Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Bent-core V-shaped mesogens consisting of salicylaldimine mesogenic segments: synthesis and characterization of mesomorphic behaviour

C. V. Yelamaggad Corresponding author[a]; I. Shashikala[a]; D. S. Shankar Rao[a]; S. Krishna Prasad[a]
[a] Centre for Liquid Crystal Research, Bangalore 560 013, India

To cite this Article Yelamaggad Corresponding author, C. V. , Shashikala, I. , Rao, D. S. Shankar and Prasad, S. Krishna(2004) 'Bent-core V-shaped mesogens consisting of salicylaldimine mesogenic segments: synthesis and characterization of mesomorphic behaviour', Liquid Crystals, 31: 7, 1027 — 1036

To link to this Article: DOI: 10.1080/02678290410001716015

URL: http://dx.doi.org/10.1080/02678290410001716015

LIQUID CRYSTALS, VOL. 31, NO. 7, JULY 2004, 1027–1036

Taylor & Francis
Taylor & Francis Group

Bent-core V-shaped mesogens consisting of salicylaldimine mesogenic segments: synthesis and characterization of mesomorphic behaviour

C. V. YELAMAGGAD*, I SHASHIKALA, D. S. SHANKAR RAO and
S. KRISHNA PRASAD

Centre for Liquid Crystal Research, P.B.No.1329, Jalahalli, Bangalore 560 013,
India

(*Received 26 September 2003; in final form 26 February 2004; accepted 3 March 2004*)

A series of bent-core V-shaped mesogens consisting of salicylaldimine mesogenic segments have been synthesized and their mesomorphic behaviour characterized. In an attempt to understand structure–property relationships, the lengths of the terminal alkoxy chains have been varied from C_2 to C_{12}, C_{16} and C_{18}, resulting in 13 new bent-core V-shaped molecules. The thermal behaviour of these new compounds has been investigated by optical microscopy, calorimetry and X-ray diffraction studies. In general the compounds show conventional mesophases similar to those shown by calamitic LCs. The materials exhibit good thermal stability, even though their melting and clearing transition temperatures are high as a result of the presence of intramolecular hydrogen bonding between the H-atom of the hydroxyl group and the N-atom of the imine functionality. The phase appearing in the first member of the series with ethoxy chains is a nematic, while the C_3 to C_6 derivatives exhibit a smectic A phase as well as a nematic phase. The higher homologues, C_7 to C_{12}, C_{16} and C_{18}, show only the smectic A phase. X-ray studies reveal that the SmA phase has a partially bilayer (interdigitated) structure. Remarkably, in some cases, the smectic A phase supercools well below room temperature. It is apparent from our studies that increasing the length of the alkoxy chains promotes smectic behaviour, in agreement with the general observation made for such bent-core molecules.

1. 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 generally well understood. LCs with rod-like molecules exhibit nematic (N) and/or smectic (Sm) mesophases whereas LCs with flat disc-shaped molecules show N and/or columnar (Col) mesophases [3]. Over the past ten years or so there has been a resurgence of interest 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 shapes [4]. Such materials have been termed 'non-conventional LCs', some examples of which are oligomeric LCs, bent-core molecules, polycatenars, and dendrimers.

Of all the non-classical molecular architectures known to support liquid crystalline behaviour, bent-core molecules [5] attract a great deal of attention as they exhibit liquid crystallinity even though their molecular geometry deviates significantly from the classical rod or disc shapes. In fact, such molecules have been known since the days of Vorlander, who with Apel [6, 7] reported the first synthesis of bent-core 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 in the 1,2-positions gives bent-core V-shaped molecules [5*a*], whereas bent-core banana-shaped materials are formed when two mesogenic segments are covalently connected either to a benzene ring in the 1,3-positions or by an odd-numbered alkylene spacer (figure 1) [5*b*]. However it is now well established that the mesomorphic behaviour of these two classes of bent-core molecules are different and this may be attributed to the angle between the

*Author for correspondence; e-mail: yelamaggad@yahoo.com

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2004 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290410001716015

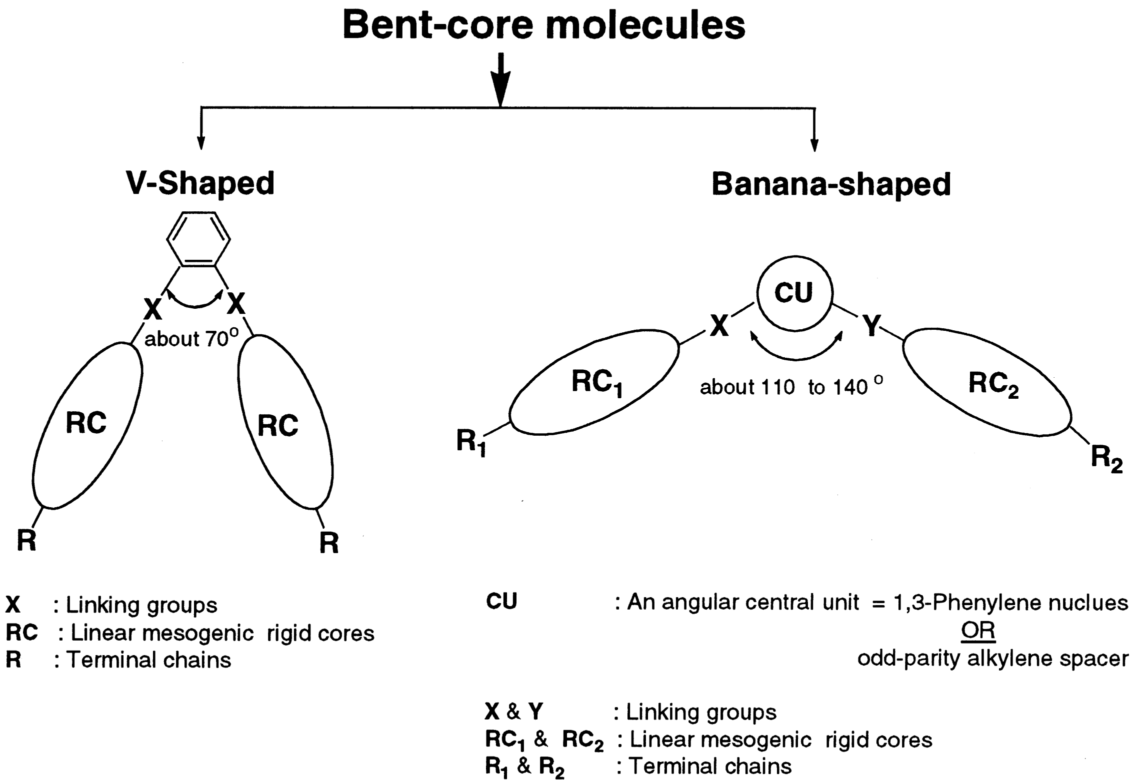
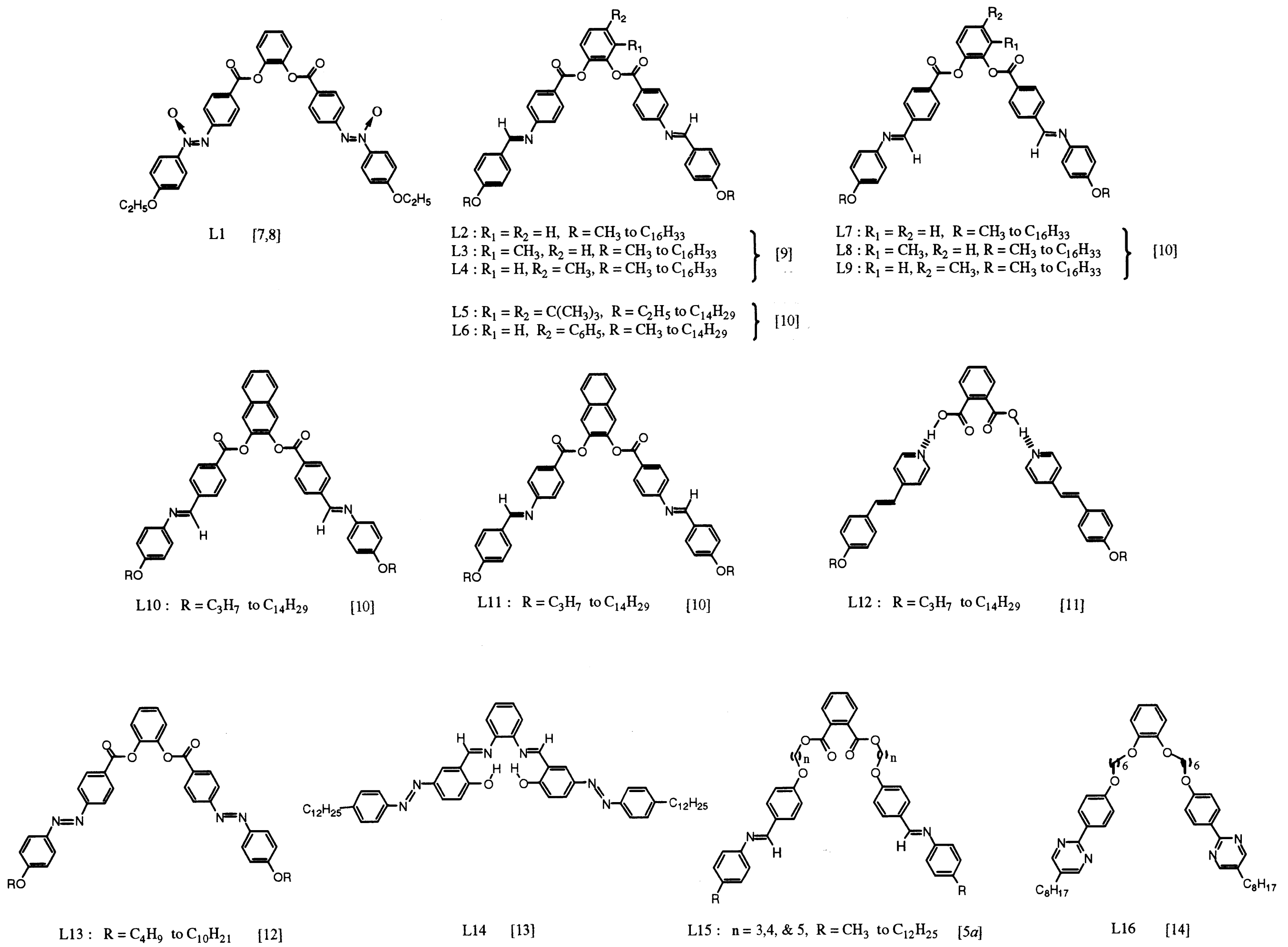


Figure 1. A general template for the molecular structures of bent-core V-shaped and banana-shaped molecules.

mesogenic segments (arms) attached to the central benzene nucleus (see figure 1). As we shall see later in detail, bent-core V-shaped molecules are known to exhibit mesophases similar to those shown by classical calamitic LCs, whereas banana-shaped mesogens exhibit new smectic phases including two-dimensional phases, which are not comparable to or miscible with the phases formed by calamitics. In this paper we focus attention on bent-core V-shaped molecules only.

Bent-core V-shaped compounds are also known as fused twins [4*e*] or U-shaped molecules [5*b*]. However, in this paper we shall adopt the term bent-core V-shaped mesogens. As mentioned already, Vorlander and Apel [7] were the first to report a bent-core V-shaped molecule, namely 1,2-phenylene bis[4-(ethoxyphenylazoxy)benzoate] (which we refer to as L1, and see figure 2 for molecular structure) and recently shown to exhibit a nematic phase [8]. Later, in 1991 Kuboshita *et al.* [9] reported the synthesis and characterization of the 1,2-phenylene bis[4-(4-alkoxybenzylideneamino)-benzoate]s (L2 series) and their 3- and 4-methyl substituted variants (L3 and L4 series). These three series of compounds were found to display nematic (N), smectic A (SmA), and smectic B (SmB) phases. In 1993 Matsuzaki and Matsunaga [10] reported different series of bent-core V-shaped molecules, namely the 4-*tert*-butyl-/phenyl-1,2-phenylene bis[4-(4-alkoxybenzylideneamino)benzoate]s (L5 and L6 series), the 1,2-phenylene bis[4-(4-alkoxyphenyliminomethyl)benzoate]s (L7 series) and their 3- and 4-methyl substituted variants (L8 and L9 series), the 2,3-naphthylene bis[4-(4-alkoxyphenyliminomethyl)benzoate]s (L10 series) and the bis[4-(4-alkoxybenzylideneamino)benzoate]s (L11 series). These 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 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 (L12). Recently, Prasad has reported a number of azobenzene-based bent-core V-shaped molecules (L13), which were found to exhibit N, SmA and crystal E phases [12]. More recently, Rao and Paul have described the synthesis and characterization of several bent-core molecules [13]. Among these, a bent-core V-shaped tetradentate ligand (L14), 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 compounds, there have been



L1 [7,8]

L2 : $R_1 = R_2 = H$, $R = CH_3$ to $C_{16}H_{33}$
L3 : $R_1 = CH_3$, $R_2 = H$, $R = CH_3$ to $C_{16}H_{33}$
L4 : $R_1 = H$, $R_2 = CH_3$, $R = CH_3$ to $C_{16}H_{33}$ [9]

L5 : $R_1 = R_2 = C(CH_3)_3$, $R = C_2H_5$ to $C_{14}H_{29}$
L6 : $R_1 = H$, $R_2 = C_6H_5$, $R = CH_3$ to $C_{14}H_{29}$ [10]

L7 : $R_1 = R_2 = H$, $R = CH_3$ to $C_{16}H_{33}$
L8 : $R_1 = CH_3$, $R_2 = H$, $R = CH_3$ to $C_{16}H_{33}$
L9 : $R_1 = H$, $R_2 = CH_3$, $R = CH_3$ to $C_{16}H_{33}$ [10]

L10 : $R = C_3H_7$ to $C_{14}H_{29}$ [10]

L11 : $R = C_3H_7$ to $C_{14}H_{29}$ [10]

L12 : $R = C_3H_7$ to $C_{14}H_{29}$ [11]

L13 : $R = C_4H_9$ to $C_{10}H_{21}$ [12]

L14 [13]

L15 : n = 3,4, & 5, $R = CH_3$ to $C_{12}H_{25}$ [5*a*]

L16 [14]

Figure 2. Molecular structures and references for various bent-core V-shaped molecules reported in the literature.

some interesting reports on new types of bent-core structure in which two mesogenic segments are connected to a benzene ring at the 1,2-positions through alkylene spacers, and these have been called bent-core V-shaped dimers. Attard and Douglass [5*a*] reported the early examples of such bent-core V-shaped dimeric LCs, the benzene-1,2-di(4-carboxybenzyliedene-4′-*n*-alkylanilines) (L15) in which the central benzene ring is connected to two Schiff's base mesogenic segments in the 1,2-positions through alkylene spacers. Among the four series of compounds described, the members of the two homologous series containing odd-parity alkylene spacers were found to show N and SmA phases as a function of terminal chain length. Materials having an even-parity alkylene spacer were found to be purely smectogenic. Xray studies revealed a 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 a C_6 alkylene spacer (L16). This compound was found to exhibit smectic-like layer ordering in the nematic phase, and unusual enthalpy changes 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], Schiff's base [9, 10], stilbazole [11], and azobenzene [12] mesogenic segments have been connected covalently in the 1,2-positions of a benzene ring to obtain bent-core V-shaped mesogens. In order to understand the underlying structure–property relationships further, different cores must now 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. To continue of our investigations of salicylaldimine-based non-conventional LCs, and in particular bent-core molecules [15], here we report the synthesis and characterization of the bent-core V-shaped molecules, the 1,2-phenylene bis[*N*-(2-hydroxy-4-*n*-alkoxyloxybenzylidene)-4′-aminobenzoate]s in which salicylaldimine segments have been connected covalently to catechol.

2. Results and discussion

2.1. *Synthesis and molecular structure characterization*

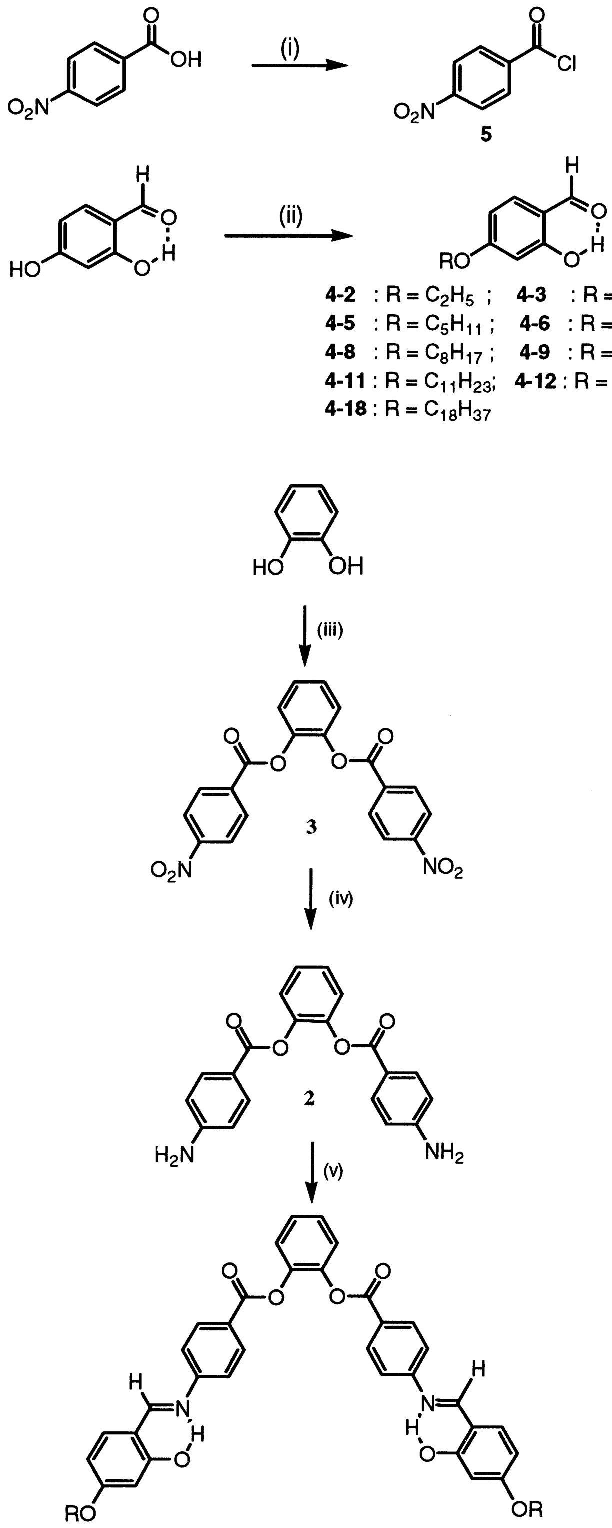
The target bent-core materials were synthesized as shown in the scheme. We envisaged that the proposed molecules could be obtained by condensing 4-*n*-alkoxy-2-hydroxybenzaldehydes (**4–5** to **4–18**) with diamine **2**, the 2-(4-aminobenzoyloxy)phenyl 4-aminobenzoate. Accordingly, diamine **2** was prepared by the catalytic hydrogenation of dinitro compound **3**, 2-(4-nitrobenzoyloxy)phenyl 4-nitrobenzoate, using Pd-C (10%) catalyst, which in turn was prepared by treating two moles of 4-nitrobenzoyl chloride (**5**) with one mole of catechol. The aldehydes **4–5** to **4–18** were synthesized by controlled O-alkylation of 2,4-dihydroxybenzaldehyde with 1-bromoalkanes using $KHCO_3$ as a mild base. Finally the aldehydes and diamine obtained were condensed under mild acidic conditions to obtain the proposed bent-core V-shaped compounds in reasonably good yield (70–80%).

The molecular structures of the bent-core compounds (**1–2**, to **1–12**, **1–16** and **1–18**) and their intermediates (**2**, **3** and **4–2** to **4–12**, **4–16** and **4–18**) were confirmed using spectroscopic analyses. As expected, the IR and ^{1}H NMR spectra of the target molecules are similar. The IR spectra show absorption bands in the region of ν_{max}/cm^{-1} 2917–2966, 1729–1749 and 1591–1597 due to C–H (paraffinic), C=O and C=N stretching vibrations, respectively. In the ^{1}H NMR spectra, the hydroxy (–OH) proton is seen at a high frequency, i.e. in the region $\delta = 13.3–13.2$, as it is involved in intramolecular hydrogen bonding. The imine (–CH=N–) proton gives a singlet in the region $\delta = 8.5–8.48$. The 18 aromatic protons appear as one doublet (d), and three multiplets (m) in the ranges $\delta = 8.1–8.12$, 7.46–7.40 to7.35–7.2, 7.29–7.25 to 7.2–7.19 and 6.57–6.47 to 6.47–6.43, respectively. The oxymethylene and other protons of the paraffinic chains appear at the expected positions with the appropriate splitting patterns. The ^{13}C NMR (SEFT, Spin Echo Fourier Transform) experiment was carried out for two representative compounds **1–11** and **1–16**. The spectra of both compounds were clearly identical and therefore we discuss only the spectral data for the compound **1–11**. In the ^{13}C SEFTspectrum, at higher frequencies (downfield) compound **1–11** shows seven positive signals (above the base line) at $\delta = 164.98$, 164.76, 164.52, 153.94, 143.33, 126.98 and 113.41, which are due to one carbonyl carbon and six quaternary carbons of the molecule. Eight negative peaks (appearing below the base line) at $\delta = 163.7$, 134.7, 132.3, 127.4, 124.3, 121.8, 108.8, and 102.2 are due to methine carbons. Thus the ^{13}C signals (see experimental section for details) were found to be in agreement with the proposed molecular structure. These spectral data, coupled with microanalytical data, unambiguously establish the molecular structures of the bent-core V-shaped molecules obtained in the present investigation.

2.2. *Thermal behaviour*

In order to establish the effects of varying the terminal alkoxy chain length on the mesomorphic behaviour, 13 homologues were synthesized and their mesomorphic behaviour characterized. The preliminary optical observations were performed using untreated clean glass slides. For confirmation of assignments, two differently surface-coated slides, one treated for homogeneous alignment, the other for homeotropic alignment were used. The transition temperatures and associated enthalpy changes are listed in the table. The first member of the series **1–2**, having ethoxy chains, exhibits an enantiotropic N phase that was identified from the observation of a characteristic marble texture when slides treated for planar orientation were used (figure 3). In a homeotropically-aligned sample, the N phase shows a pseudoisotropic texture, which flashed when subjected to shearing stress. The next homologue **1–3**, with propyloxy chains, was found to be dimorphic exhibiting an enantiotropic N phase and a monotropic SmA phase, while compounds **1–4** to **1–6** show two enantiotropic phases. The presence of the SmA phase was confirmed from the microscopic observation of the characteristic focal-conic texture in slides treated for planar orientation, and a dark field of view in slides treated for homeotropic orientation. When untreated slides were used, both the focal-conic and psuedoisotropic textures were observed. As can be seen in the table, all the higher homologues **1–7** to **1–12**, **1–16** and **1–18** exhibit only smectic behaviour. However it is interesting to note that compounds **1–5** to **1–10** behave differently from the other homologues, particularly, during cooling; as a representative case we describe the thermal behaviour of compound **1–10**.

For compound **1–10** optical microscopy reveals that during the first heating the crystal (Cr) melts to a SmA phase, which remains to the isotropic (I) phase, and upon subsequent cooling the characteristic focal-conic texture appears. No other textural change nor crystallization of the samples were seen before room



4-2 : R = C_2H_5 ; **4-3** : R = C_3H_7 ; **4-4** : R = C_4H_9 ;
4-5 : R = C_5H_{11} ; **4-6** : R = C_6H_{13} ; **4-7** : R = C_7H_{15} ;
4-8 : R = C_8H_{17} ; **4-9** : R = C_9H_{19} ; **4-10** : R = $C_{10}H_{21}$;
4-11 : R = $C_{11}H_{23}$; **4-12** : R = $C_{12}H_{25}$; **4-16** : R = $C_{16}H_{33}$;
4-18 : R = $C_{18}H_{37}$

1-2 : R = C_2H_5 ; **1-3** : R = C_3H_7 ; **1-4** : R = C_4H_9 ; **1-5** : R = C_5H_{11} ; **1-6** : R = C_6H_{13} ;
1-7 : R = C_7H_{15} ; **1-8** : R = C_8H_{17} ; **1-9** : R = C_9H_{19} ; **1-10** : R = $C_{10}H_{21}$; **1-11** : R = $C_{11}H_{23}$;
1-12 : R = $C_{12}H_{25}$; **1-16** : R = $C_{16}H_{33}$; **1-18** : R = $C_{18}H_{37}$

Scheme. Reagents and conditions: (i) PCl_5, reflux, 3 h; (ii) 1-bromoalkanes, $KHCO_3$, acetone, reflux, 12 h; (iii) **5**, pyridine, THF, 0°C (30 min) to rt, 12 h; (iv) H_2, Pd/C (10%), EtOAc, 15 psi, rt, 16 h; (v) **4–2** to **4–12**, **4–16** or **4–18**, EtOH, AcOH (catalytic), reflux, 2 h.

Table. Transition temperatures[a] (°C) and enthalpies ($J\,g^{-1}$) of 1,2-phenylene bis[*N*-(2-hydroxy-4-*n*-alkoxybenzylidene)-4′-aminobenzoate]s: Cr_1 and Cr_2 = crystal; SmA = Smectic A; N = Nematic phase; I = isotropic phase.

Compound	*R*	Cr_1	Heating Cooling	Cr_2	Heating Cooling	SmA	Heating Cooling	N	Heating Cooling	I
1–2	C_2H_5	●	195.8 (76.4) 128.9 (33.8)	—		—		●	207.6 (0.24) 200.7 (0.22)	●
1–3	C_3H_7	●	176.7 (66.9) 99.8 (27.1)	—		●	— 138.5 (0.4)	●	189.5 (0.3) 182.6 (0.3)	●
1–4	C_4H_9	●	164.8 (58.3) 149.7 (20.4)	—		●	176.1 (2) 168.5 (1.9)	●	193.7 (0.3) 191 (0.3)	●
1–5	C_5H_{11}	●	120.3 (54.1)^{c}	—		●	186.6^{b} 183.5 (4.1)	●	190.4 (6.3)^{b} 187.9 (0.5)	●
1–6	C_6H_{13}	●	124 (63.5)^{c}	—		●	184.1^{b} 179 (3.8)	●	187.5 (4.5)^{b} 182.4 (0.5)	●
1–7	C_7H_{15}	●	100.6 (46.8)	●	120.2 (25.4)^{c}	●	199 (4.4) 197.1 (4.0)	—		●
1–8	C_8H_{17}	●	103.1 (43.6)^{c}	—		●	195.4 (6.7) 194.2 (5.5)	—		●
1–9	C_9H_{19}	●	99 (48.7)	●	124.3 (55.9)^{c}	●	205.3 (6.5) 203.8 (5.5)	—		●
1–10	$C_{10}H_{21}$	●	98.4 (50.9)^{c}	—		●	207.3 (6.3) 206.5 (5.9)	—		●
1–11	$C_{11}H_{23}$	●	98.4 (49.7) 44.6 (19)	—		●	207.8 (6.4) 206.9 (6.4)	—		●
1–12	$C_{12}H_{25}$	●	95.9 (58.1) 49.1 (46)	—		●	208 (7.4) 207.1 (7.4)	—		●
1–16	$C_{16}H_{33}$	●	97.9 (86.7) 40.1 (40.8)	—		●	202.0 (6.7) 201.7 (6.4)	—		●
1–18	$C_{18}H_{37}$	●	92.8 (88.4)^{d}	●	103.9 (98.2) 53.8 (55.7)	●	181.4 (3.3) 180.5 (3.3)			●

[a] Peak temperatures in the DSC traces obtained during the first heating and subsequent cooling at 5°C min^{-1}.

[b] Although the SmA–N transition was observed under the microscope, this transition was not resolved in the DSC scan during heating; hence the ΔH value represents the combined enthalpy for both SmA–N and N–I transitions.

[c] DSC scans show that the SmA phase super-cools to −55°C, the lowest temperature that can be attained by the instrument but crystallizes at about room temperature during the subsequent heating cycle.

[d] An additional crystal–crystal transition was observed at 69.7°C (63.1 $J\,g^{-1}$).

temperature was reached (figure 4). The differential scanning calorimetric trace obtained during cooling (figure 5, C1) showed that the SmA phase persists to −55°C, the lowest temperature achievable with our instrument. On heating the sample from −55°C, an exothermic peak at 20°C and two endothermic peak at 97 and 205°C (figure 5, H2) appear. The exothermic

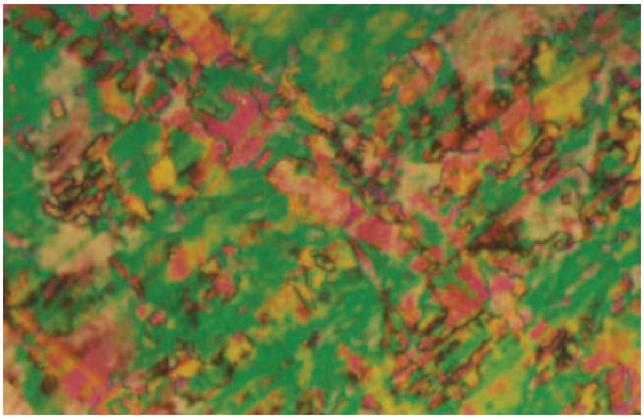


Figure 3. Photomicrograph of the marble texture observed for the N phase of the bent-core compound **1–2** at 180°C during cooling (magnification ×320).

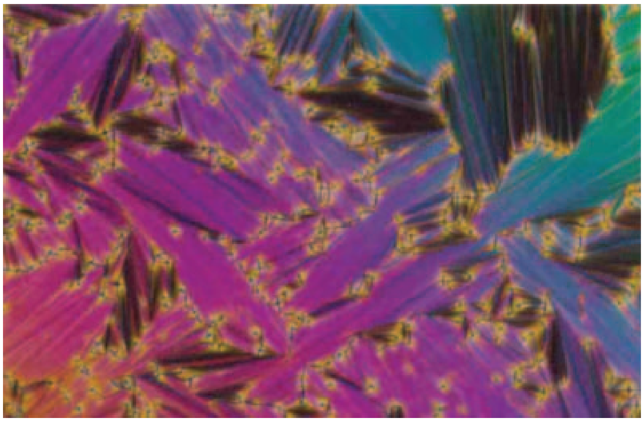


Figure 4. Photomicrograph of a typical focal-conic texture of the SmA phase observed for the bent-core V-shaped material **1–10** at room temperature (30°C) (magnification ×320).

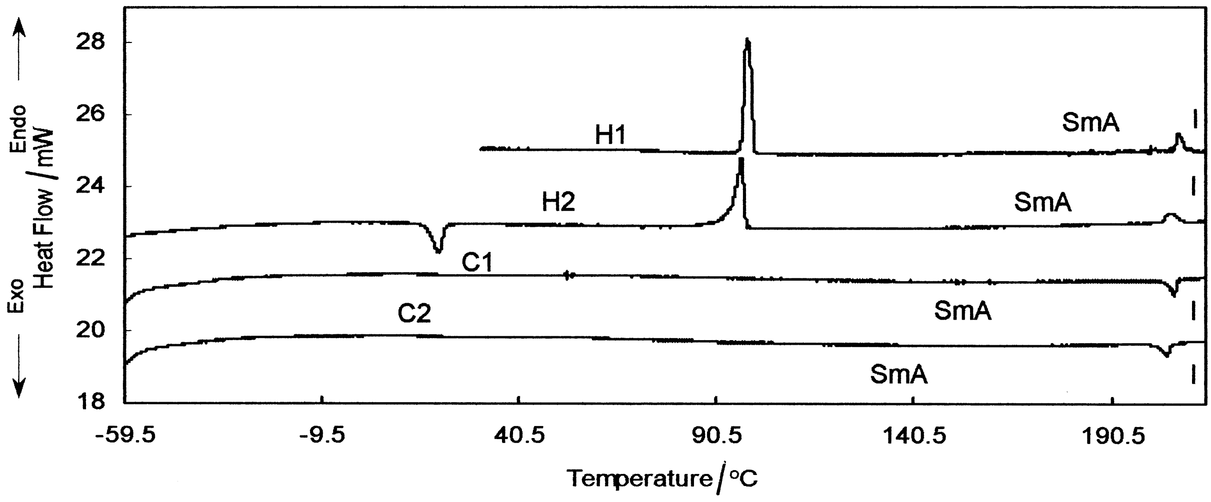


Figure 5. DSC traces obtained for the compound **1–10** at a rate of 5°C min^{-1}. H1 and H2 are first and second heating scans; C1 and C2 are first and second cooling scans.

peak is associated with the crystallization of the sample while the two endothermic transitions are due to crystal–melt and SmA–I transitions. The process of heating perhaps acts as a mechanical disturbance which results in crystallization. On the subsequent (second) cooling (figure 5, C2) of the compound from the isotropic phase, similar results were obtained as in the case of first cooling. Thus the transitions are highly reproducible during repeated heating and cooling cycles with the exception of the slight drift in clearing temperature. Similar observations were made for all the compounds **1–7** to **1–12**, **1–16** and **1–18**, with the SmA phases existing over a wide temperature range on cooling.

It is well known that the SmA phase, as well as showing the most commonly encountered monolayer structure, can also exist as other variations in which the constituent molecules are arranged in partially bilayer or bilayer structures. In order to determine the structure of the SmA phase formed by these compounds, X-ray diffraction studies were carried out on one lower (C_4: **1–4**) and one higher (C_{16}: **1–16**) homologue as representative cases, using an image plate detector (MAC Science DIP1030) as described elsewhere [16]. Unoriented samples contained in sealed Lindemann glass capillaries were irradiated with CuK_α rays obtained from a sealed tube generator (Enraf-Nonius) in conjunction with double mirror focusing optics. Figures 6 (*a*) and 6 (*b*) show the one-dimensional intensity vs. 2θ profiles extracted from the 2D-diffraction patterns (see inset of the figure) taken in the SmA phase for the compounds **1–4** and **1–16** at 164 and 190°C, respectively. As can be seen, the profiles for the two compounds are similar with two sharp peaks in the low angle region and a diffuse peak in the wide angle region. The spacings are 2.12, 1.06 and 0.46 nm for the C_4 homologue and 3.8, 1.9 and 0.47 nm for the C_{16} homologue; in both cases the spacings of the first two reflections are in the ratio 1:2.

To determine how the V-shaped molecules pack to give rise to these spacings, we first determined the dimensions of the molecules using a configuration energy minimization program (Chem3D, Cambridge). We first consider a possible arrangement in which the V-shaped molecules stack into layers such that their 'bow-string' direction is along the layer normal, in a similar fashion as to bent-core banana molecules see figure 7 (*a*). In order to account for the uniaxial nature of the phase (as has been shown by the observation of a 'Maltese cross' in the homeotropic configuration), the 'arrow direction' of the bow must be pointing in random directions in the plane. In materials composed of banana molecules a phase with such a structure is in fact observed and is referred to as the B_1 or the columnar phase. The B_1 phase however has in addition a two-dimensional modulation within the layer and as a consequence exhibits additional reflections at low angles. With the new material, we observe no additional reflections in the low angle region. Furthermore the measured layer spacing is much smaller than the bow-string length of 2.7 nm for the C_4 homologue. These two features eliminate the possibility that the mesophase is of the B_1 type. A second possibility is that the bow-string direction lies in the plane of the layer, see figure 7 (*b*). The length to be considered in this case is that along the arrow direction, which has been calculated to be 1.8 nm for the C_4 homologue. Thus the observed spacing of 2.12 nm would mean an

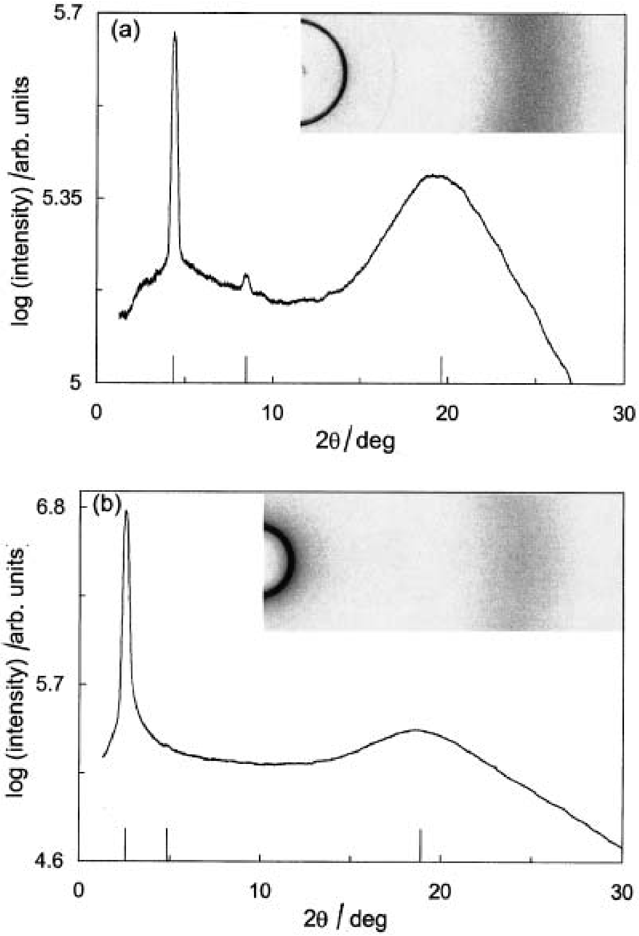


Figure 6. The XRD pattern and one-dimensional intensity versus 2θ profiles and obtained for the SmA phase of the compounds (*a*) **1–4** and (*b*) **1–16** at 164°C and 190°C, respectively. Notice in both the cases a diffuse peak in the wide angle region indicating liquid-like order, and two sharp reflections with spacings in the ratio 1:2 implying a lamellar structure.

interdigitation of the molecules between neighbouring layers. Of course, to avoid the layer being polar along the layer normal direction there will be as many 'up' molecules as 'down'. The structure of the mesophase for the C_{16} homologue is identical to that of the C_4 homologue and, therefore, we believe that the SmA phases exhibited by other homologues of the series also have a partially bilayer structure.

A comparison of the phase behaviour of the compounds synthesized here with the structurally related Schiff's bases, namely, the 1,2-phenylene bis[4-(4-*n*-alkoxybenzylideneamino)benzoate]s (L2 series), is noteworthy. As mentioned earlier, the L2 series of compounds have been reported to exhibit N and/or SmA and/or SmB phases [9]. However the bent-core molecules of the present investigation show N and/or SmA phases. The absence of the SmB phase and the high clearing temperatures of the present compounds could be attributed to the presence of the salicylaldimine moieties, which themselves are rigid owing to the existence of intramolecular hydrogen bonding. As can be seen in figure 8, the thermal range of the N phase is dramatically reduced even with a slight increase in the length of the alkoxy chains. This observation is in accordance with the general result that increasing the length of alkoxy chains promotes smectic behaviour in bent-core V-shaped mesogens.

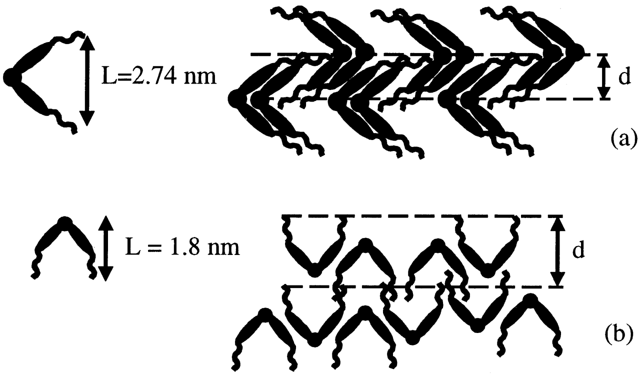


Figure 7. (*a*) A possible stacking of bent-core V-shaped molecules into layers with their 'bow-string' direction along the layer normal, similar to that of the layer stacking of banana-shaped molecules (*b*) Another possible arrangement in which the bow-string direction of the constituent molecules lies in the plane of the layer and the observed spacing suggests an interdigitation of the molecules.

3. Summary

In conclusion, we have studied the mesophase behaviour of a series of bent-core V-shaped mesogens, the 1,2-phenylene bis[*N*-(2-hydroxy-4-*n*-alkoxyloxybenzylidene)-4′-aminobenzoate]s, in which salicylaldimine segments have been connected covalently to catechol. The effect of the length of the alkoxy chains on the

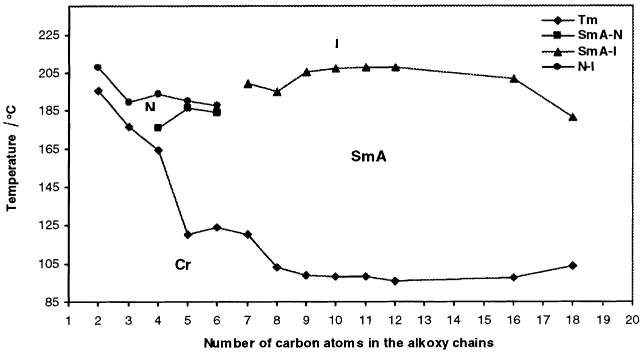


Figure 8. Dependence of the transition temperatures on the number of carbon atoms in the terminal alkoxy chains.

mesomorphic behaviour was examined by preparing 13 compounds in which the carbon number of the alkoxy chains is varied from 2 to 12, 16 and 18. The first member of the series with ethoxy chains exhibits only the nematic phase while intermediate homologues with C_3–C_6 alkoxy chains were found to display smectic A as well as nematic phases, with a significant increase in the thermal range of the smectic A phase. The higher homologues having C_7–C_{12}, C_{16} and C_{18} alkoxy chains show only the smectic A phase. Thus the mesomorphic behaviour of the present series of compounds is reminiscent of that seen for other bent-core V-shaped mesogens reported in the literature; specifically, increasing the length of alkoxy chains promotes smectic behaviour. When compared with corresponding Schiff's bases, the compounds exhibit higher melting and clearing transition temperatures and do not show the smectic B phase. This may be attributed to the presence of the salicylaldimine moieties which themselves are rigid owing to the existence of intramolecular hydrogen bonding.

4. Experimental

4.1. *Characterization*

1-Bromoalkanes and 2,4-hydroxybenzaldehyde were obtained from Aldrich while 4-nitrobenzioc acid and catechol were purchased from a local source and used without purification. Solvents were obtained from local sources and dried following standard procedures. The intermediate compounds were purified following column chromatographic separation techniques using silica gel (100–120 mesh) as a stationary phase while target compounds were purified by recrstallization. Thin layer chromatography was performed on aluminium sheets pre-coated with silica gel (Merck, Kieselge10, F254). IR spectra were recorded using a Perkin-Elmer Spectrum 1000 FTIR spectrometer. NMR spectra were recorded using Bruker DRX-500 (500 MHz) or DPX-200 (200 MHz) spectrometers. For ^{1}H NMR spectra, the chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane as internal standard. Microanalyses were obtained using a Eurovector elemental analyser model EA3000. The target molecules were investigated for liquid crystalline behaviour using a polarizing optical microscope (Leitz DMRXP) in conjunction with a programmable hot stage (Mettler FP90), and by differential scanning calorimetry (Perkin-Elmer DSC7).

4.2. *Synthesis*

4.2.1. *2-(4-Nitrobenzoyloxy)phenyl 4-nitrobenzoate (**3**)*

A solution of 4-nitrobenzoyl chloride (10.1 g, 54.5 mmol, 3 equiv.) in THF (30 ml) was added dropwise to a pre-cooled (5–10°C) solution of catechol (2 g, 18 mmol, 1 equiv.) in pyridine (25 ml) under nitrogen over a period of 15 min. The reaction mixture was allowed to attain room temperature (30°C) and stirring was continued for 24 h. The reaction mixture was concentrated, the thick mass obtained poured into ice-cold 2N HCl, and the resulting yellow solid filtered off. This solid product was dissolved in CH_2Cl_2 (50 ml), and the solution was washed with 5% aqueous NaOH (10 ml × 2), water (10 ml × 2) and dried over anhyd. Na_2SO_4. Evaporation of the solvent furnished a crude product that was purified by column chromatography using silica gel (100–200 mesh). Elution with EtOAc/hexane (1/10) furnished a yellow solid, which was further purified by repeated recrystallization from an absolute ethanol/CH_2Cl_2 mixture (9/1); yield 5.2 g (71%), pale yellow solid, m.p. 168.4°C, $R_f = 0.53$ in EtOAc/hexane (2/3). IR (KBr pellet): $\nu_{\max}$ in cm^{-1} 1741, 1519, 1498 and 1273. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.25 (s, 8H, Ar), 7.42 (s, 4H, Ar). FAB mass: $[M]^+$ calcd for $C_{20}H_{12}N_2O_8$. Elemental analysis: calcd (found) C 58.71 (58.38), H 2.96 (2.59), N 6.85 (6.77)%.

4.2.2. *2-(4-Aminobenzoyloxy)phenyl 4-aminobenzoate (**2**)*

A solution of compound **3** (5 g, 12.2 mmol) in dry EtOAc (50 ml) with activated Pd-C (10%) (0.5 g) was subjected to hydrogenation at 15 psi pressure over a period of 16 h. The reaction mixture was filtered through a celite and the filtrate was evaporated to dryness under vacuum, furnishing the pure product; pale brown solid, yield: 4.1 g (quantative), m.p: 186.4°C $R_f = 0.03$ in EtOAc/hexane (2/3). IR (KBr pellet): $\nu_{\max}$ in cm^{-1} 3354, 1698, 1635, 1595, 1514, 1283 and 1172. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.89 (d, $J = 8.6$ Hz, 4H, Ar), 7.29 (d, $J = 9.3$ Hz, 4H, Ar) and 6.58 (d, $J = 8.6$ Hz, 4H, Ar).

4.2.3. *General procedure for the preparation of 1,2-phenylene bis[N-(2-hydroxy-4-n-alkoxybenzylidene)-4′-aminobenzoate]s (**1–2** to **1–12**, **1–16** and **1–18**)*

A mixture of compound **2** (0.59 mmol, 1 equiv.), 4-*n*-alkoxy-2-hydroxy benzaldehydes (**4–2** to **4–12**, **4–16** or **4–18**) (1.18 mmol, 2 equiv.), absolute ethanol and a few traces of acetic acid was heated under reflux until a yellow solid precipitated (2 h). The crude product thus obtained was filtered off repeatedly washed with hot absolute ethanol. It was purified by repeated recrystallization from ethanol/CH_2Cl_2 (9/1). Representative characterization data are provided for compound **1–11**.

1,2-Phenylene bis[N-(2-hydroxy-4-*n*-undecyloxybenzylidene)-4′-aminobenzoate] (**1–11**): a yellow solid, IR

(KBr Pellet): $\nu_{\max}$ in cm^{-1} 2920, 1731, and 1595. ^{1}H NMR (200 MHz, $CDCl_3$): δ 13.29 (s, 2H, $2\times OH$), 8.48 (s, 2H, $2\times$CH–N), 8.10 (d, $J = 8.52$ Hz, 4H, Ar), 7.43–7.33 (m, 4H, Ar), 7.26–7.20 (m, 6H, Ar), 6.49–6.43 (m, 4H, Ar), 3.99 (t, $J = 6.53$ Hz, 4H, $2\times OCH_2$), 1.86–1.72 (m, 4H, $2\times CH_2$), 1.43–1.27 (m, 32H, $16\times$–CH_2) and 0.88 (t, $J = 6.4$ Hz, 6H, $2\times CH_3$). ^{13}C NMR (500 MHz, $CDCl_3$, spin echo FT): δ 164.98(C), 164.76 (C), 164.52 (C), 163.73 (CH), 153.94 (C), 143.33 (C), 134.70 (CH), 132.35 (CH), 127.41 (CH), 126.98 (C), 124.30 (CH), 121.83 (CH), 113.41 (C), 108.76 (CH), 102.21 (CH), 69.05 (OCH_2), 32.59 (CH_2), 30.27 (–CH_2), 30.04 (CH_2), 29.74 (CH_2), 26.67 (CH_2), 23.37 (CH_2) and 14.97 (CH_3). Elemental analysis: calcd (found) C 74.92 (74.43), H 7.64 (7.42), N 3.12 (2.79)%.

We sincerely thank Prof. S. Chandrasekhar for encouragement. I.S. gratefully acknowledges the Council of Scientific and Industrial Research (No. 01(1727)/02/EMR-II) for the award of a Senior Research Fellowship.

References

[1] REINITZER, F., 1888, *Monatsh. Chem.*, **9,** 421.

[2] CHANDRASEKHAR, S., SADASHIVA, B. K., and SURESH, K. A., 1997, *Pramana*, **9,** 471.

[3] (*a*) CHANDRASEKHAR, S., 1994, *Liquid Crystals*, 2nd Edn (Cambridge: Cambridge University Press); (*b*) DE GENNES, P. G., and PROST, J., 1993, *The Physics of Liquid Crystals* (Oxford: Oxford Science Publication); (*c*) BAHADUR, B., 1990, *Liquid Crystals Application and Uses*, Vol.1–3, (Singapore: World Scientific).

[4] (*a*) TSCHIERSKE, C., 1998, *J. mater. Chem.*, **8**, 1485; (*b*) TSCHIERSKE, C., 2001, *J. mater. Chem.*, **11**, 2647; (*c*) TSCHIERSKE, C., 2001, *Annu. Rep. prog. Chem.*, *C*, **97**, 191; (*d*) TSCHIERSKE, C., 2002, *Curr. opin. colloid interface Sci.*, **7**, 69; (*e*) DEMUS, D., 1989, *Liq. Cryst.*, **5**, 75.

[5] (*a*) ATTARD, G. S., and DOUGLASS, A. G., 1997, *Liq. Cryst.*, **22**, 349 and references therein; (*b*) PELZL, G., DIELE, S., and WEISSFLOG, W., 1999, *Adv. Mater.*, **11**, 707 and references therein.

[6] VORLANDER, D., 1929, *Ber. Dtsch. Chem. Ges.*, **62,** 2831.

[7] VORLANDER, D., and APEL, A., 1932, *Ber. Dtsch. Chem. Ges.*, **65,** 1101.

[8] PELZL, G., WIRTH, I., and WEISSFLOG, W., 2001, *Liq. Cryst.*, **28,** 969.

[9] KUBOSHITA, M., MATSUNAGA, Y., and MATSUZAKI, H., 1991, *Mol. Cryst. Liq. Cryst.*, **199,** 319.

[10] MATSUZAKI, H., and MATSUNAGA, Y., 1993, *Mol. Cryst. liq. Cryst.*, **14,** 105.

[11] KATO, T., ADACHI, H., FUJISHIMA, A., and FRECHET, J. M. J., 1992, *Chem. Lett.*, 265.

[12] PRASAD, V., 2001, *Liq. Cryst.*, **28,** 145.

[13] RAO, N. V. S., and PAUL, M. KR., 2003, *Mol. Cryst. liq. Cryst.*, **393,** 57.

[14] YOSHIZAWA, A., and YAMAGUCHI, A., 2002, *Chem. Commun.* 2060.

[15] (*a*) YELAMAGGAD, C. V., HIREMATH, U. S., ANITHA NAGAMANI, S., SHANKAR RAO, D. S., and KRISHNA PRASAD, S., 2001, *J. mater. Chem.*, **11**, 1818; (*b*) SHANKAR RAO, D. S., NAIR, G. G., KRISHNA PRASAD, S., ANITHA NAGAMANI, S., and YELAMAGGAD, C. V., 2001, *Liq. Cryst.*, **28**, 1239; (*c*) NAIR, G. G., KRISHNA PRASAD, S., HIREMATH, U. S., and YELAMAGGAD, C. V., 2001, *J. appl. Phys.*, **90**, 48; (*d*) YELAMAGGAD, C. V., ANITHA NAGAMANI, S., SHANKAR RAO, D. S., KRISHNA PRASAD, S., and JAKLI, A., 2002, *Liq. Cryst.*, **29**, 1181; (*e*) YELAMAGGAD, C. V., ANITHA NAGAMANI, S., HIREMATH, U. S SHANKAR RAO, D. S., and KRISHNA PRASAD, S., 2002, *Liq. Cryst.*, **29**, 1401.

[16] KRISHNA PRASAD, S., SHANKAR RAO, D. S., CHANDRASEKHAR, S., and KUMAR, S., 2003, *Mol. Cryst. liq. Cryst.*, **396,** 121.