Soft Matter

Optically Biaxial, Re-entrant and Frustrated Mesophases in Chiral, Non-symmetric Liquid Crystal Dimers and Binary Mixtures

Vediappen Padmini,^[a, b] Palakurthy Nani Babu,^[a] Geetha G. Nair,^[a] D. S. Shankar Rao,^[a] and Channabasaveshwar V. Yelamaggad*^[a]

Abstract: Sixteen optically active, non-symmetric dimers, in which cyanobiphenyl and salicylaldimine mesogens are interlinked by a flexible spacer, were synthesized and characterized. While the terminal chiral tail, in the form of either (R)-2-octyloxy or (S)-2-octyloxy chain attached to salicylaldimine core, was held constant, the number of methylene units in the spacer was varied from 3 to 10 affording eight pairs of (R & S) enantiomers. They were probed for their thermal properties with the aid of orthoscopy, conoscopy, differential scanning calorimetry and X-ray powder diffraction. In addition, the binary mixture study was carried out using chiral and achiral dimers with the intensions of stabilizing optically biaxial phase/s, re-entrant phases and important phase sequences. Notably, one of the chiral dimers as well as some mixtures exhibited a biaxial smectic A (SmA_b) phase appearing between a uniaxial SmA and a re-entrant uniaxial SmA phases. The mesophases such as chiral nematic

Introduction

Over the past two decades or so, tremendous progress has been made towards the development of non-conventional liquid crystals (LCs) through the rational molecular design and bottom-up synthesis.^[1-31] These hybrid mesogens differ in their shape-anisotropy and phase transitional behavior from the conventional LCs. They comprise molecular entities such as flexible units, that is, tails and spacers (hydrocarbons/fluorocarbons/hydrophobic–hydrophilic units/carbisilanes/polysilanes etc.) and functional rigid mesogenic and/or non-mesogenic/

[a]	Dr. V. Padmini, Dr. P. N. Babu, Dr. G. G. Nair, Dr. D. S. S. Rao,
	Dr. C. V. Yelamaggad
	Centre for Nano and Soft Matter Sciences
	P. B. No. 1329, Prof. U. R. Rao Road, Jalahalli, Bengaluru 560013 (India)
	Fax: (+ 91)80-28382044
	E-mail: yelamaggad@cens.res.in
	yelamaggad@gmail.com
[b]	Dr. V. Padmini
	Department of Organic Chemistry
	School of Chemistry, Madurai Kamaraj University
	Madurai 625021, Tamil Nadu (India)
D	Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/ asia 201600918

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(N*) and frustrated phases viz., blue phases (BPs) and twist grain boundary (TGB) phases, were also found to occur in most of the dimers and mixtures. X-ray diffraction studies revealed that the dimers possessing oxybutoxy and oxypentoxy spacers show interdigitated (SmA_d) phase where smectic periodicity is over 1.4 times the molecular length; whereas in the intercalated SmA (SmA_c) phase formed by a dimer having oxydecoxy spacer the periodicity was found to be approximately half the molecular length. The handedness of the helical structure of the N* phases formed by two enantiomers was examined with the aid of CD measurements; as expected, these enantiomers showed optical activities of equal magnitudes but with opposite signs. Overall, it appears that the chiral dimers and mixtures presented herein may serve as model systems in design and developing novel materials exhibiting the apolar SmA_b phase possessing D_{2h} symmetry and nematic-type biaxiality.

self-complementing (H-bonding) cores. In fact, these represent a rich family of LC materials as they have provided strategies to incorporate the functional molecular components of choice. They, being multifunctional hybrid materials, have the ability to revolutionize materials science,^[1-9] the medical field^[12, 32-38] and applied research,^[11, 13, 19, 23] as they self-assemble and self-organize inherently into novel hierarchical fluid structures with exceptionally improved and easily tuneable/addressable characteristics; moreover, they respond well to external stimuli.

It is well demonstrated that liquid-crystal morphologies of these systems can be modulated to a large extent by varying the numbers, polarity, compatibility, size, shape, etc. of rigid cores as well as the length and parity of the spacers.^[1–30] For example, the influence of the latter parameter is prominently seen in LC dimers in which two mesogens are covalently bound to each other in an end-to-end manner via a flexible spacer.^[28–31,39–57] In particular, their phase transitional properties are governed by the spacer parity as it determines the conformation (geometry/overall molecular shape) of the dimeric mesogens. The dimers with an even-parity spacer, existing in its *all-trans* form, possess a zig-zag shape wherein the constituent mesogens remain parallel to each other. On the contrary, the dimers comprising an odd-parity spacer have a bent-conformation/banana-shape in which the mesogenic cores incline



with respect to one another.^[28-31] They can be broadly classified into two categories: (a) symmetric dimers, wherein two mesogenic cores are chemically similar and (b) non-symmetric dimers, which comprise two chemically different mesogens.^[28-30] Symmetric dimers are known to show a rich smectic polymorphism; remarkably, the existence of a twist-bend nematic (N_{tb}) phase signifying a structural correlation between the uniaxial nematic (N) and the chiral nematic N* phases has been reported in an achiral symmetric dimer having an oddnumbered spacer.[47] Non-symmetric dimers, unlike their symmetric counterparts, show intercalated and interdigitated phases. Molecular chirality profoundly influences the phase transitional properties of both symmetric and non-symmetric dimers.^[28-31,52] A wide variety of both types of chiral dimers have been studied to primarily figure out the influence of the number of carbon atoms of the central flexible spacer, besides other structural parameters, on the chirality of the LC phases.^[28-31,52]

We have been actively involved in the design, synthesis and characterization of such chiral oligomers primarily to understand the structure–property correlations; in particular, our work has largely focused on optically active non-symmetric dimers as they exhibit new mesophases, unprecedented sequences, frustrated phases, etc.^[52, 54, 55] In 2009, for example, we observed that a chiral non-symmetric LC dimer made by covalently tethering cyanobiphenyl and salicyladimine cores via

a heptamethylene spacer exhibits a new phase sequence, namely, blue phase (BP)-chiral nematic (N*)-twist grain boundary (TGB)-uniaxial smectic A (SmA)-biaxial smectic A (SmA_b)uniaxial smectic A (SmA) phases; the SmA phase exhibiting reentrance is believed to stem from dipolar and steric factors.^[54] Inspired by these findings, we intended to undertake a systematic investigation on the variants of this dimer so as to understand the correlation between molecular structure and LC properties. Herein, we report on the synthesis and characterization of sixteen non-symmetric dimers (eight enantiomeric pairs); in this study, the aforesaid dimer is also included for the sake of comparison and completeness. As shown in Scheme 1, each pair of enantiomers comprise (R)-2-octyloxy and (S)-2-octyloxy chiral tails and the number of methylene units in the flexible spacer has been varied from 3 to 10. Besides, we have prepared binary systems by mixing one of the (R)-enantiomers, I(R)-7, and a known analogous achiral dimer^[58] in varying proportions.

Results and Discussion

Synthesis and molecular structural characterization

Scheme 2 shows the synthetic steps followed to prepare the eight pairs of enantiomers. To begin with, 4'-hydroxy-4-cyanobiphenyl was alkylated with α,ω -dibromoalkanes in the pres-



I 140.8 (1.1) N 127.1 SmA 96.5 SmA_b 82.5 (64.3) Cr

Scheme 1. Molecular structures of fifteen optically active, nonsymmetric dimers synthesized and characterized (a) and the known dimers, I(R)-7 [54] and I-5 [58] used for binary mixture studies (b).

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Scheme 2. Synthesis of optically active, non-symmetric dimers. Reagents and conditions: (i) Dibromoalkane, K₂CO₃, KI (cat.), butanone, reflux, 12 h; (ii) 2,4-dihydroxybenzaldehyde, K₂CO₃, KI (cat.), butanone, reflux, 12 h; (iii) (S)-(+)-2-octanol, Ph₃P, DIAD,THF, rt, 18 h; (iv) (R)-(-)-2-octanol, Ph₃P, DIAD,THF, rt, 18 h; (v) H₂, (1 atm, balloon), 10 % Pd-C, THF, rt, 4 h; (vi) ethanol, acetic acid (cat.), reflux, 4 h.

ence of anhydrous K_2CO_3 in butanone to obtain 4'-((ω -bromoalkyl)oxy)-4-cyanobiphenyls (1 a-h) in good yields.[59-61] The reaction of 2,4-dihydroxybenzaldehyde with cyanobiphenyls (1 a-h) in the presence of a mild base in butanone yielded the respective O-alkylated products, namely, 4'-((ω -(4-formyl-3-hydroxyphenoxy)alkyl)oxy)-4-cyanobiphenyls (2 a-h).^[58-62] Under Mitsunobu reaction conditions,^[63] 4-nitrophenol was O-alkylated with the (S)- and (R)-2-octanol, to obtain (R)-4-(octan-2-yloxy)nitrobenzene (3) and (5)-4-(octan-2-yloxy)nitrobenzenes (5),^[64–68] these nitro materials were catalytically hydrogenated using H₂ (1 atm, balloon) and Pd/C (10%) in THF, to obtain the respective (R)-4-(octan-2-yloxy)aniline (4) and (S)-4-(octan-2yloxy)aniline (6) in notable yields.^[64-68] In the final step, anilines 4 and 6 were condensed with aldehydes 2a-h in the presence of a weak acid in ethanol to obtain the targeted optically active, non-symmetric dimers in excellent yields. The synthetic procedure for the target dimers and their molecular structural characterization data are given in the Supporting Information.

Thermal properties

Eight pairs of enantiomers prepared were examined for their thermal behavior with the aid of polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and powder Xray diffraction (XRD). It may be mentioned here that POM and DSC techniques were used as prime and complementary tools for determining the thermal characteristics of all dimers, whereas XRD was used to measure the layer spacings (*d*) of the smectic phases of a few chosen, representative materials. LC phases were identified based on the observation of fluid birefringent textures under POM; specific LC phase assignment and phase sequences were determined based on the observation of characteristic textures and their pattern transformation when undergoing phase transitions.^[68] The peak temperatures recorded in DSC thermograms due to phase transitions were found to be consistent with those of POM studies. The transition temperatures and the corresponding enthalpy values obtained from DSC measurements are given in Table 1.

From the accumulated results (Table 1) it is apparent that all the dimers with an even-numbered methylene spacer show, unlike the corresponding odd-members, enantiotropic mesomorphism. This is expected given the fact that dimers with an even-membered spacer attain an overall linear conformation, which favors the parallel arrangement of the mesogenic cores resulting in their self-assembly into the LC state. As a representative case, an energy-minimized space-filling model of an even-member I(R)-4 with a zig-zag shape is shown in Figure 1 a where the mesogenic cores lie along the long molecular axis of the dimer. Both the POM and DSC studies confirmed that the enantiomers I(R)-4 and I(S)-4, wherein the two mesogenic groups are separated by an oxybutoxy moiety, exhibit analogous enantiotropic LC behavior, as expected. DSC traces recorded for both the samples are shown in Figure 2. When thin films of the samples I(R)-4 and I(S)-4 were held between clean (untreated) glass plates and cooled from the isotropic phase, they display a fan-like texture of the N* phase (Figure 3a) at ~179 °C ($\Delta H = 5.3 \text{ Jg}^{-1}$); here, within individual fans the helix orients uniformly. As expected, the oily streaks characteristic of

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Table 1. Phase sequence, transition temperatures (${}^{\circ}C)^{[a]}$ and the corresponding enthalpies (Jg^{-1}) of chiral dimers belonging to **II-n,R** and **III-n,S** series. Cr= Crystal; SmA=uniaxial smectic A phase; SmA_b=biaxial smectic A phase; TGB=twist grain boundary phase; N*=chiral nematic phase; and BP=blue phase.

Dimer	Phase sequence	
	Heating	Cooling
I(R)-3	Cr 102.4 (68.1) l	-
I(S)-3	Cr 102.3 (64.3) I	-
I(R)-4	Cr 133.9 (56.9) SmA 174.9 ^[b] TGB ^c -N* 179.9 (5.4) I	l 178.7 (5.3) N*-TGB 173.8 SmA 116.4 (51.2) Cr
I(S)-4	Cr 134.2 (45.2) SmA 174.6 ^[b] TGB ^[c] -N* 179.9 (5.4) l	l 179 (5.3) N*-TGB 173.9 SmA 116.4 (51.5) Cr
I(R)-5	Cr 109.7 l	l 91.1 (0.4) BP 83.5 N*-TGB ^(c) 81.7 ^(b) SmA 44.1 (12.4) Cr
I(S)-5	Cr 109.3 l	l 91.8 (0.4) BP 83.7 N*-TGB ^(c) 81.5 ^(b) SmA 44 (19.2) Cr
I(<i>R</i>)-6	Cr 113.7 (62.4) N* 156.3 (5.1) I	l 155.5 (4.9) N* 95.8 (35.8) Cr
I(S)-6	Cr 116.6 (57.8) N* 156.6 (5.1) I	l 155.7 (5) N* 92.9 (25.5) Cr
I(R)-7*	Cr 74.2 (50.6) N* 100.1 (0.4) I	l 99.2 (0.4) BP 90 N*-TGB ^(c) 74 ^(b) SmA 53.9 ^(b) SmA _b 51.2 ^(b) SmA (re-entrant) 29.1 ^(b) Cr
I(S)-7	Cr 73.7 (49.3) N* 100 (0.4) I	l 99.4 (0.4) BP 89.8 N*-TGB ^(c) 73.8 ^(b) SmA 53.6 ^(b) SmA _b 51.1 ^(b) SmA (re-entrant) 35 ^(b) Cr
I(R)-8	Cr 114 (68.2) N* 140.7 (5.2) I	l 139.7 (5.1) N* 95.9 (42.6) Cr
I(S)-8	Cr 112.7 (53.5) N* 140.1 (5.1) I	l 138.7 (5.3) N* 98.4 (56.4) Cr
I(R)-9	Cr 105.7 (49.6) l	l 103.4 (0.4) BP 94.4 N* 56.9 (31.6) Cr
I(S)-9	Cr 105 (45.6) l	I 103.6 (0.5) BP 94.2 N* 56.7 (25.1) Cr
I(<i>R</i>)-10	Cr 115.3 (56.3) SmA 129.9 (1.9) N* 138.8 (4.8) I	l 137.6 (4.6) N* 127.8 (1.8) SmA 94.4 (49.60 Cr
I(S)-10	Cr 113.1 (55) SmA 129.7 (1.8) N* 138.7 (4.9) I	l 136.9 (4.8) N* 127.6 (1.8) SmA 88.9 (47.9) Cr
× 1/		

* Known dimer, but included in this study for the sake of comparison and completeness. [a] Peak temperatures in the DSC thermograms obtained during the first heating and cooling cycles at a rate of 5 °C min⁻¹. [b] The phase transition was observed under a polarizing microscope and too weak to get recognized in DSC. [c] A transient phase.

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Figure 1. Space-filing energy minimized (all-*trans*) models of an even-membered dimer **I**(*R*)-4 (a) and an odd-membered dimer **I**(*R*)-3 (b). Note that owing to the presence of four methylene units in the spacer, the dimer **I**(*R*)-4 attains nearly a linear geometry, whereas **I**(*R*)-3 with three methylene groups gains a bent-shape.

the Grandjean plane texture (Figure 3b) were observed when the fan-like texture was subjected to a mechanical stress. On cooling the samples further, the N* phase transforms to the SmA phase through a fleeting TGB phase. The presence of the both TGB and SmA phases was clearly identified from the optical textures obtained on slow cooling from the N* phase. The SmA phase showed the co-occurrence of both focal-conic fan and homeotropic domains. When the samples were subjected to homeotropic boundary conditions, the SmA phase displayed a pseudo-isotropic texture exclusively; by contrast, it showed a focal-conic texture solely when tested in glass substrates treated for planar orientation. The TGB phase showed a striking filament texture when the pseudo-isotropic texture of the lowtemperature SmA phase was heated slowly. In fact, all the three phases, that is, N*, TGB and SmA phases, existed together for a short while; this was evidenced by the observation of textures corresponding to these three LC phases appearing



Figure 2. DSC thermograms of the first heating–cooling cycles recorded at a rate of 5° Cmin⁻¹ for dimers **I**(**R**)-**4** (blue traces) and **I**(**S**)-**4** (red traces). Note that these dimers, being enantiomers, behave identically, and thus peak positions due to their phase transitions are exactly matching.

concurrently (Figure 3 c). The next two enantiomeric pairs, namely, I(R)-6&I(S)-6, and I(R)-8&I(S)-8, show an identical mesomorphic behavior stabilizing an enantiotropic N* phase only; the presence of this phase was established, as earlier, by polarizing microscopy. The dimers I(R)-10 and I(S)-10, wherein mesogenic cores are interconnected through the decamethylene spacer, show thermodynamically stable N* and SmA phases that was evidenced by textural observation.

Powder XRD studies have shown that the SmA phase formed by polar mesogens (i.e., with a terminal cyano group)

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generally consist of antiparallel pairs.[28,61,69-71] The pairing of polar mesogens results from the strong intermolecular longitudinal association so as to minimize the dipolar energy contribution effectively. Such organization of mesogenic cores gives rise to either a partially bilayered SmA (SmA_d) phase where the layer spacing (d) is greater than the molecular length (L), or a bilayer SmA (SmA₂) phase with the layer thickness $d \approx 2L$. Indeed, dimeric molecules, depending upon the lengths of terminal tail and spacer, may also adopt an intercalate SmA structure wherein the spacers and terminal chains are mixed randomly; in this case, the layer spacing is approximately half the molecular length ($d = \frac{1}{2}L$). Thus, the SmA phase, which can be regarded as an one-dimensional (1D) mass density wave along the director, was examined by powder XRD. In particular, XRD measurements were performed on the unaligned SmA phase of dimers I(R)-4, I(S)-5 and I(R)-10 as a representative cases. The samples were placed in Lindemann glass capillaries of 1 mm diameter by capillary action in the isotropic state. Subsequently, both ends of the capillaries were flame sealed. The samples were heated to their isotropic state and cooled slowly; the XRD data were acquired as a function of temperature in the SmA phase region.

The profiles acquired at different temperatures of both samples were found to be nearly identical; specifically, the 1D intensity versus diffraction (2 θ) profiles obtained at different temperatures were found to be nearly the same. Figure 4a represents such profiles obtained at 160 °C, 70 °C and 125 °C for dimers I(R)-4, I(S)-5 and I(R)-10, respectively. The temperature dependence of the layer spacing profiles derived from the low-angle Bragg reflections is shown in Figure 4b. Each profile consists of a diffuse peak in the wide-angle area $(2\theta \approx 20^{\circ})$ and a sharp, intense (first-order) reflection, in the small-angle region ($0 < 2\theta < 5^{\circ}$), evidently establishing the layer structure. In fact, the presence of only the first-order layer reflection suggests that the density profile along the layer normal is close to sinusoidal. In Table 2, the spacings related to the low-angle reflection (d), wide-angle peak positions and the molecular length (L) of the dimers in their all-trans geometry and the d/Lratio are presented. The wide-angle reflection with the spacing value centered at 4.5 Å is characteristic of the liquid-like arrangement of the mesogens within the layers. As expected, the wide-angle diffuse maximum remains unaltered on passing



Figure 4. (a) The 1D intensity vs. 2θ profiles obtained for the SmA phase of dimers **I**(*R*)-4, **I**(*S*)-5 and **I**(*R*)-10 at 160 °C, 70 °C and 125 °C, respectively; note that each trace comprises a sharp reflection in the low-angle region and a diffuse peak in the wide-angle region. (b) The layer spacing (*d*) obtained as a function of temperature in the SmA phase of **I**(*R*)-4, **I**(*S*)-5 and **I**(*R*)-10.

from higher to lower temperature of the SmA phase implying that the short-range remains liquid-like. It can be seen from Table 1 that for dimers I(R)-4 and I(S)-5 the spacing (*d*) corresponding to the wave vector of the mass density wave is longer than the estimated all-*trans* length of the molecule with the *d/L* ratio being in the range of 1.5 to 1.7 Å, indicating a partial bilayer structure for the SmA phase where, due to the microphase segregation, chemically compatible (like) parts of the



Figure 3. Microphotographs of the optical textural patterns of the LC phases stabilized by even-membered dimeric molecule I(R)-4: (a) the fan-like texture of the N* phase obtained at 175 °C; (b) the oily streaks characteristic of the Grandjean plane texture of the N* phase observed when the fan-like pattern-(a) was sheared; (c) the texture seen across the N*-SmA transition at about 174 °C; note that the textures of the SmA (*pseudo*-isotropic texture), TGB (filaments) and N* (left portion: non-specific) are co-occurring.

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Table 2. XRD and related data of the SmA of dimers I(R)-4, I(S)-5 and I(S)-10: The estimated *all-trans* molecular length (*L*) together with the spacings (*d*) of the low-angle reflection, the wide-angle peak positions and d/L ratio are given.

Mesogen [L/Å]	<i>T</i> [°C]	Layer spacing - <i>d</i> (low-angle peak position) [Å]	Wide-angle peak position [Å]	d/L
	160	55.77		1.467
	155	55.40		1.457
	150	55.12		1.450
I(R)-4	145	54.89	16	1.444
(38)	140	54.67	4.0	1.462
	135	54.54		1.435
	130	54.49		1.433
	125	54.34		1.430
1(5)-5	70	56.61		1.715
(22)	65	56.58	4.5	1.714
(55)	60	56.582		1.714
	125	22.44		0.4987
	120	22.45		0.4991
	115	22.46		0.4992
	110	22.48		0.4997
	105	22.49		0.4998
	100	22.50		0.5000
	95	22.30		0.4957
	90	22.31		0.4958
I(R)-10	85	22.318	16	0.4959
(45)	80	22.32	4.0	0.4960
	75	22.31		0.4958
	70	22.30		0.4956
	65	22.28		0.4952
	60	22.30		0.4955
	55	22.29		0.4954
	50	22.29		0.4954
	45	22.27		0.4950
	40	22.28		0.4951

molecules overlap. Thus, the dimers I(R)-4 and I(S)-5 show the interdigitated smectic A (SmA_d) phase resulting from self-assembly of antiparallel pairs of mesogens (Figure 5a) formed by electrostatic interaction among the polar cyanobiphenyl cores.^[28,71] It can be seen from the data presented in Table 1 that the *d*-values obtained as function of temperature in the SmA phase of dimer I(R)-10 are significantly smaller than the estimated all-trans molecular length, and thus the d/L ratio is ~0.49 Å. Indeed, this ratio is characteristic of an intercalated SmA (SmA_c) phase where, within a layer, different entities of molecules overlap (Figure 5b). It is well known that if the length of the terminal tail is shorter than, or comparable to, the length of the central spacer, an intercalated structure is formed. This type of structure is considered to be favored not only by the electrostatic quadrupolar interaction among the groups having guadrupole moments of opposite signs but also due to entropy gain.^[28,71] Thus, X-ray diffraction experiments reveal the formation of SmA_d and SmA_c phases by the dimers which is governed by the relative lengths of the spacer and terminal tail.

Now we describe and discuss the thermal properties of four pairs of enantiomers having an odd-numbered methylene spacer. The data accumulated in Table 1 clearly reveal that these odd-members, unlike even-membered dimeric mole-



Figure 5. (a) A sketch of a partial bilayer SmA (SmA_d) phase formed by the dimer having an oxytetramethyleneoxy (even) spacer: **I**(*R*)-**4**; *L* = 38 Å. Note that antiparallel pairs (dotted square) self-assemble to yield SmA_d phase; the measured spacing (*d*) is longer than the estimated *all-trans* length of the dimer and thus the *d/L* ratio is \approx 1.4 Å. (b) A schematic representation of an intercalated SmA (SmA_c) phase of dimer **I**(*R*)-**10** where, within the chain region, random mixing of terminal tails and the spacers occurs. Here, the layer periodicity is equal to half the all-*trans* molecular length of **I**(*R*)-**10** (45 Å); thus, *d/L* ratio is \approx 0.49 Å.

cules, by and large, disfavor the LC behavior that can be ascribed to the bent-conformation (Figure 1b) and thus reduced shape-anisotropy of the mesogens. The enantiomers I(R)-3 and I(S)-3, where the mesogenic cores are interconnected by an oxytrimethyleneoxy spacer, were found to be non-mesomorphic showing a direct transition from crystal to isotropic liquid state. The next pair of dimers, I(R)-5 and I(S)-5, showed monotropic LC behavior; upon heating, they transformed directly from the crystalline state to isotropic liquid while upon cooling, they stabilized BP, N*, TGB (transient) and SmA phases; the presence of the latter three mesophases was clearly established by POM study as described before. Compound I(R)-9 and I(S)-9 behaved nearly in the same way with the exemption of the TGB phase. The occurrence of BP, over a thermal range of about seven degrees, was evidenced by optical textural observation. These dimers, placed between untreated glass slides and cooled slowly (0.1 °C min⁻¹) from the isotropic phase, show a striking, characteristic texture of the BP (BP-I/BP-II) composed of micron-sized bright platelets of different color. The bright color of platelets indicates selective reflection of the periodic structure. Indeed, the platelet pattern transforms in to a Grandjean plane texture when the top glass substrate was sheared gently. It is generally observed that blue phases occur only in strongly chiral LC systems with short helical pitch. Chirality, being purely a symmetry property (absence of inversion symmetry), can be either be present or absent. However, quantitative measures of chirality have been made by considering the pitch of the helix.^[52] In the case of N* phase, the structure which is always chiral, is termed strongly or weakly chiral by considering whether the pitch is shorter or longer, respectively. Thus, the pitch of the N* phase appearing below the BPs formed by these strongly chiral dimers must be short.

The (S)-enantiomer I(S)-7 with an oxyheptoxy (7) spacer exhibits, analogous to the (R)-enantiomer I(R)-7,^[54] a very rich

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phase sequence. It shows BP, N*, TGB, SmA, SmA_b and SmA phases with the uniaxial smectic A phase showing re-occurrence. Before discussing the aforesaid phase sequence, we first comment on the chiroptical properties of the N* phase of both the enantiomers, I(R)-7 and I(S)-7, investigated by circular dichroism (CD) spectroscopy. CD activity is generally observed when the optically active medium absorbs left- and righthanded circular polarized light differently. The N* phase, due to its helical superstructure where the constituent nematic layers twist continuously with respect to each other, exhibits some unique optical phenomena such as circular dichroism (CD) and Bragg-like light reflection.^[72a-d] In a homogeneously aligned N* phase, the mesogenic molecules adopt a macroscopic helical order; that is, the director rotates in a helical fashion around a perpendicular axis. The helical sense of the N* phase, being a chirality-dependent issue, can be right- or left-handed; in other words, it indicates the director's rotation from layer to layer. Needless to say, the configuration of the chiral element(s) of the constituent mesogens dictates the handedness to the structure. The dimers I(R)-7 and I(S)-7, being enantiomers of a chiral compound, should show optical

activities of equal magnitudes but with opposite signs. Therefore, the helical screw sense of the N* phase of dimers I(R)-7 and I(S)-7 must to be opposite to each other. To investigate this, a CD study was undertaken as the circularly polarized light (CPL), being chiral, interacts differently with the N* phase formed by enantiomers I(R)-7 and I(S)-7. To begin with, prefabricated cells of known thickness were used to quantify the measurements; however, the CD peaks (saturated) obtained were found to be out of the measurable range of the equipment. This problem was circumvented by using thin films of the samples; thus, the CD experiments carried out are purely qualitative measures. Enantiomers I(R)-7 and I(S)-7, sandwiched between two quartz plates, were heated slightly above their isotropic temperatures and pressed to obtain thin films where the samples are uniformly spread. Next, the samples were cooled to the N* phase and mechanically sheared to obtain a planar alignment of the molecules. While cooling the sample, the temperature-dependent CD spectra were recorded in the entire temperature range of the N* phase. It may be mentioned here that in the isotropic phases, negligibly weak CD signals, when compared to those of the N* phase, were seen. This implies that the CD activity stems from the chiral induction in the LC structure but not from the molecular chirality.

It is well known that, in the absorption region, the visible CD band may combine linear dichroism (LD) and birefringence. However, this possibility was ruled out by recording the temperature-dependent CD spectra of the samples subjected to 90° in-plane rotation. The recorded spectra were found to be virtually identical to those obtained in the original position of the samples, suggesting that CD activity is

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genuinely due to the macroscopic helical structure of the N* phase but not because of LD. Moreover, the CD spectrometer used by us also measures LD directly and hence the samples were subjected to such a measurement; no LD activity was found. Figure 6a and 6b, respectively, show the CD spectra obtained for dimers I(R)-7 and I(S)-7; they comprise an intense CD band in the wavelength (λ) range of 490–480 nm with a small shoulder at ~435 nm. The intense CD band is arising due to the $n-\pi^*$ transition of the chromophores present in the chiral environment; in other words, the chromophores of dimers show optically active electronic transitions in the visible region of the CD spectrum. The presence of a positive CD band has been generally attributed to a right-handed screw sense for the N* phase derived from lyotropic systems and cholesterol-based mesogens;^[52,72b-d] we therefore presume that the helices in the N* phases of enantiomer I(R)-7 and I(S)-7, exhibiting positive and negative CD bands, have a right- and lefttwisted structure, respectively.

We now discuss the thermal behavior of dimer I(S)-7. When a thin film of the compound held between a clean glass slide and a coverslip was gradually cooled (0.1 °C min⁻¹) from the



Figure 6. CD spectra recorded as a function of temperature in the N* phase formed by the mirror-image isomers I(R)-7 (a) and I(S)-7 (b)

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isotropic phase, a texture appears sharply manifesting optically in the form of a misty blue texture (without any structure in it) (Figure 7 a) characteristic of the blue phase III (BPIII). Subsequently, bright platelets of different colors begin to appear on top of the foggy pattern (Figure 7b) and eventually fill the field of view implying the occurrence of another BP; the presence of crinkled lines between the plates is indicative of BPI. As expected, the Grandjean plane pattern appears if the BPI is subjected to mechanical stress. On cooling the sample from BPI, the N* phase, through a transient TGB phase, comes into existence at \sim 73 °C with an uncharacteristic optical texture which upon shearing placidly changes to oily streaks typical of the Grandjean plane texture (Figure 7 c) where the helical axis lies perpendicular to the glass plates (along the viewing direction). Upon lowering the temperature of the sample further, a change to a focal-conic fan coexistent with pseudo-isotropic domains occurs. The focal-conic fan texture supports a layered structure, whereas homeotropic regions imply an orthogonal organization of the molecules with respect to the layer planes. These textural patterns hint towards the existence of the SmA phase having uniaxial symmetry; the presence of this phase was confirmed indubitably by the observation of a dark field of view in slides treated for homeotropic anchoring conditions and a focal-conic fan texture (Figure 7 d) in glass substrates treated to induce homogeneous orientation. The presence of a short-lived TGB phase was determined by the observation of filamentary texture when the homeotropically aligned SmA phase was slowly heated towards N* phase (Figure 7 e); eventually, the filamentary texture coalesces to give a short-lived non-specific texture.

Further cooling of the sample caused a transition to another mesophase sharply at 53.6 °C with a notable change in the optical textural pattern; as shown in Figure 7 f, the homeotropic (pseudo-isotropic) region and homogeneous (focal-conic) pattern of the preceding SmA phase transform to a low birefringence schlieren texture and a stripped focal-conic texture, respectively. The schlieren texture in the homeotropic orientation is suggestive of the director field in the plane of the cells. These optical textural features are typical of an orthogonal biaxial SmA (SmA_b) phase^[53, 54, 58, 73-84] which possesses an additional director (m) in the plane of the layers (see a later section for details). For the sake of confirmation, the sample was examined in cells treated for homeotropic and homogeneous anchoring. As expected, a focal-conic texture having faint stripes on top of fans was observed (Figure 7 g) when the sample was studied using substrates treated for homogeneous configura-



Figure 7. Photomicrographs of the textures observed under POM for the mesophases of odd-membered dimeric molecule **I(5)-7**: (a) the misty blue texture of the BP-III coming into view immediately below the isotropic phase; (b) the platelet texture of the BP-I appearing over the blue fog of BP-III; (c) the oily streaks typical of the Grandjean plane texture of the N* phase (85 °C); (d) the focal-conic fan texture of the planarly aligned SmA phase (65 °C); (e) filamentary texture of the TGB phase originating from the homeotropic domains of the SmA phase; (f) texture of the SmA_b phase (53 °C) comprising both schlieren pattern (with vigorous flickering) and focal conics (having fine striations across the fans), respectively, stemming from the homeotropic and homogeneous alignment of the dimer; (g) focal-conic texture of the planarly aligned SmA_b phase where faint bars can be observed (52.5 °C) (see the marked area); (h)-(i) the schlieren texture with two- and four-brush defects (see the circled area) and the stripped pattern seen for the homeotropically oriented SmA_b phase (52.5 °C).

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tion. Subjecting the sample to homeotropic boundary conditions yielded a schlieren texture comprising both two-brush (strength $s = \pm \frac{1}{2}$) and four-brush ($s = \pm 1$) defects with a strong director fluctuation (Figure 7h); besides, in some regions of the cell, a striped texture over the schlieren texture with alternate bright and dark bands moving across the sample also existed (Figure 7 i). The occurrence of both integer and half-integer defects, particularly of the $s = \pm \frac{1}{2}$ defect, rules out the LC phase being a smectic C (SmC) phase where the tilted organization of mesogens allows the disclination of integer strength exclusively. Using a tilting plate compensator, the quantitative in-plane birefringence (Δm) was measured, which gave a value of 0.002 (52.5 °C) which is smaller than that measured for the dimer I(R)-7.[54] As the temperature is lowered further, the sample exhibits, at 51.2°C, an optical texture where the schlieren and the striped patterns disappear sharply leaving a dark (pseudo-isotropic) field of view; in the planarly aligned regime, a focal-conic texture typical of an uniaxial SmA phase was observed where transition bars across the fans (seen for the SmA_b phase) vanish totally; upon shearing gently, a pseudo-isotropic pattern was observed solely, implying a complete homeotropic alignment of the mesogens. The existence of the SmA phase below the SmA_b phase was substantiated based on the observation of a focal-conic pattern and dark texture when the sample was examined, respectively, in between glass slides treated for homogeneous and homeotropic anchoring. Thus, the POM study reveals that dimer I(S)-7 exhibits a re-entrant phase sequence, SmA-SmA_b-SmA, below the BP-N*-TGB phases.

Optical conoscopy is an important tool that greatly helps in distinguishing uniaxial and biaxial LC phases. In this technique, the sample is observed between crossed polarizers with the optical axis remaining along the direction of light propagation. Experiments were carried out on a homeotropically anchored sample wherein the molecules are uniformly oriented with the director (n) normal to the substrate. A cell was fabricated using an indium tin oxide (ITO)-coated glass plate and an ordinary glass plate; the inner surfaces of these substrates were treated with octadecyltriethoxysilane for homeotropic orientation of the molecules. The cell comprised two aluminium 10 μ m-thick strips separated by ~0.5 mm. The sample was heated to its isotropic state and filled into the cell by capillary action. After cooling slowly from the isotropic phase to the higher temperature of SmA phase, conoscopic observation was made between the crossed polarizers set to 45° to the direction of the in-plane electric field (sine-wave field, $310 V_{ppr}$ 90 Hz); as expected, a typical crosslike uniaxial interference pattern (Maltese cross) was observed. As the temperature was lowered further, a biaxial pattern in which the isogyres split was obtained at ~53 °C and the gap between the isogyres remained unaltered until about 51.5 °C. On reducing the temperature further, the arms of the cross (isogyres) begin to come closer and merge at ~51 °C to give a Maltese cross indicating that the lower temperature phase is indeed unaxial. The orthoscopic and conoscopic patterns seen for the SmA phase (at 57 °C), SmA_b phase (53.5 °C) and re-entrant SmA (50.5 °C) are respectively shown in Figure 8a-c and 8d-f. While the well-

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Figure 8. Photomicrographs of the orthoscopic (a–c) and conoscopic (d–f) patterns observed for the LC phases of a homeotropically aligned dimer **I(S)-7**: the SmA phase at 57 °C (a,d); the SmA_b phase at 53.5 °C (b,e); re-entrant SmA phase 50 °C (c,f). Note that in the conoscopic pattern (e) of the SmA_b phase isogyres are separated.

separated isogyres are seen for the SmA_b phase (Figure 8e), the SmA (Figure 8 d) and re-entrant SmA (Figure 8 f) phases exhibit uniaxial interference patterns. Indeed, the conoscopic patterns were also observed in the absence of an external field where the splitting of isogyres in the SmA_b phase was found to be very weak. In view of all of the foregoing observations it can be concluded that the dimer **I(S)-7** shows the BP-N*-TGB-SmA-SmA_b-SmA sequence with the uniaxial smectic A phase being re-entrant.

As mentioned earlier, the thermal behavior and overall conformation of LC dimers decisively depends upon the length and parity of the spacer. Figure 9 presents, in the form of a horizontal bar chart, the dependence of the LC behavior of the cooling cycle of (R)-enantiomers, except the dimer I(R)-3 as it is non-mesomorphic, on the number of carbon atoms in the central spacer. It especially shows the odd-even effect, the influence of length and parity of the spacer on the phase sequences, transition temperatures, and clearing temperatures. In general, the thermal behavior of the present series of compounds was found to be identical to that of LC dimers reported hitherto.^[28-31,52] For example, the clearing temperatures of the even-members with short-spacer lengths (n = 4, 6, and 8) vary considerably showing higher values. However, upon increasing the spacer length (n = 10) this effect seems to attenuate; by contrast, the compounds with an odd-numbered methylene spacer show lower clearing temperatures. As discussed

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Figure 9. A horizontal bar graph depicting the dependence of mesomorphic behavior during cooling cycle (phase sequence, phase transition temperatures and clearing temperatures) on the number of carbon atoms of the central spacer of (*R*)-enantiomers. Note that the TGB phase is not included in the profile as it exists over a very short thermal range.

previously, such behavior can be interpreted in terms of the overall conformation (linear- or bent-shape) of the molecules governed by the geometry and flexibility of the central spacer, which basically affects the mutual orientation of the mesogenic entities. Another interesting aspect to be noted is that all the odd-members (with n = 5, 7, and 9), except dimers I(R)-3/I(S)-3, show BPs; this behavior is in complete agreement with the general observation that chiral dimers with an odd-parity spacer show BPs, which is not the case with even-membered dimers, suggesting that the chirality of the liquid crystal structure shows a dependence on the parity of the spacer.^[28] Perhaps, odd-members, being bent-shaped, reduce the pitch of LC phases due to a smaller twist elastic constant that is associated to their lower orientational order.^[28]

Binary mixture study

A binary mixture study was undertaken mainly to explore the possibility of stabilizing the SmA_b phase and/or SmA-SmA_b-SmA (re-entrant) phase sequence. Among the various types of smectic LC (layered) phases, which essentially differ in their molecular packing, symmetry of 1D and 2D lattices, and tilt angle with respect to the layer normal, the optically uniaxial, monolayered SmA phase having $D_{\infty h}$ symmetry is the simplest and perhaps one of the most exhaustively studied smectic phases.^[69,70] In this phase, the mesogens within the layer are oriented along the layer normal (director n) and freely rotate about their long molecular axis. On the contrary, one of the most sought after phases in the SmA LCs is the SmA_b phase^[54, 58, 73-76] as it is supposed to be a very promising and viable medium for future advanced technologies.^[84] In this phase, the constituent molecules are oriented along the layer normal (director n), but have an additional director (m) in the plane of the layers due to the restricted rotation of mesogens around their long molecular axis. The symmetry of this phase, however, is proposed^[85] to be dependent on the type of constituent mesogens: D_{2h} or C_{2V} if the molecules are board-like (sanidic) or banana-shaped, respectively. In other words, the apolar SmA_b phase formed by sanidic molecules possesses D_{2h} symmetry and nematic-type biaxiality, while banana-like mesogens stabilize the SmA_b phase of C_{2V} symmetry where at least one direction is polar. However, it is interesting to note that the former type of SmA_b phase occurs less commonly^[54, 58, 73–75] as compared to the latter structure.^[76-83] In fact, the present study is the extension of our previous work reported on a chiral dimer I(R)-7 that showed the SmA_b phase in an unique and unprecedented phase sequence, that is, SmA-SmA_b-SmA (re-entrant). As expected, such a phase sequence could be only observed in the (S)-enantiomer, I(S)-7, of the above dimer, indicating that designing the mesogens capable of stabilizing the SmA_b phase or the aforesaid phase sequence is not a trivial task necessitating the development of either single-component LC systems or mixtures; however, a literature survey suggests that the latter strategy is proven to be fruitful and less cumbersome.^[74,77,83]

Binary mixtures derived from mixing of two pure mesogens closely resembling in their molecular structure and geometry (conformation) are known to stabilize thermodynamically stable LC phases of the constituent compounds.^[86] For example, it has been observed that a binary mixture made from two nematogens with nearly identical chemical structures and geometries show an enantiotropic nematic phase.[86-88] These observations prompted us to select two mesogens exhibiting the SmA_b phase. Scheme 1 shows the molecular structures of the two LCs, along with their LC behavior, used for the preparation of binary mixtures. Precisely, the achiral dimer I-5, 4'-((5-(4-(((4-(decyloxy)phenyl)imino)methyl)-3-hydroxyphenoxy)pentyl)oxy)-[1,1'-biphenyl]-4-carbonitrile,^[58] was mixed with the chiral dimer I(R)-7.^[54] The weight ratio percentages in the nine binary mixtures of I-5 and I(R)-7, respectively, are 10:90 (M1-9), 20:80 (M2-8), 30:70 (M3-7), 40:60 (M4-6), 50:50 (M5-5), 60:40 (M6-4), 70:30 (M7-3), 80:20 (M8-2) and 90:10 (M9-1); thus, weight percentages will be used throughout this text. Thorough mixing of the dimers I-5 and I(R)-7 was achieved by blending in their isotropic state. The dimers were weighed in their crystalline form using a microbalance with an accuracy of 1 mg; subsequently, the mixtures were heated to about 145°C on a hot plate (equipped with a thermometer) and stirred continuously for about 5 min to obtain well-homogenized bi-component systems.

The thermal behavior and phase transition temperatures of the mixtures determined using POM in conjunction with a hot stage are listed in Table 3. The phase diagram, which illustrates LC phases (sequences) exhibited by different mixtures of two mesogens over a range of temperatures, is also shown in Figure 10. As can be seen, the compositions move from pure dimer **I-5** on the left, through nine mixtures, to pristine **I**(*R*)-7 on the right of the diagram. It must be mentioned here that **I-5** mixes well with the chiral dimer **I**(*R*)-7 at all the concentrations, as evidenced by sharp phase transitions (width ~500 mK) observed under POM. This implies a good structural and geometrical compatibility of both compounds. In all mixtures, the SmA_b and/or re-entrant SmA phases exist as metastable (monotropic) LC phases. The first three mixtures M1-9,

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Table 3. LC Phase sequences and transition temperatures (°C)^[a] of nine binary mixtures formed by mixing achiral dimer **I-5** (10 to 90 wt%) with optically active dimer **I(R)-7** (90 to 10 wt%). Cr=Crystal; SmA=uniaxial smectic A phase; SmA_b=biaxial smectic A phase; TGB=twist grain boundary phase; N*= chiral nematic phase; BP=blue phase; I=isotropic liquid state.

Mixture Wt% ratio I-5:I(<i>R</i>)-7	Phase sequence	
	Heating	Cooling
M1-9 (10:90)	Cr 67.9 SmA 73 TGB ^[b] -N* 103.1 I	l 101.5 BP 92.8 N*-TGB ^[b] 70.2 SmA 52.1 SmA _b 51.2 SmA (re-entrant) 35 Cr
M2–8 (20:80)	Cr 69.5 SmA 79 TGB ^[b] -N* 106.1 l	l 104.3 BP 100 N*-TGB ^[b] 75.2 SmA 56.2 SmA $_{\rm b}$ 48.2 SmA (re-entrant) 30 Cr
M3–7 (30:70)	Cr 69.0 SmA 79.8 TGB ^(b) -N* 108 I	l 104.1 BP 100 N*-TGB ^(b) 75.9 SmA 60.1 SmA _b 43.1 SmA (re-entrant) 30 Cr
M4–6 (40:60)	Cr 83.8 SmA 86.5 TGB ^(b) -N* 113 I	l 112 BP 109 N*-TGB ^(b) 83.3 SmA 61.8 SmA _b 42 Cr
M5–5 (50:50)	Cr 100 SmA 105.7 TGB ^(b) -N* 128 I	l 126 N*-TGB ^[b] 104.2 SmA 77.7 SmA _b 65.3 Cr
M6-4 (60:40)	Cr 97 SmA 102.1 TGB ^(b) -N* 122.6 I	l 122 N*-TGB ^[b] 101.8 SmA 73.1 SmA _b 60.9 Cr
M7–3 (70:30)	Cr 100.9 SmA 108.4 TGB ^(b) -N* 127 I	l 126.3 N*-TGB ^[b] 107.2 SmA 76.2 SmA _b 63.5 Cr
M8–2 (80:20)	Cr 106.2 SmA 122.4 TGB ^(b) -N* 136.9 I	l 136 N*-TGB ^(b) 122.3 SmA 82.1 SmA _b 76.1 Cr
M9–1 (90:10)	Cr 107 SmA 124.9 TGB ^[b] -N* 138 I	l 137.7 N*-TGB ^[b] 124.3 SmA 92.1 SmA _b 74.9 Cr
[a] The phase transition	ns and the corresponding temperatures were deduced	ced from polarizing microscope study. [b] A transient phase



Figure 10. The phase diagram of the mixtures of dimers I-5 and I(R)-7.

M2-8 and M3-7, behave exactly analogous to that of chiral dimer I(R)-7 exhibiting a rich poymesomorphic sequence, that

is, BP-N*-TGB-SmA-SmA_b-SmA (re-entrant) that was adjudged mainly based on the textural observation under POM.

On slow cooling the isotropic liquid of these mixtures held between clean glass slides and observed under a POM, a characteristic blue fog texture of the amorphous BPIII phase appears and following this a colorful platelet texture featuring crinkled lines among the plates of BPI grows instantaneously. On cooling further, the N* phase comes into existence, which upon shearing showed oily streaks. Upon lowering the temperature, a transition from N* phase to SmA phase occurs with textural pattern comprising both focal-conic fan and homeotropic textures; Figure 11a represents such an pattern observed for the mixture M3-7 [I-5:I(R)-7; 30:70]. If the sample is heated slowly from the homeotropically aligned SmA phase, the filaments of the TGB phase grow which eventually coalesce to an unfamiliar texture. On cooling the sample further, the SmA phase transforms into the SmA_b phase with homeotropic regions exhibiting a schlieren pattern with a strong director fluctuation (Figure 11 b). Indeed, the schlieren texture consisted of both two- and four-brush strength defects. Besides, in some



Figure 11. Photomicrographs of the optical textures seen for the LC phases of binary mixture M3-7 [I-5:I(*R*)-7; 30:70]: (a) texture of SmA phase comprising both focal-conic fan texture and homeotropic regions (65 °C); (b) texture of the SmA_b phase consisting of both stripped focal-conic fan and schlieren patterns (55 °C); (c) the pattern observed for the homeotropically oriented SmA_b phase (56 °C) where alternate bright and dark bands persist over the schlieren texture.

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of regions of the sample, a striped texture with alternate bright and dark bands could also be observed (Figure 11 c). In the planar regions, very fine striations appear across the elongated fans of the focal-conic texture (Figure 11). As the sample in the homeotropic case was cooled further, the SmA phase reappears where the striped and the schlieren textures vanish completely leaving a dark field of view. Conoscopic studies were carried out to confirm the existence of biaxial and uniaxial SmA phases. The homeotropic cells required for the experiments were fabricated first, as described before, and then the samples were inserted in them. The observations between crossed polarizers were made in the SmA, SmA_b and SmA (reentrant) phases. As a representative case, the conoscopic patterns seen for mixture M2-8 [I-5:I(R)-7; 20:80] are shown in Figure 12a-c. As can be seen, the high- and low-temperature (reentrant) SmA phases show uniaxial interference patterns (Figure 12a,c), while for the middle SmA_b phase the isogyres split to give a biaxial pattern (Figure 12b). It can be seen that the thermal range of SmA_b phase in M1-9 is about 1°C, which is less than that present in the case of dimer I(R)-7 (\approx 2.7 °C). Interestingly, the SmA_b phase, at the expense of re-entrant SmA phase, becomes thermally more stable in the mixtures M2-8 and M3-7; in the latter case, the phase exists over a temperature range of 18°C.



Figure 12. Photomicrographs of the conoscopic patterns observed for homeotropically aligned smectic phases of mixture M2-8 [**I-5:1(***R***)-7**; 20:80]: (a) The SmA phase (70 °C); (b) the SmA_b phase (52 °C); (c) re-entrant SmA phase (40 °C). Note that isogyres are moderately separated in the conoscopic pattern (b) of the SmA_b phase.

The mixture M4-6 shows the sequence BP-N*-TGB-SmA-SmA_b while cooling from the isotropic phase. In this case, unlike in the abovementioned mixtures, the re-entrant SmA vanishes completely whereas the SmA_b phase stabilizes over a wider thermal range of ~ 20 °C. The next five mixtures namely, M5-5, M6-4, M7-3, M8-2 and M9-1 display a phase sequence viz., N*-TGB-SmA-SmA_b upon cooling wherein the BP gets extinguished. In mixtures M5-5, M6-4, M7-3 and M8-2 the SmA_b phase occurs in the thermal range of 6-12°C which is slightly less than $(14^{\circ}C)$ that is present in the pure dimer I-5. However, in the case of M9-1 it increases to $\sim 17\,^\circ \text{C}.$ Thus, all the mixture prepared herein exhibit $\mathsf{SmA}_{\mathsf{b}}$ phase and in some cases it appears in a sequence of SmA-SmA_b-SmA (re-entrant). This implies that the phase transitional behavior of binary mixtures of the non-symmetric dimers is possibly determined by molecular structural similarity and conformation. Such structural parameters facilitate thorough core-core interactions of mesogens leading to their excellent miscibility.

Conclusion

In this article, the results of our extensive studies encompassing the synthesis and evaluation of phase transitional behavior of sixteen non-symmetric polar dimers, in the form of eight enantiomeric pairs are presented; the study also includes preparation and characterization of binary mixtures. The dimers were made by covalently linking an electron-deficient cynobiphenyl core and an electron-rich salicylaldimine unit through a conformationally flexible alkylene spacer. Each pair of enantiomers has been derived from (R)-2-octyloxy and (S)-2-octyloxy tails. The number of methylene units in the flexible spacer has been varied from 3 to 10 yielding eight pairs. Thus, the effect of varying the length and parity of the spacer on thermal properties has been examined with the aid of polarized optical microscopy, differential scanning calorimetry and powder X-ray diffraction. The length and parity of the spacer greatly influences the thermal behavior of dimers. The members with oddparity (5, 7 and 9) spacers, except a pair of non-mesomorphic enantiomers with oxypropoxy (3) spacer, show commonly blue phases (BPs) and chiral nematic (N*) phase, while a pair of enantiomers with oxypentoxy (5) spacer shows additionally a twist grain boundary (TGB) phase and smectic A (SmA) phases. Notably, the (S)-enantiomer with oxyheptoxy (7) spacer shows, analogous to its counterpart (R)-enantiomer reported earlier by us, TGB, SmA, biaxial SmA (SmA_b), and re-entrant SmA (SmA_{re}) phases as well. The orthoscopic and conoscopic patterns confirm occurrence of the SmA-SmA_b-SmA_{re} sequence. All the dimers with even-membered (4, 6, 8 and 10) spacers stabilize the N* phase, while the members bearing 4 and 10 methylene units in the spacer show additionally TGB and/or SmA phases. X-ray measurements reveal the interdigitated or intercalated arrangement of mesogens in the SmA phase, which is not only associated with the interplay among the relative lengths of the spacer and terminal tail but also linked to electrostatic quadrupolar interactions between dissimilar mesogenic entities. CD experiments were carried out to reveal the handedness of the N* phases stabilized by two enantiomers; mirror-imaging CD bands of virtually equal magnitude but with opposite sign were obtained, confirming the enantiomeric purity of the isomers. To develop materials capable of showing the SmA_b phase or a rare phase sequence (i.e., SmA-SmA_b-SmA_{re} sequence), binary mixtures of two known, achiral and chiral, dimers were prepared and characterized. The occurrence of interesting phase sequences such as BP-N*-TGB-SmA-SmA_b-SmA_{re}, BP-N*-TGB-SmA-SmA_b and N*-TGB-SmA-SmA_b were established; notably, the latter two sequences appear to be unreported hitherto. Thus, the dimers and mixtures studied herein serve as model systems for the design and development of smectic phase having D_{2h} symmetry and nematic-type biaxiality.

Experimental Section

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Materials, methods and instrumentation

Unless otherwise stated, all reagents procured from commercial chemical companies were used as received. 4-Nitrophenol, anhy-

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drous potassium carbonate, potassium iodide, acetic acid, etc. were purchased from local sources, whereas 2,4-dihydroxy benzaldehyde, (R)-2-octanol, (S)-2-octanol, triphenylphosphine, diisopropyl-azodicarboxylate, 10% Pd-C, and α,ω -dibromoalkanes were obtained from overseas companies. Absolute ethanol was distilled twice with magnesium ethoxide (magnesium turnings and iodine); butanone was stored over anhydrous K₂CO₃ for 24 h and then subjected to fractional distillation. THF was dried over sodium and benzophenone under inert atmosphere. Ethyl acetate and hexanes obtained from local sources were distilled twice before use. Ultrapure nitrogen (99.99%) was used for maintaining the inert atmosphere. For column chromatography, silica gel (60-120 and 100-200 mesh) was used as the stationary phase. Thin layer chromatography (TLC) was performed on aluminum-backed sheets precoated with silica gel (0.2 mm, Merck, Kieselgel 60, F254); this technique was employed to assess the purity of the compounds, especially to monitor the progress of the reactions. The TLC plates were either stained with iodine vapor or exposed to ultraviolet light for the detection of organic spots.

All intermediates and target materials were characterized with aid of FTIR, UV-Vis, and NMR spectroscopies as well as elemental analysis. In fact, prior to the characterization, the final compounds (dimers) were dissolved in THF and micro-filtered to remove fine particles and threads. ¹H spectra were recorded in CDCl₃ solvent at ambient temperature using a Bruker AMX-400 (400 MHz) spectrometer. The coupling constants (J) are given in Hz. Chemical shifts are reported in ppm on a scale downfield from TMS with the residual proton resonance of the solvent as the internal standard (CHCl₂: δ 7.27 ppm). The spectral data are given in the format: chemical shift (δ), integration, multiplicity; splitting signals are presented as: s = singlet, d=doublet, dd=doublet of doublet, brs=broad singlet and t = triplet. ¹³C NMR spectra were recorded on an AMX-400 (100.6 MHz) spectrometer with complete proton decoupling and the chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl3: δ 77.0 ppm). FT-IR spectra of the compounds (in KBr pellets) were recorded in the region of 4000-400 cm⁻¹ using a PerkinElmer Spectrum 1000 FT-IR spectrometer, and the spectral positions are given in wavenumber (cm⁻¹) unit. UV-Vis absorption spectra were measured on a PerkinElmer Lambda 20 UV-Vis spectrometer. The elemental analysis of compounds was carried out with aid of an Eurovector E300 analyzer. Molecular lengths of dimers were measured (in Å) from the energy minimized (all-trans) conformation using the ChemBio3D Ultra 12.0 program. Space filling models of molecular structures were minimized using MM2 computations.

An Olympus BX50 (BX50F4 model) optical polarizing transmitted light microscope attached to a digital camera and a Mettler FP82HT hot stage, programmed by an FP90 central processor, was used for determining the phase sequences, LC phases and transition temperatures. A PerkinElmer Diamond differential scanning calorimeter (DSC) attached to a PC system operating on Pyris software was employed to determine the phase transition temperatures and the associated enthalpies. DSC thermograms of both heating and cooling cycles of the dimers were recorded at a rate of 5°Cmin⁻¹ under the constant flow of nitrogen gas. X-ray diffraction studies were carried on powder samples in Lindemann capillaries with $\mathsf{Cu}_{\mathsf{K}\alpha}$ radiation using an Image Plate Detector (MAC Science, Japan) equipped with a double mirror focusing optics. X-Ray diffraction studies were performed on powder samples in Lindemann capillaries with Cu_{Kx} ($\lambda = 0.15418$ nm) radiation using a PANalytical X'Pert PRO MP X-ray diffractometer comprising a focusing elliptical mirror and a fast resolution detector (PIXCEL).

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FULL PAPER

Eight new pairs of enantiomeric

dimers, synthesized by joining cyanobiphenyl and salicylaldimine cores via a flexible spacer of varying length and parity, including binary mixtures derived from such dimeric motifs, are evidenced to show helical, frustrated, optically biaxial and re-entrant liquid crystal phases by orthoscopic, conoscopic, differential scanning calorimetric and X-ray powder diffraction techniques.



Soft Matter

Vediappen Padmini, Palakurthy Nani Babu, Geetha G. Nair, D. S. Shankar Rao, Channabasaveshwar V. Yelamaggad*



Optically Biaxial, Re-entrant and Frustrated Mesophases in Chiral, Nonsymmetric Liquid Crystal Dimers and **Binary Mixtures**

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