Blue Phase, Smectic Fluids, and Unprecedented Sequences in Liquid Crystal Dimers

Channabasaveshwar V. Yelamaggad,*,[†]
Indudhara Swamy Shashikala,[†] Guangxun Liao,[§]
Doddamane S. Shankar Rao,[†] Subbarao Krishna Prasad,[†]
Quan Li,[§] and Antal Jakli[§]

Centre for Liquid Crystal Research, Jalahalli, Bangalore 560 013, India, and Liquid Crystal Institute, Kent State University, Kent, Ohio 44240

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In supramolecular chemistry, the interplay among molecular architecture, chirality, molecular order, and macroscopic properties is of great interest from fundamental and life science view points as well as for attractive application in materials science.[1] Liquid crystals (LCs) display macroscopic chiral structures, viz. blue phases (BP), chiral nematic (N*), twist grain boundary (TGB), and chiral smectic C (SmC*) phases, when they possess chiral molecules.[2] However, recently, there has been a spectacular exception that achiral bent-core mesogens display polar order and macroscopic chirality spontaneously in the form of electrically switchable smectic (SmCP or B_2) phases,[3] two-dimensional (Col or B_1)[4] fluids, and helical superstructures (B_7).[5] The origin of chirality (polar order) in these structures is an arguably important topic but is presently attributed to two symmetry-breaking instabilities: a directed packing and a tilt of the molecules.[5,6] Obviously, from the viewpoint of scientific curiosity, the concept of molecular chirality can be introduced in achiral banana-shaped molecules to understand the effect on the thermal behavior, which results from the interplay between molecular dissymmetry and bent conformation.

In this direction, there have been several interesting reports of the bent-core molecules either being doped with chiral host rodlike LC media[7] or having asymmetric carbon centers in the form of chiral alkyl tails[8] or present within the molecule.[9] Remarkably, the bent cores are found to alter the chirality (the helical twisting power, HTP) of the host optically active molecules,[7] whereas the bent cores with chiral tails show either the SmCP [8a,b] or SmC*[8c] originating from the polar order due to molecular chirality or directed packing of bent cores, respectively. In addition, new phase sequences have been discovered in such chiral molecular systems.[9] On the basis of the widespread theme of covalently linking mesogens of different shapes to control microscopic and macroscopic structures that bridge the gap between different class of liquid crystals,[10] we report here the synthesis and thermal behavior of all together new LC dimers featuring an achiral bent core tethered to a chiral pro-mesogenic rodlike segment through a flexible spacer varying in its length and parity. We reasonably envisaged that the bulkiness of the cholesterol entity and parity of the spacer enforce, respectively, the stereochemical restraints and conformations of these molecules, leading to interesting thermal behavior.[11] The molecular structures of the eight dimers, the Schiff bases **1a**−**4a** and their salicyladimine analogues **1b**−**4b**, synthesized by acid-catalyzed condensation of various aldehydes with an amine (see the Supporting Information for details) are shown in Figure 1. The phase-transition behavior of these dimers assessed with the help of several complimentary studies is summarized in Table 1.

The LC property of the dimers has a remarkable dependence on the all-trans shape conformation of the molecules as a result of the parity of the flexible spacer joining the two different anisometric segments, which we elaborate as follows. The imines **1a**, **3a**, and **4a** and their salicylaldimine analogues **1b**, **3b**, and **4b** having an even-parity (the sum of *n* and C of CO) spacer display a remarkable transitional behavior. These compounds, for example, **1a** and **1b**, either placed between clean glass slides or treated for planar or homeotropic geometry, and then cooled slowly (0.1 to 2 °C/min) from the isotropic (I) phase, show a mesophase (M) having foggy appearance with a very faint color background in both the transmission as well as the reflection modes (images a and b of Figure 2). The optical transmission as well as electrical resistivity (at 100 kHz) (Figure 2c; see the Supporting Information for the plots for **1b**) and differential scanning calorimetric (DSC) studies (see the Supporting Information) evidence an I−M phase transition. On cooling

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* Corresponding author. Tel.: 91-80-28381119. Fax: 91-80-28382044. E-mail: yelamaggad@yahoo.com.

[†] Centre for Liquid Crystal Research.

[§] Kent State University.

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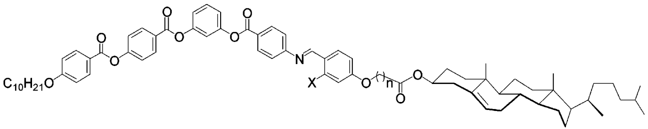

1a : n = 3, X = H; **2a**: n = 4, X = H; **3a**: n = 5, X = H; **4a**: n = 7, X = H
1b : n = 3, X = OH; **2b**: n = 4, X = OH; **3b**: n = 5, X = OH; **4b**: n = 7, X = OH

Figure 1. Molecular structures of chiral bent-rod imines **1a**−**4a** and salicylaldimines **1b**−**4b**.

Table 1. Phase-Transition Temperatures (°C)[a] and Enthalpies (J/g) of Dimers[b]

	phase sequence
1a	I 170.2 (0.7) BP 148[c] N* 124.1 (9.5) M_{x1}[d] T_g[e]
1b	I 183.8 (0.6) BP 164[c] N* 154.2 (11) M_{x1}[d] T_g[e]
2a	I 135.5 (9.1) Col_r 75.1 (5.8) Cr
2b	I 147.7 (8.8) Col_r 81 (6.4) Cr
3a	I 164 (0.6) BP 148[c] N* 118.4 (5.6) Col_{r1}[d] 112.6 (1.1) Col_{r2}[d] 108.9 (2.3) M_{x2}[c] 93 (28) Cr
3b	I 174.5 (0.8) BP 152[c] N* 141.3 (10.5) M_{x3}[d] 52[c] T_g
4a	I 151.3 (1) BP 137[c] N* 114.7 (6.7) Col_r[d] 77.7 (9) Cr
4b	I 161.1 (0.6) BP 144[c] N*[d] 138.9 (9) Col_r[d] 94.8 (17.8) Cr

[a] Peak temperatures in the DSC profiles obtained during the first heating and cooling cycles at a rate of 5 °C/min (except for **3a**). [b] BP = blue phase III; N* = chiral nematic phase; M_{x1}, M_{x2} and M_{x3} = unknown tilted smectic mesophases; Col_r (B_1) = rectangular columnar phase; Col_{r1} and Col_{r2} = two different columnar phases; T_g = glassy state; I = isotropic phase [c] The transition to this phase was observed under the polarizing optical microscope and was too weak to be recognized in the DSC thermogram. [d] A monotropic phase. [e] The freezing of the mesophase into the glassy state happens over a range of temperatures.

these samples below the M phase, the N* phase with a typical Grandjean planar texture having a bright blue color appears. In a planar wedge cell (0.1° wedge angle) preparation, the N* phase showed, unlike the M phase, Grandjean−Cano (GC) lines as expected. In the UV−vis spectra, the absorption signals were weak for both the Iso and M phases, whereas the N* phase showed a strong absorption maximum (λ_{max} = 433−480 nm) (Figure 2d; see the Supporting Information for the spectra of **1b**). The M phase showed a broad CD band (more than 100 nm centered around 418 nm). The intensity of this band increased monotonically on lowering the temperature (Figure 2e; see the Supporting Information for the plot for **1b**). These complementary studies suggest that the M phase of dimers **1a**, **1b**, **3a**, **3b**, **4a**, and **4b** is amorphous blue phase (BPIII), which exists over a wide thermal (14−22 °C) range, the highest range ever known for any single component system including a T-shaped mesogen.[2,13] This observation seems to compliment a recent invention[7c] that guest bent cores induce BP (I and II) in the host rodlike LCs. In this case, the BP thermal range could hardly exceed 2 °C, because of the limited miscibility of the guest−host systems. Remarkably, in our study, the covalent linking of such guest−host systems ensured the wide thermal range of BP.

The dimers **1a** and **1b** exhibit an identical tilted smectic phase (M_{x1}) below the N*. On cooling **1b** from the isotropic phase, M_{x1} appears with a spherulitic pattern (Figure 3a) for planar or homeotropic conditions. The X-ray diffraction (XRD) pattern obtained for **1b** at 140 °C (Figure 3b) exhibits a sharp reflection with d (spacing) = 48.1 Å in the low-angle region and a diffuse one in the wide-angle region (d = 4.9 Å). Because the measured length (l) of **1b** in its all-trans geometry is ~58 Å, much higher than d = 48.1 Å, this suggesting that the M_{x1} phase has a tilted structure. An electro-optic switching study was performed for this sample contained in a 5 μm cell coated for planar alignment. When a square wave field was applied (2−3 V/μm), monostable domains appear and an electroclinic (linear) type of switching was observed (images c and d of Figure 3) without any threshold. The field causes changes in the textural pattern; focal-conic defects appear that remain even after the field is removed. On application of a triangular wave field (up to 10 V/μm or even higher), the spontaneous polarization (P_s) peak could not be seen, although a broad hump persisted (see the Supporting Information).

The dimers **2a** and **2b** with C_5-(odd) spacers exhibit a diverse behavior, with much lower transition temperatures compared to other dimers. This clearly indicates they have a pronounced bent conformation see the Supporting Information. When cooled from the isotropic phase, they show a dendritic pattern that coalesces to a mosaic texture quite similar to that for the B_1 phase, also regarded as a columnar phase (see the Supporting Information). XRD studies carried out for a representative sample **2b** confirmed the existence of a 2D rectangular lattice (see the Supporting Information). Such a structure originates from the formation of ribbonlike segents of the smectic layers that organize such that the bent direction of the molecules in adjacent ribbons is antiparallel, leading to an escape from the macroscopic polar order.[4b]

The imine **3a** displays a rich but complicated polymorphic sequence. When the sample is cooled from the N* phase, first a mesophase appears at 118.4 °C with a fan-shaped focal-conic-like texture (Figure 4a) that subsequently transforms to another phase at 112.6 °C, marked by the appearance of very fine striations on the focal-conics (Figure 4b). The thermal signatures due to these transitions were seen in the DSC profile obtained during the cooling mode at a rate of 2 °C/min; their enthalpies were found to be 5.6 and 1.1 J/g, respectively (see the Supporting Information). The XRD 1D diagrams of these two phases obtained at 115 °C (Figure 4c) and 110 °C (see the Supporting Information) show a similar pattern featuring three sharp reflections, with d values 43.1, 30.3, and 18.6 Å and 45, 30.1, and 18.6 Å, respectively, in the small-angle region in addition to diffuse wide-angle scattering with d = 4.8 Å. In both cases, the low-angle reflections were indexed as {2,0}, {1,1}, and {4,1}, indicating a 2D rectangular lattice characteristic of the Col_r (B_1) phase. Because the textural patterns are different on the basis of on the DSC data, we suggest the presence of two columnar phases: Col_{r1} and Col_{r2}. Furthermore, these phases were found to be inert to the electrical field. On the sample being cooled below the Col_{r2} phase, a tilted smectic (M_{x2}) phase occurs at 109 °C (ΔH = 2.3 J/g) that subsequently transforms in to a crystalline state (93 °C).

The M_{x2} phase shows a nonspecific grainy pattern (see the Supporting Information) unlike the M_{x1} phase. However, the XRD profile (see the Supporting Information) derived from the 2D pattern showed a reflection with a spacing of 45.1 Å (whereas l = 65 Å) in the small-angle region and a diffuse peak in the wide-angle region at 4.7 Å, suggesting a tilted organization of molecules within the smectic layer. On application of a triangular wave field (8−10 V/μm), ferro-

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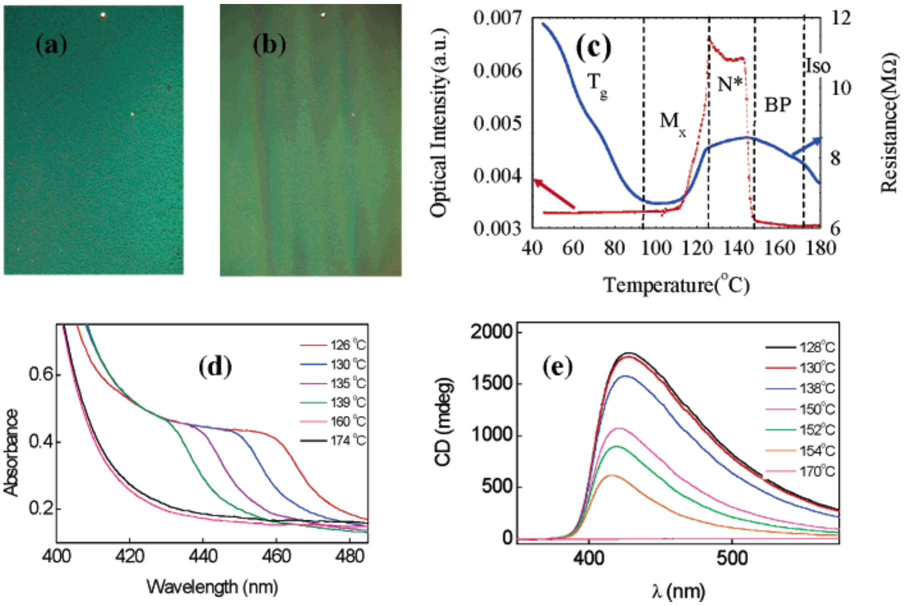

Figure 2. (a, b) Photomicrograph of the BPIII seen at 173 °C under polarizing microscope in the transmission and reflection modes, respectively, for the dimer **1b**; (c) the intensity as well as resistance measurement profiles obtained for **1a**; (d, e) UV−vis and CD spectra obtained for **1a** (as a function of temperature) in the region of I-BPIII-N*.

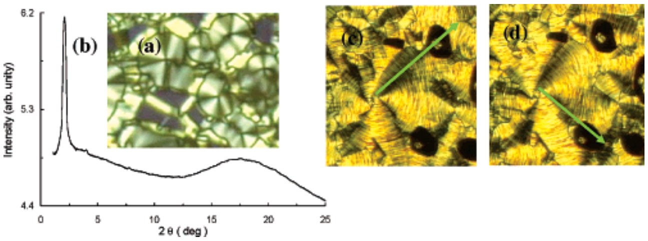

Figure 3. (a) Microphotograph of the texture, (b) 1D intensity vs 2θ profile, and photomicrographs of the domains (c) $E = 0$ and (d) $E = 2$ V/μm obtained for the M_{x1} phase of **1b**.

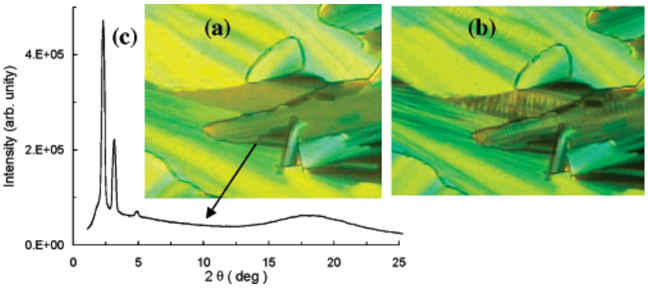

Figure 4. (a) Microphotograph of the texture, (c) 1D intensity vs 2θ profile obtained for the Col_{r1} phase of **3a** at 115 °C. (b) Microphotograph taken for the Col_{r2} phase of **3a** at 110 °C.

electric switching was observed with a P_s value of about 15 nC/cm^2 (see the Supporting Information). In case of close-packed bent-core structures, the P_s is typically well more than 100 nC/cm^2, which requires larger thresholds. Thus, the P_s of the M_{x2} phase is solely due to the chirality and tilt of the molecules, suggesting that it may have a structure similar to that of the SmC* phase, although optical textures do not confirm it. This structure may originate from the alternate arrangement of bulky cholesterol units to avoid splay of the director or bend of the layers, thereby preserving the head−tail symmetry. Thus, a phase sequence I−BPIII−N*−Col_{r1}−Col_{r2}−M_{x2}, the first of its kind, was established and further evidenced by the optical intensity and resistance measurement studies as shown in the Supporting Information. The occurrence of a polar smectic phase (like SmC*) below the Col phase is intriguing[9] and was unknown hitherto. The dimer **3b** displayed a rather simple phase sequence, viz. I−BPIII−N*−M_{x3}−T_g (a detailed study on the M_{x3} phase has been reported recently[14]), in which the Col structure is absent. The important feature of **3b**, as mentioned earlier, is that the BPIII exists over a wide thermal range (∼20 °C).

The dimers **4a** and **4b** possessing a C_8-spacer exhibit a Col_r (B_1) phase below the N* phase. The existence of a Col_r (B_1) phase was evidenced by the observation of the textural pattern coupled with XRD data (see the Supporting Information). Thus, these compounds form a Col structure at the expense of a smectic phase, clearly indicating that the length of the spacer also influences the transitional behavior. It is worth mentioning that the phase sequences of all dimers are highly reproducible over multiple heating and cooling cycles, indicating their remarkable thermal stability.

In summary, we have reported the synthesis and characterization of novel dimers in which an achiral bent-core is covalently tethered to a bulky chiral rodlike mesogen through an odd−even parity alkylene spacer. Such a molecular design, the first of its kind, favors the formation of an amorphous BP phase over the longest thermal range ever reported. In addition, this dimeric design leads to polar smectic fluids and new phase sequences originating from the interplay between the shape anisotropy of the two mesogenic segments as well as parity and length of the flexible spacer.

Supporting Information Available: General information, synthesis and characterization, experimental details, and additional physical characterization data; Figure 5 showing ferroelectric switching, optical intensity, and resistance measurement studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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