Arrhenius expression. The activation energy calculated is about 10 kJ mol^{-1}. Notice that the data closer to the transition deviate from the Arrhenius behaviour.

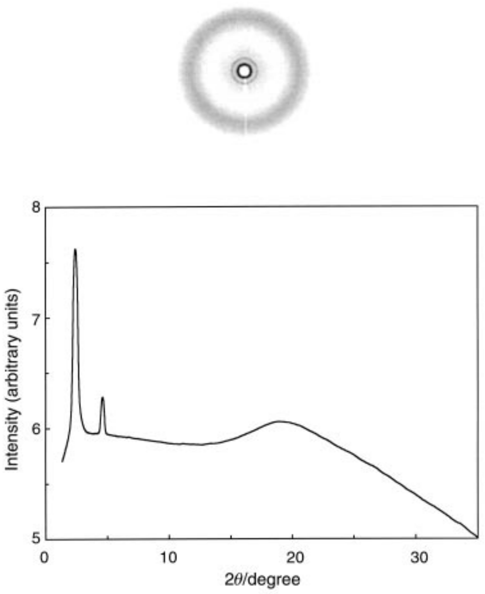


Fig. 7 X-Ray diffraction pattern (top) and the intensity *versus* 2θ profile (bottom) of the sample at 160 °C.

In conclusion, we have presented the synthesis, mesomorphic properties and electro-optic investigations of the first example of a salicylaldimine-based achiral banana-shaped liquid crystal. The novelty of the molecule originates from fact that the molecular structure consists of a thermally and hydrolytically stable salicylaldimine unit as a linear rigid segment attached to an angular central 1,3-disubstituted benzene nucleus. As we had expected the compound seems to be promising with regard to its stability to heat and moisture owing to the presence of intramolecular hydrogen bonding. It is well known that mesogens consisting of a salicylaldimine segment will have a higher clearing temperature, whereas the compound **1** has a clearing temperature that is comparable to any other related bent-core systems. Interestingly, it exhibits a switchable banana-mesophase (B_2) over a 60 °C temperature range. A systematic investigation focusing on molecular design and synthesis leading to such stable bent-cores is very much essential to stabilize switchable banana-mesophases existing over wide and convenient operating temperature ranges required for many practical applications. Presently we are investigating the higher and lower homologues of the compound **1**.

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