NJC

PAPER



Cite this: DOI: 10.1039/c8nj03520b

Received 14th July 2018, Accepted 3rd December 2018

DOI: 10.1039/c8nj03520b

rsc.li/njc

I. Introduction

Liquid crystal (LC) oligomers (oligomesogens) formed by covalently tethering two or more mesogenic cores through flexible spacer(s) have been attracting considerable scientific attention largely due to the fact that they constitute a novel class of nonconventional mesomorphic materials providing a plethora of opportunities to modulate the thermal properties and other functional characteristics with great ease.^{1–4} Interestingly, in a recent review article by Richard J. Mandle, one of the most remarkable phase transitional properties of oligomesogens, which was hitherto masked, has been revealed: the existence of the twist-bend nematic (N_{tb}) phase, which signifies a structural correlation among the well-known uniaxial nematic (N) and the chiral nematic (N*) phases, has been reported to

Highly frustrated liquid crystal phases in optically active dimers: synthesis and rich phase transitional behavior⁺

Rashmi Ashwathama Nayak,^{‡*^a} Sachin A. Bhat,^a G. Shanker,^b D. S. Shankar Rao^a and C. V. Yelamaggad ^b*^a

Herein we report on the synthesis and characterization of four new series of optically active, nonsymmetric dimers in which cholesterol is covalently linked to a Schiff base core through an ω-oxyalkanoyl spacer. While the Schiff base core is substituted with *n*-butyloxy, *n*-hexyloxy, *n*-octyloxy, *n*-decyloxy and *n*-dodecyloxy tails, three even-parity spacers, namely, 4-oxybutanoyl, 6-oxyhexanoyl, 8-oxyoctanoyl, and an odd-parity spacer, namely, 5-oxypentanoyl, have been used to join the two cores. The experimental results show that the length and parity of the spacer and the length of the terminal tail play a vital role in deciding the phase sequences of the dimers. In general, the dimers possessing an even-parity spacer display enantiotropic LC phases such as chiral nematic (N*), twist grain boundary (TGB), smectic A (SmA), chiral smectic C (SmC*) and twist grain boundary phase with SmC* slabs (TGBC*). Some of these dimers display TGBC* over a wide temperature range. The dimers with an odd-parity (5-oxypentanoyl) spacer display, unlike their even-membered counterparts, blue phases (BPIII/II/I); besides, they stabilize N* and/or unknown smectic (SmX) phases. The circular dichroism (CD) measurements were carried out as a function of temperature on the planar texture formed by three even-membered dimers and an odd-membered dimer. The occurrence of a strong negative CD band in the N* phase of the even-membered dimers suggests a left-handed screw sense of the macroscopic helical structure, and the scenario is opposite in the case of an odd-membered dimer.

exist in a variety of LC oligomers.² Fundamentally, the intrinsic self-assembly of oligomesogens into LC phases is rather different from that of the conventional (monomeric) low molar mass LCs.¹ For example, the first (simplest) constituent of oligomers, namely LC dimers, wherein two mesogens are bound to each other via a flexible (polymethylene) spacer, displays atypical mesomorphism which varies from those of the corresponding monomeric mesogens.^{1a,d,3,4} In fact, their thermal behavior depends not only on the chemical nature of two constituent mesogenic segments but also on the length and parity of the central spacer.³ While the symmetric LC dimers, made by joining two chemically identical mesogenic units, display a rich smectic polymorphism, the non-symmetric LC dimers comprising two chemically dissimilar mesogens show intercalated structures. Indeed, both classes of dimers show an archetypal spacer parity directed odd-even effect.^{1a,d,3} That is, the clearing (LC phase to isotropic phase) transition temperatures and the associated entropies show a pronounced alternation when the spacer parity is varied with even or odd number of methylene units. This behavior has generally been ascribed to the dependence of the overall shape of the dimeric molecules on the parity of the spacer in all-trans conformation. A dimer with an even-parity spacer attains a rod-like shape where the mesogenic units are antiparallel,



View Article Online

^a Centre for Nano and Soft Matter Sciences, P. B. No. 1329, Prof. U. R. Rao Road, Jalahalli, Bengaluru 560013, India. E-mail: yelamaggad@cens.res.in, yelamaggad@gmail.com

^b Department of Chemistry, Jnana Bharathi Campus, Sneha Bhavan,

Bangalore University, Bengaluru, 560056, India

 [†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c8nj03520b
 ‡ Present address: CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road,

Pune-411 008, India.

whereas in a dimer with an odd-numbered spacer, the mesogens are inclined with respect to each other to give an overall bent shape to the molecule. The bent shape of the odd-spaced dimer obviously decreases the molecular shape anisotropy and thus the order of the LC phase (due to inefficient packing), so clearing temperatures and the associated enthalpy/entropy values are lower in such dimers.

In recent years, chirality⁵ in LC dimers has become one of the major research topics not only for fundamental research reasons but also from the technological point of view.^{1a,d,3,4} This is mainly because molecular asymmetry imparting form chirality to LC dimers has profoundly influenced their thermal properties. In fact, several remarkable phase transitional properties have been witnessed in a wide variety of both symmetric and nonsymmetric LC dimers.^{1a,d,3,4} This is especially noteworthy in the case of optically active, nonsymmetric dimers in which cholesterol is covalently linked to a conventional calamitic (two-ring mesogenic) core via a flexible spacer of varying length and parity. Their unique molecular structural characteristics, mostly stemming from the presence of cholesterol, have not only enabled them to display exceptional phase sequences, highly frustrated fluid structures, reentrant phases, etc., but also provided distinctive strategies and platforms to modulate the properties of LC phases featuring technological values.⁴ Jin and co-workers were the first to work on cholesterol-based Schiff base dimers, I-1 to I-4 (Chart 1), reporting the occurrence of the richest variety of mesophases in one of the dimers (I-1) which included the fluid incommensurate smectic (Sm_{ic}) phase.⁶ Inspired by these findings, a wide variety of cholesterol-based dimers numbering over 400 have been realized where mesogenic cores such as Schiff base,6,7,8c,d o-hydroxy Schiff base (salicylaldimine),⁸ isoflavone,⁹ sydnone,¹⁰ azobenzene,¹¹ bent core,¹² cinnamate,¹³ chalcone,¹⁴ 1,4-diphenyl-1*H*-1,2,3-triazole,¹⁵ biphenyl,¹⁶ diphenylbutadiene,¹⁷ tolane,¹⁸ 1,3,4-oxadiazole/ 1,2,4-oxadiazole/1,3,4-thiadiazole,¹⁹ and pentaalkynylbenzene²⁰ have been interlinked with cholesterol to understand the structure-property correlations. In essence, the molecular architecture of cholesterol-based dimers is such that it provides strategies to design multifunctional soft materials through the incorporation of suitable molecular fragments such as spacers, mesogens and terminal segments.

As mentioned earlier, optically active nonsymmetric dimers derived from the combination of cholesterol and Schiff base^{6,7,8c,d}



Chart 1 Molecular structures of novel Schiff base LC dimers reported by Jin and co-workers (ref. 6 and 7*a*) and similar dimers with reversed imine linkage and n-alkoxy terminal tails investigated in the present study.

segments display the richest variety of mesophases. Hitherto accumulated experimental results show that the mesomorphism of such dimers is extremely sensitive to the nature of Schiff base and its terminal substituents. On the other hand, it is well known that the thermal behavior of Schiff base LCs can be altered effectively if the imine (azomethine) linkage is reversed.²¹ Hence, in continuation of our earlier study on such LCs,^{7c} we intended to realize cholesterol-based Schiff base dimers where the orientation (direction) of the imine linkage is reversed. Accordingly, we have synthesized and investigated the thermal behavior of four series of cholesterol-based dimers comprising Schiff base wherein the direction of imine linkage is inverted (see Chart 1). The even-parity spacers such as 4-oxybutanoyl(trimethylene), 6-oxyhexanoyl(pentamethylene) and 8-oxyoctanoyl(heptamethylene), and an odd-parity spacer 5-oxypentanoyl(tetramethylene) have been used to join the two mesogenic segments. Given the fact that a slight change in the nature and length of the terminal chain affects both transition temperatures and mesophase sequences that will be formed, in the present study the Schiff base unit is substituted with *n*-butyloxy, *n*-hexyloxy, *n*-octyloxy, *n*-decyloxy and *n*-dodecyloxy tails. These new dimers are represented by the mnemonic DSB-n,R where DSB denotes dimeric Schiff base, n indicates the total number of methylene carbons solely (excluding the carbonyl carbon) in the spacer and **R** signifies the *n*-alkoxy tail. A general molecular structure of the four series of cholesterol-based nonsymmetric dimers (DSB-3,R, DSB-4,R, DSB-5,R and DSB-7,R) realized in the present study is shown in Chart 1.

II. Synthesis and molecular structural characterization

Four series of target Schiff base dimers, **DSB-3,R**, **DSB-4,R**, **DSB-5,R** and **DSB-7,R**, were prepared as shown in Scheme 1. Cholesteryl ω -bromoalkanoates (**1a-d**) were prepared in excellent yields by the esterification of cholesterol with freshly synthesized 4-bromobutanoyl, 5-bromopentanoyl, 6-bromohexanoyl or 8-bromooctanoyl chlorides as described in the literature.^{16b,22} These alkanoates **1a-d** were reacted with 4-nitrophenol to get the corresponding nitro derivatives **2a-d** which were subsequently subjected to catalytic hydrogenation (10% Pd–C; H₂ 1 atm., balloon), yielding the key amines **3a-d**.

4-*n*-Alkoxybenzaldehydes (4a–e), prepared by *O*-alkylating 4-hydroxybenzaldehyde with the requisite *n*-alkyl bromides in the presence of a mild base, were condensed with amines 3a–d in the presence of a mild acid to obtain four series of dimers. The spectroscopic data and the results of elemental analyses were found to be consistent with the proposed molecular structures of all the intermediates and final compounds. The detailed synthetic procedures and molecular structural characterization data of the target LC dimers and their intermediates are presented in the ESI.†

III. Results and discussion

The thermal behavior of these four series of dimers, DSB-3,R, DSB-4,R, DSB-5,R and DSB-7,R, and their key intermediates,



Scheme 1 Reagents and conditions: (i) *n*-bromoalkanoyl chlorides, pyridine, THF, 0-5 °C to rt (82–88%). (ii) 4-Nitrophenol, anhydrous K₂CO₃, butanone, reflux 12 h (76–84%). (iii) H₂ (1 atm., balloon), 10% Pd–C, THF, rt, 4 h (87–94%). (iv) *n*-Bromoalkanes, anhydrous K₂CO₃, butanone, reflux 12 h (85–90%). (v) EtOH, AcOH (catalytic), reflux, 1 h (66–85%).

2a–d and **3a–d**, was established using standard complementary techniques. Generally, the samples placed between a clean untreated glass slide and a cover slip were used for the POM study. However, for confirmation of the LC phase assignment, two differently surface-coated slides, one treated for homogeneous orientation and the other for homeotropic alignment of the mesogens, were employed. The intermediates **2a–d** and **3a–d** show LC phases; in particular, these compounds exhibit N*, TGB and SmA phases that were adjudged based on the optical textural observation under POM (Fig. S1, ESI†). The phase sequences, transition temperatures and enthalpies of these intermediates are summarized in Table S1 (ESI†). In the following sections, the LC properties of dimers belonging to DSB-3,R, DSB-4,R, DSB-5,R and DSB-7,R series have been discussed.

IIIa. Thermal behavior of DSB-3,R series

The thermal properties of dimers belonging to the **DSB-3,R** series are presented in Table 1, which reveals that all the dimers are mesomorphic. Fig. 1a depicts the effect of the length of the terminal tail on the LC behavior of dimers observed during the cooling cycle. The mesophase identification and phase sequence confirmation were achieved purely based on

textural observations under POM. The textures seen for different LC phases of dimers are shown in Fig. 2a-i. It is especially apparent from the results that all the five dimers of the series display enantiotropic mesomorphism. The first member DSB-3,4 exhibits SmA and N* phases. When a thin film of this compound was placed between two glass plates and cooled from the isotropic phase, focal-conic fan texture appeared, which, when sheared, showed the characteristic Grandjean texture of the N* phase. On cooling the sample further, a transformation to a focal-conic fan texture of the SmA phase occurs. The next member DSB-3,6 shows the TGB phase in addition to the SmA and N* phases. The TGB phase gave a filament texture on heating from a homeotropic SmA phase, as expected. Indeed, if the sample is heated at a higher rate (>3 $^{\circ}$ C min⁻¹), the N*, SmA and TGB phases coexist. Interestingly, the dimer DSB-3,8 stabilizes the TGBC* phase along with the TGB and N* phases. On cooling from the isotropic state, it displayed a focal-conic fan texture which on mechanical stress transformed into a Grandjean planar texture (Fig. 2a) of the N* phase.²³ The planar texture of the N* phase on further cooling transformed into a TGB phase (which may have either a SmA or a SmC block) at

Table 1Phase sequences, transition temperatures ($^{\circ}C$)^a and enthalpies of transitions (kJ mol⁻¹) of DSB-3,R series

| | Phase sequence | |
|----------|---|--|
| | Heating | |
| Dimers | Cooling | |
| DSB-3,4 | Cr 141 (19.2) SmA 168.6 ^b N* 230.4 (3.7) I I 229.6 (3.5) N* 167.1 ^b SmA 116 (8.3) Cr | |
| DSB-3,6 | Cr 148 (35.3) SmA 156.2 ^b TGB 158.7 ^b N* 220.4 (3.4) I I 219.5 (2.8) N* 157.1 ^b TGB 154.8 ^b SmA 98.2 (25.2) Cr | |
| DSB-3,8 | Cr 118.5 (38.4) TGBC* 172.1 ^b TGB 195.2 ^b N* 214.3 (3.8) I I 213.4 (3.7) N* 194.2 ^b TGB 169.9 ^b TGBC* 80.8 (11.2) Cr | |
| DSB-3,10 | Cr 119.9 (31.6) SmC* 173.1 ^b SmA 197.4 ^b TGB 202.4 (0.3) N* 208.8 (4.7) I L 207.9 (4.6) N* 201.4 (0.3) TGB 195.7 ^b SmA 172.3 ^b SmC* 87 (25.5) Cr | |
| DSB-3,12 | Cr 117.8 (40.6) SmC* 173.2 ^b SmA 202^{b} TGB 203 (0.5) N* 204.3 (3.4) I I 203.4 (3.5) N* 201.9 (0.4) TGB 200.1 ^b SmA 170.2^{b} SmC* 82.6 (19.9) Cr | |

^{*a*} Transition temperatures determined by both POM and peak values of the DSC traces during the first heating/cooling cycles at 5 $^{\circ}$ C min⁻¹ rate. ^{*b*} The phase transition was observed under the microscope, but it was too weak to be resolved by DSC.



Fig. 1 (a) A plot of transition temperature as a function of the number of carbon atoms in the terminal tail for mesogens belonging to the **DSB-3,R** series. (b) DSC traces obtained for the first and second heating–cooling cycles of mesogen **DSB-3,10** at a rate of 5 °C min⁻¹. Notice that the traces of two heating–cooling cycles closely match, suggesting that these compounds are thermally stable.

about 194 °C as evidenced by the observation of a planar texture (Fig. 2b). Upon cooling the sample further, a square grid pattern (Fig. 2c) appeared at 169.9 °C over the gray planar texture, indicating the presence of a TGBC* phase.²³ Despite several attempts, this dimer could not be aligned homeotropically, and thus, the expected filament and undulated filament textures of the TGB and TGBC* phases, respectively, could not be observed. However, in a wedge type cell treated for planar orientation, Grandjean Cano (GC) dislocation lines were observed in the N* (Fig. 2d), TGB (Fig. 2e) and TGBC* (Fig. 2f) phases, demonstrating that there is a helical twist normal to the plates in these phases; notably, in the TGBC* phase the GC lines superposed on the square grid pattern (Fig. 2f). These observations rule out the possibility that the origin of the square grid is due to some instability in the helical structure of the SmC* phase. In fact, in the TGBC* structure, besides the presence of a helical superstructure due to the TGB helix, there exists another helical structure due to the bulk SmC* phase; the helical axis of the latter is perpendicular to that of the TGB helix.

The dimers **DSB-3,10** and **DSB-3,12** showed an identical mesomorphic behavior. In fact, the richest polymorphic sequence was observed for both of these dimers, which we describe as follows. When a thin film of any of the two dimers, placed between clean glass slides, was cooled gradually from the isotropic state, the N* phase was found to emanate from the

dark background at a well defined temperature. Its presence was clearly recognized by a focal-conic fan texture which transformed into a Grandjean planar texture when the top glass substrate was pressed very gently. Upon cooling the pressed sample further, the TGB phase (having either SmA or SmC block) appeared with a planar texture. On lowering the sample temperature further, the planar texture of the TGB phase sharply changed to a pattern comprising both a focalconic fan texture and a pseudo-isotropic texture; these textural features strongly suggest the presence of the SmA phase.²³ In fact, upon heating the homeotropically aligned (pseudoisotropic texture of) SmA phase, a striking filament texture of the TGB phase was observed. When the SmA phase was cooled further, an optical texture comprising the banded focal-conic fans and cloudy pattern featuring a faint schlieren texture, arising due to planar and homeotropic orientations of the dimers, respectively, were observed, which suggests the presence of the SmC* phase. Hence, the occurrence of N*-TGB-SmA-SmC* phase sequence was evidenced using slides treated for planar and homeotropic alignments. As expected, the TGB phase showed a filament texture when slides treated for homeotropic alignment were employed. The presence of the SmA phase displayed the focal-conic texture in slides treated for planar orientation, as shown in Fig. 2g, and a dark field of view in slides treated for homeotropic alignment. The focal-conic fan



Fig. 2 Photomicrographs of the optical textures seen for the mesophases of dimers belonging to the DSB-3,R series: (a) the Grandjean planar texture of the N* seen for DSB-3,8 (206 °C); (b) the planar texture of the TGB phase of DSB-3,8 (180 °C); (c) the square grid pattern of the TGBC* phase emerging from the planar texture of the TGB phase of DSB-3,8 (169 °C); (d) the Grandjean Cano (GC) dislocation lines observed for the N* phase of DSB-3,8 (200 °C); (e) GC dislocation lines noticed for the TGB phase of DSB-3,8 (190 °C); (f) the square grid pattern superposed on the GC dislocation lines seen for the TGBC* phase of DSB-3,8 (150 °C); (g) the focal-conic fan texture of the homogeneously aligned SmA phase of DSB-3,10 (190 °C); (h) an equidistant line pattern superimposed on the focal-conics of SmC* fans of DSB-3,10 (165 °C); (i) the dull yellow greyish schlieren texture of the homoeotropically oriented SmC* phase of DSB-3,12 (151 °C).

texture with dechiralization lines on top of it was observed solely, as shown in Fig. 2h, for the homogeneously aligned SmC* phase. However, for the homeotropic orientation it showed a schlieren texture surrounded by a dull yellow greyish uniform pattern (Fig. 2i); the schlieren texture mostly contained four-brush disclinations (strength S = 1). As a representative case, the DSC traces obtained for **DSB-3,10** during two consecutive heating and cooling cycles are shown in Fig. 2b where the close resemblance among the traces can be seen. Thus, the calorimetric results corroborate the microscopic observation that these dimers are thermally stable. It is important to note that the dimer **DSB-3,8** shows the TGB and TGBC* phases over a wide thermal width, *viz.* ~ 24 °C and ~ 85 °C, respectively.

IIIb. Thermal behavior of the DSB-4,R series

The phase sequences, transition temperatures and associated enthalpies of the **DSB-4,R** series of dimers having an odd-parity spacer are summarized in Table 2. The data shown here were derived from DSC traces of the first heating–cooling cycles obtained at a rate of 5 °C min⁻¹. Fig. 3a shows the DSC traces obtained for one of the dimers. Fig. 3b shows the dependence of the transition temperatures of the dimers on the number of carbon atoms in the terminal tail. All five members of the series exhibited enantiotropic mesophases. The first two members, DSB-4,4 and DSB-4,6, showed an identical thermal behavior that was evidenced based on the characteristic optical textures of the mesophases. As a representative case, the microphotographs of textural patterns observed for the mesophases of dimer DSB-4,4 are shown in Fig. 4a-f. When a thin film of the sample, placed between a glass slide and a coverslip, was cooled slowly $(0.1 \,^{\circ}\text{C min}^{-1})$ from the isotropic phase, a platelet texture grew on top of the black background and filled the field of view (Fig. 4a), suggesting the presence of BPI or BPII. In fact the cubic BPI and BPII phases, comprising double twist cylinders, possessed 3D orientational ordering with periods nearly equal to 500 nm that is of the order of the wavelength of visible light. Thus, they Bragg-scattered light in the visible range. They comprised differently oriented domains exhibiting the textural pattern characterized by a mosaic of different colors.²³ The textural pattern seen under the POM suggests the existence of a cubic blue phase which can be either BPI or BPII.²³ With further cooling, the N* phase began to grow instantaneously on top of the platelet texture (Fig. 4b) and filled the field of view quickly displaying an atypical bright texture, which upon gentle shearing showed the Grandjean planar texture of the N* phase (Fig. 4c).

| | Phase sequence |
|-----------|---|
| | Heating |
| Compounds | Cooling |
| DSB-4,4 | Cr 102.6 (16.4) N* 169.8 (0.2) I |
| | I 167.8 BPI/II-N* (0.2) ^b 79.4 (5.9)Cr |
| DSB-4,6 | Cr 109.3 (33.2) N* 166.7 (0.6) I |
| | I 166.0 BPI/II-N* $(0.5)^b$ 76.8 (20.9) Cr |
| DSB-4,8 | Cr 107.7 (25.7) SmX 124.6 ^c N* 160.9 (0.7) I |
| | I 160.3 (0.6) BPIII 151 ^c N*108.3 ^c SmX 59.8 (19.1) Cr |
| DSB-4,10 | Cr 126.5 (52.7) SmX 144.7 ^c N* 157.1 (0.7) I |
| , | I 156.3 (0.6) BPIII 144.2 ^c N* 123.2 ^c SmX 60.8 (34.6) Cr |
| DSB-4,12 | Cr 124.4 (52) SmX 139.5 ^c N* 155.3 (1.4) I |
| , | I 154.8 (1.4) BPIII ^c 150 N*133.3 ^c SmX 55 (43) Cr |

^{*a*} Transition temperatures determined by both POM and peak values of the DSC traces during the first heating/cooling cycles at 5 °C min⁻¹ rate. ^{*b*} The I-BP and BP-N* phase transitions were seen under POM, but they were too weak to be detected by DSC; thus, the ΔH value represents the combined enthalpy for the I-BP and BP-N* transitions. ^{*c*} The phase transition was observed under the microscope, but it was too weak to be resolved by DSC.

Mesophase characterization by optical textural observation revealed that the dimers DSB-4,8, DSB-4,10 and DSB-4,12 display nearly the same transitional behavior; the occurrence of three distinct phase transitions was evidenced. For example, the dimer DSB-4,8, either placed between clean glass slides or treated for planar or homeotropic geometry, and cooled slowly from the isotropic (I) phase, showed a LC phase having a dark bluish-foggy appearance as shown in Fig. 4d, which is a characteristic texture of the BPIII.²³ A signature due to I-BPIII transition with $\Delta H = 0.6$ kJ mol⁻¹ (Table 2) seen in the DSC trace corroborated the optical observation. On cooling the sample further, at 151 °C the BPIII texture changed to a pattern, which on gentle shearing showed the Grandjean planar texture typical of the N* phase (Fig. 4e). Thus, the BPIII existed over 9 °C thermal range; it can be noted here that the other two dimers DSB-4,10 and DSB-4,12 stabilized this phase over \sim 12 °C and \sim 5 °C, respectively. It must be mentioned here that the existence of the BPIII phase in these dimers (DSB-4,8, DSB-4,10 and DSB-4,12) and the BPI/II phase in lower members DSB-4,4 and DSB-4,6 is in good agreement with the general observation that chiral, non-symmetric dimers possessing an

odd-membered spacer show BPs;^{1d,24-26} this implies that the chirality/pitch of the LC structure is vital²⁷ which shows a dependence on the parity of the spacer.²⁶ This observation can be ascribed to the bent shape of dimers (Fig. 5, top portion) which are less elongated when compared to their even spacer counterparts (Fig. 5, bottom portion). In particular, this can be understood in terms of the smaller helical pitch for the oddmember which stems from the smaller twist elastic constant that in turn linked to their lower orientational order. In other words, the higher orientational order found for even-members precluded stabilization of BPs by them. When the sample (DSB-4,8) was continued to cool from the Grandjean planar texture of the N* phase, a mesophase, hereafter referred to as the SmX phase, set in at \sim 108 °C. It manifests optically in the form of oily streak texture having a bluish background as shown in Fig. 4f. It can be mentioned here that the optical textural patterns for these mesophases were found to be identical when the samples were either examined using clean glass slides or treated for planar or homeotropic orientation. Thus, the exact nature of the SmX phase could not be revealed by optical study alone.

In order to probe the structure of the SmX phase, XRD measurements were carried out on an unaligned (powder) sample DSB-4,8. While cooling the sample, the XRD patterns as a function of temperature were collected in the SmX phase region. The diffractograms obtained for all the temperatures were found to be practically identical; as a typical case, the pattern obtained at 90 °C is shown in Fig. 6a. It consists of two low angle reflections, the first one very intense (d_1) and the other very weak (d_2) , and a diffuse reflection at wide angles. The wide angle diffuse peak centered at 4.9 Å corresponds to the intermolecular separation within the smectic layer arising due to the liquid like order. The spacings (d_1) derived from the low angle Bragg reflections obtained at different temperatures are depicted in Fig. 6b. Indeed, this spacing (d_1) corresponds to the smectic layer thickness in the SmX phase. The second peak with the spacing ($d_2 = 20.8$ Å) nearly half the molecular length of the dimer must be arising from the combination of different parts of the molecule; in fact, such a feature has been observed for many cholesterol-based dimers.^{4,6,7*a*,*b*} The spacing d_1 of the low-angle reflections and the d_1/L ratio calculated by considering the molecular length L in an all-trans conformation are presented



Fig. 3 (a) DSC thermograms obtained for the first and second heating–cooling cycles of mesogen **DSB-4,6** at a rate of 5 $^{\circ}$ C min⁻¹. (b) Plot of transition temperature as a function of the number of carbon atoms in the terminal tail for LC dimers of the **DSB-4,R** series.



Fig. 4 Microphotographs of the optical textures observed for different LC phases of dimers belonging to the DSB-4,R series: (a) the platelet texture of BPI/BPII seen for DSB-4,4 (167.8 °C); (b) the textural pattern showing the co-existence of both BPI/BPII and N* phases for dimer DSB-4,4 (167 °C); (c) the oily streak texture of the N* seen for DSB-4,4 (110 °C); (d) the blue fog texture of the BPIII seen for DSB-4,8 (155 °C); (e) the oily streak texture of the N* phase observed for DSB-4,8 (120 °C); (f) the uncharacteristic texture observed for the SmX phase of DSB-4,8 (80 °C).



Fig. 5 The most stable (energy minimized) space-filling models of an oddmembered dimer **DSB-4,4** (top) and an even-membered dimer **DSB-3,4** (bottom).

in Table S2 (ESI[†]). It is apparent from the collected data that at higher temperatures the layer spacing d_1 is slightly more when compared to the estimated all-*trans* molecular length (42 Å); thus, the d_1/L ratio is slightly more than one. However, at lower temperatures the layer spacing d_1 is less than the molecular length and thus the d_1/L ratio is less than one, suggesting tilting of the molecules within the smectic layers, which increases on

lowering the temperature. Accordingly, the SmX phase can be considered as a tilted smectic phase.

IIIc. Thermal behavior of the DSB-5,R series

Table 3 shows the phase transition temperatures and the corresponding enthalpy changes of the **DSB-5,R** series of dimers. All the dimers of the series show enantiotropic LC phases. The dependence of the transition temperatures of the dimers on the number of carbon atoms in the terminal chain is shown in Fig. 7a. It is worth mentioning here that these dimers, like the other three series, were found to be thermally stable during repeated heating and cooling cycles through the mesophase–isotropic transition, as confirmed by both optical and the DSC experiments. For example, as shown in Fig. 7b, the DSC traces recorded for the two consecutive heating–cooling cycles were virtually identical. The textures seen for different LC phases of some of these dimers are shown in Fig. 8a–f.

Compounds **DSB-5,4** and **DSB-5,6** behaved identically, showing three LC phases. The occurrence of enantiotropic N*, TGB and SmA phases was ascertained based on their characteristic



Fig. 6 (a) X-ray intensity profile obtained for the SmX phase of **DSB-4,8** at 90 °C showing two reflections (d_1 and d_2) at low angles and a diffuse peak at the wide angle region. (b) The temperature dependence of the layer spacing d_1 in the SmX phase.

textural pattern observed under POM. The focal-conic fan texture growing just below the isotropic phase and a planar texture having oily streaks seen for the N* phase are shown in Fig. 8a and b, respectively. The planar texture of the TGB phase appearing for a very short thermal range is shown in Fig. 8c which immediately transforms into the SmA phase where a pattern comprising both focal-conic fan texture and a pseudoisotropic texture could be seen. Fig. 8d shows the filament texture of the TGB phase obtained upon heating the pseudoisotropic texture of the SmA phase. The next dimer DSB-5,8 showed a dimesomorphic sequence involving a transition from the TGBC* phase to the N* phase; a square grid texture pattern of TGBC* observed at 120 °C is shown in Fig. 8e. Compound DSB-5,10 showed three enantiotropic LC phases, namely TGBC*, TGB and N* phases, that was adjudged based on textural observation as described before. The last member of the series, DSB-5,12, like the dimers DSB-3,10 and DSB-3,12 of the DSB-3,R series, showed a rich variety of LC phases. That is, it exhibited four mesophases, N*, TGB, SmA and SmC* phases. As a representative case, the microphotograph of the optical texture of the planarly aligned SmC* phase featuring dechiralisation lines on top of the focal conic fan texture is shown in Fig. 8f. Needless to say, the occurrence of these LC phases was unequivocally

established with the help of POM wherein each mesophase showed characteristic optical textural patterns when viewed through the polarizing microscope. Given the fact that the TGB phase is short-lived, the N* and SmA phases coexisted along with it, which was evident from fact that the respective textures of these three LC phases existed concurrently.

IIId. Thermal behavior of the DSB-7,R series

The transitional properties of the five dimers belonging to the **DSB-7,R** series are presented in Table 4. Fig. 9a shows the dependence of the thermal properties on the number of carbon atoms in the terminal chain of the **DSB-7,R** series of dimers. These dimers, despite the fact that they comprise the Schiff base core, exhibited good thermal stability that was noted during the optical and calorimetric studies. In fact, the peaks of phase transitions observed in DSC thermograms for any number of heating-cooling cycles were found to be highly reproducible; for example, as shown in Fig. 9b, repeated heating-cooling scans of the sample **DSB-7,12** showed almost identical thermograms. From the collected data, the following inference can be made. In general, all the compounds of the series show enantiotropic LC phases. They commonly show the N* phase in spite of variation in their terminal tail length.

Table 3 Transition temperatures (°C)^a and enthalpies of transitions (kJ mol⁻¹) of the **DSB-5,R** series

| Compounds | Phase sequence | |
|-----------|---|---------|
| | Heating Cooling | |
| | | DSB-5,4 |
| DSB-5,6 | Cr 119.8 (23) SmA 165.4 ^c TGB-N* 199.5 (2.7) ^b I L 199.1 (2.6) ^b N*-TGB 165.1 ^c SmA 99.5 (23.6) Cr | |
| DSB-5,8 | Cr 118.5 (45.8) TGBC* 142.1 ^c N* 194.5 (5.1) I L 193.7 (5) N* 139.7 ^c TGBC* 79.7 (27.6) Cr | |
| DSB-5,10 | Cr 111.1 (44.4) TGBC* 158.2 ^c TGB 177.5 ^c N* 188.9 (4.8) I L 188.2 (4.8) N* 175.7 ^c TGB 156.6 ^c TGBC* 68.4 (17.3) Cr | |
| DSB-5,12 | Cr 101.7 (37.7) SmC* 164.3' SmA 181 (0.8) TGB-N* 184.3 (4.6) ^b I I 183.7 (4.5) ^b N*-TGB 180.1 (0.6) SmA 162.8' SmC* 69.1 (20.7) Cr | |

^{*a*} Transition temperatures determined by both POM and peak values of the DSC traces during the first heating–cooling cycles at 5 °C min⁻¹ rate. ^{*b*} The TGB phase is a transient phase that was seen under POM only; the TGB-N*/N*-TGB transitions were too weak to be detected by DSC and thus, the ΔH value represents the combined enthalpy TGB-N*/N*-TGB transitions. ^{*c*} The phase transition was observed under the microscope, but it was too weak to be detected by DSC.



Fig. 7 (a) The influence of the number of carbon atoms in the terminal chain on the transition temperature for the **DSB-5,R** series; (b) DSC traces obtained for the first and second heating–cooling cycles of mesogen **DSB-5,10** at a rate of 5 $^{\circ}$ C min⁻¹.



Fig. 8 Photomicrographs of the optical textures seen for the mesophases exhibited by dimers of the **DSB-5,R** series: (a) the focal-conic fan texture of the N* of dimer **DSB-5,4** developing on top of the isotropic liquid (207 °C); (b) the oily streak texture of the N* phase formed after shearing the focal-conic fan texture of the N* phase of **DSB-5,4** (185 °C); (c) the planar texture of the TGB phase of dimer **DSB-5,6** (165 °C); (d) the filament texture of the TGB phase obtained when a homeotropically aligned SmA phase of the dimer **DSB-5,6** is heated (155 °C); (e) the square grid pattern of TGBC* observed for **DSB-5,8** (120 °C); (f) the dechiralization lines on the top of the broken focal-conic texture of the SmC* phase of **DSB-5,12** (100 °C).

This was identified based on the observation of characteristic Grandjean planar texture (Fig. 10a), formed upon shearing the natural fan-like texture developed while cooling the samples from the isotropic state.

The first three members **DSB-7,4**, **DSB-7,6** and **DSB-7,8** displayed SmA and TGB phases additionally. As expected, the SmA phase showed, when examined using untreated glass microscope slides, the regions of focal-conic fan and homeotropic textures. The TGB phase displayed the filament texture (Fig. 10b) on heating from a homeotropic SmA phase. The next dimer **DSB-7,10** showed TGB and TGBC* phases besides the N* phase. When the Grandjean planar texture of the N* phase was

Table 4 Transition temperatures (°C)² and enthalpies of transitions (kJ mol^-1) of the DSB-7,R series

| | Phase sequence |
|-----------|---|
| | Heating |
| Compounds | Cooling |
| DSB-7,4 | Cr 130.6 (41.4) SmA 166.3 ^b TGB-N* 190.1 (2.8) ^c I L 188 3 (2.7) ^c N*-TGB 164 9 ^b SmA 89 1 (16.0) Cr |
| DSB-7,6 | Cr 120.3 (51.6) SmA 166.8 (0.4) TGB-N* 183.7 (3.5) ^c I 182.6 (3.3) ^c N*-TGB 164.9 (0.3) SmA 75.1 (20.1) Cr |
| DSB-7,8 | Cr 117.4 (37.4) SmA 150.4 ^b TGB-N* 175.9 (3.6) ^c I I 174.5 (3.2) ^c N*-TGB 149.6 ^b SmA 98.3 (38.9) Cr |
| DSB-7,10 | Cr 109.6 (34.2) TGBC* 134.4 ^b TGB 148.5 N* 170.4 (3.4) I I 169.5 (3.2) N* 147.1 TGB 133.0 ^b TGBC* 68.1 (13.6) Cr |
| DSB-7,12 | Cr 99.5 (35.2) TGBC* 156.4 ^b N* 164.1 (4.1) I I 163.7 (4) N* 155.0 ^b TGBC* 60.1 (24.6) Cr |

^{*a*} Transition temperatures determined by both POM and peak values of the DSC traces during the first heating–cooling cycles at 5 °C min⁻¹ rate. ^{*b*} The phase transition was observed under POM, but it was too weak to be detected by DSC. ^{*c*} The TGB phase was seen under POM only; the TGB-N*/N*-TGB transitions were too weak to be detected by DSC and thus, the ΔH value represents the combined enthalpy TGB-N*/N*-TGB transitions.

cooled, a phase transition occurred with a deep gray blurry planar texture which is the characteristic texture of the TGB phase. As the temperature was lowered, a square grid pattern developed sharply on top of grayish planar texture of the TGB phase at 133 °C, implying the presence of the TGBC* phase. In order to verify the presence of the N* and frustrated (TGB and TGBC*) phases, the sample was examined in a wedge type cell treated for homogeneous alignment. The N* and TGB phases obtained in succession while cooling from the isotropic phase showed an array of GC lines. On further cooling, the TGBC* phase came into existence with a square grid pattern appearing on top of the dislocation lines. Thus, the TGB and TGBC* phases, respectively, exist over thermal range of ~ 14 °C and \sim 65 °C which is noteworthy given the fact that such phases, being frustrated structures, are known to exist over a narrow temperature range.^{5,23} Compound DSB-7,12 stabilized the TGBC* phase besides the N* phase. On cooling the planar texture of the N* phase, the TGBC* phase occurred with a characteristic square grid textural pattern (Fig. 10c). To confirm that the origin of square grid texture is due to the TGBC* phase, the sample was examined in wedge type cell treated for planar orientation. The N* phase obtained while cooling from the isotropic phase showed an array of GC lines; on cooling the N* phase, the TGBC* phase appeared with a square grid pattern developing over these dislocation lines.

Thus, the foregoing microscopic texture observations suggest that the dimers **DSB-7,10** and **DSB-7,12** stabilize the TGB and/or TGBC* phase over a wide thermal span. To substantiate the results of POM studies, XRD experiments were performed on unaligned (powder) samples **DSB-7,10** and **DSB-7,12** taken in Lindemann capillary tube individually. The XRD profiles were recorded as a function of temperature in the TGBC* and/or TGB mesophases while cooling these dimers, mounted



Fig. 9 (a) Dependence of the transition temperature for the DSB-7,R series on the number of carbon atoms in the terminal tail. (b) DSC traces obtained for the first and second heating–cooling cycles of DSB-7,12 at a rate of 5 °C min⁻¹. Notice the occurrence of the TGBC* phase over a wide thermal range.

inside a temperature-controlled Mettler hot stage, from their isotropic phase. The diffractograms obtained for the frustrated phases of both the dimers were found to be roughly the same, each showing two small angle ($0 < 2\theta < 5^{\circ}$) reflections, the first one very intense (d_1) and the second one weak (d_2), and a diffuse reflection at wide angles ($2\theta \approx 20^{\circ}$). Table S3 (ESI†) and Fig. 11a–d illustrate the results/various aspects corresponding to XRD studies. As representative cases, the 1D intensity *vs.* 2θ profile obtained for the TGBC* phase of dimers **DSB-7,10** and **DSB-7,12** are shown in Fig. 11a and b, respectively. Table S3 (ESI†) presents the spacing d_1 of the small-angle reflections and the d_1/L ratio, where L is the estimated all-*trans* molecular length derived from a Chem3D molecular model.

While the presence of second peak (d_2) in the small angle region in each profile is an important one as it may be originating from the combination of different parts of the dimer, 4,6,7a,b the spacing d_1 pertains to the smectic layer thickness in the TGB and TGBC* phases. The large angle diffuse band centered at ~4.9 Å (Table S3, ESI^{\dagger}) corresponds to the intermolecular separation within the smectic layer arising due to the liquid like order. Fig. 11c and d depict the layer spacing d_1 of the lowest angle reflection obtained as a function of temperature in the TGB, TGBC* and TGBC* phases of dimers DSB-7,10 and DSB-7,12, respectively. It is apparent from Fig. 11c and Table S3 (ESI[†]) that the layer spacing values in the TGB phase are comparable to the length L of the dimer DSB-7,10 in its all-trans conformation; that is, the ratio of $d_1/L \sim 1$ is archetypal of the monolayer SmA phase, meaning that the TGB phase possesses SmA blocks and thus, the TGB can be recognized as the TGBA phase. The accumulated data in the subsequent frustrated (TGBC^{*}) phase clearly show that the layer spacing d_1 is less than the estimated all-*trans* molecular length and thus the d_1/L ratio is less than one. This abrupt drop in the d_1 value at the transition from the TGBA to the TGBC^{*} phase is anticipated given the fact that in the TGBC^{*} phase the smectic C^{*}-like blocks, which remains orthogonal to the helix of the TGB structure, comprise mesogens that are tilted with respect to the layer normal direction. It can be seen that on cooling the TGBC^{*} phase gradually the d_1 -value decreases in a monotonic manner, suggesting that the tilt angle of the mesogens within the smectic layers increases on lowering the temperature.

Likewise, the *L* of the dimer **DSB-7,12** estimated from its all-*trans* configuration was found to be higher than the layer spacing d_1 values obtained in the entire thermal range of the TGBC* phase (see Fig. 11d and Table S3, ESI†). This implies the tilted organization of the mesogens within the smectic layers and obviously, the layer thickness will be smaller. Thus, the XRD study ensures the tilted organization of the molecules within the smectic layers supporting the occurrence of the TGBC* phase in both dimers.

From the foregoing presentation concerning the thermal behavior of four series of cholesterol based dimers, the following key remarks can be made. It is important to mention here that these new chiral dimers comprise Schiff base wherein the imine linkage is reversed when compared to the known Schiff base dimers.^{6,7a} Besides, with the intention of establishing the structure-property relationships, the length and parity of the spacer, and the length of terminal tail have been varied.



Fig. 10 Photomicrographs of the optical textures of mesophases obtained for the dimers of the DSB-7,R series: (a) the oily streak texture of the N* phase formed by DSB-7,6 (180 °C); (b) the co-existence of textures of both SmA and TGB phases seen for DSB-7,6 (165 °C); (c) the square grid pattern observed for the TGBC* phase of DSB-7,12 (130 °C).



Fig. 11 1D intensity vs. 2θ profile obtained for the TGBC* phase of dimers **DSB-7,10** (a) and **DSB-7,12** (b). Note that both the profiles possess two reflections (d_1 and d_2) at low angles and a diffuse peak at the wide angle region. The temperature dependence of the layer spacing d_1 in the TGB and TGBC* phases of dimer **DSB-7,10** (c) and TGBC* phase of dimer **DSB-7,12** (d).

As shown in Fig. 12, an odd–even effect is prominently seen when the parity of the spacer is varied; that is, the number of carbon atoms in the spacer affects the thermal behavior of the compounds. For example, the dimers with even-parity spacer show high clearing temperature values than dimers comprising oddparity spacer. Most importantly, the LC property of dimers having odd-parity spacer differs from those of even-members. Needless to say, the observed odd–even effect can be interpreted in terms of



Fig. 12 The influence of the number of carbon atoms in the ω -oxyalkanoyl spacer on the clearing temperatures for the **DSB-3,R**, **DSB-4,R**, **DSB-5,R** and **DSB-7,R** series of dimers. In all the plots dashed lines joining points are suggestive of the general trend; it can be noted that experimental data do not cover for n = 7.

the overall molecular shape of the mesogens governed by the geometry and flexibility of the spacer. The lower clearing temperature values of the dimers with odd-parity spacer are due to their bent conformation (the reduced shape-anisotropy); on the other hand, the even-members with their rod-like conformation show the higher values. This behavior is, in fact, the characteristic thermal property of LC dimers. It is quite apparent that the lengths of terminal tail also influence the thermal behavior of the compounds. For example, in general, within each series the clearing temperature values decrease with the increase in tail length. Likewise, within the series, the length of the terminal tail influences the phase transitional behavior of the compounds.

IV. Chiroptical behavior of the N* phase

The chiral nematic (N*) phase is an orientationally ordered system characterized by a helical superstructure wherein the preferred orientation of the mesogens twists spatially around an orthogonal (helical) axis.⁵ It is, being helical, described by its pitch (*P*) (the distance corresponding to a full 360° rotation of the constituent mesogens along the helix director) and handedness; the latter typically varies when the temperature is altered. Most importantly, it exhibits special optical properties such as Bragg-like light reflection, high rotatory power and circular dichroism (CD). The CD measurement has been

demonstrated to be one of the valid probes to reveal the chiroptical behavior of the N* phase.^{27,28} The thin-film cell of planar texture, where the molecular director aligns parallel to the glass substrate surfaces and helix axis remaining perpendicular to cell window, displays a strong optical activity where birefringence contribution remains almost negligible or generally nil; thus, the CD activity resulting from planar texture of the N* phase is valid and reliable. In fact, the homogeneous texture contained in a cell interacts very effectively with the circularly polarized light (CPL) with a wavelength $\lambda = nP(n \text{ is the}$ mean refractive index); the direction of light propagation, being perpendicular to the cell walls, remains parallel to the helix axis and thus maximizes interaction of CPL with the N* phase. The helix of the N* phase reflects CPL of the same handedness while transmitting CPL of opposite handedness; that is, circular dichroism of the N* phase is the difference between the reflection coefficients for right and left hand CPL waves, instead of the absorption coefficients. The helical/twist sense (handedness) (left or right) of the phase shows the direction in which rotation of the director occurs from layer to layer. Thus, with the help of CD measurements it is possible to determine handedness of the N* phase. It should be however noted that CD experiments are delicate and thus should be carried out with extreme care. In particular, the possibility of the linear dichroism (LD) and birefringence contributions should be eliminated so as to obtain valid and reliable CD data.

CD spectra as a function of temperature were recorded in the entire N* phase regime of the four samples, viz. DSB-3,4, DSB-4,4, DSB-5,4 and DSB-7,4, chosen as representative cases from each series. The temperature-dependent CD spectra obtained in the N* phase are shown in Fig. 13a-d. Table S4 (ESI[†]) presents the CD data of the samples in terms of the number of CD signals obtained with their positions (λ_{max} , nm), signs (positive or negative) and intensities (in millidegrees). In the following, we describe the method adopted for the sample preparation and CD measurements carried out on the planarly oriented N* phase and isotropic state of samples. A minute amount (\sim 1–2 mg) of dimers sandwiched between two clean quartz plates was heated to its isotropic phase, using a programmable hot stage which gives an accuracy of about $\pm 0.6~^\circ\mathrm{C}$ variations, and the CD spectra were recorded. As shown in Fig. 13e-h (black traces), the CD activity, as expected, remains silent in this state. The samples were then cooled slowly into the N* phase and sheared mechanically over and over again not only to ensure uniform spreading but also to realize very thin film of the samples. It must be mentioned here that the preparation of such thin films of the N* phase was indispensable to overcome the saturation setback where intense CD bands beyond the measurable range of the CD spectrometer existed. Precisely, the standard cells with known thickness could not be used and thus, the CD experiments presented herein are purely qualitative. The CD spectra as a function of decreasing temperature were recorded in the entire temperature range of the N* phase. As illustrated in Fig. 13a-d, the CD phenomenon, unlike in the isotropic liquid state (Fig. 13e-h), was observed in the entire thermal width of the mesophase clearly implying that the chromophores are not influenced by the molecular chirality, but they are affected by the chirality (handedness) of the phase; in other words, the CD activity stems from the macroscopic helical arrangement of dimers. Genuinity of the CD signals observed in the N* phase was evaluated by recording at four and six different orientations performed by in-plane rotation of the sample cells by 90° and 60° , respectively. As expected, the CD spectra recorded in these experiments were found to be indistinguishable from those seen for the original position of the sample cell, meaning that there is no LD contribution. The CD equipment used in the current investigation has a built-in provision to measure the LD directly and thus, samples were subjected to LD measurement where the activity was found to be nil (see red traces in Fig. 13e-h); that is, as shown in the insets of Fig. 13e-f, the LD spectra have no meaningful signatures. The foregoing experimental results evidently suggest that the CD activity of the N* phase is indisputable and certainly not stemming from the LD artifact.

As can be seen in Fig. 13a, c and d, the even-membered dimers DSB-3,4, DSB-5,4 and DSB-7,4 commonly show an intense negative band in the range of 420 to 370 nm and a less intense positive band at \sim 280 nm. While the dimer DSB-4,4 with odd-numbered spacer shows an intense positive band in the region of 420 to 380 nm (Fig. 13b). Hence, both even- and odd-membered dimers display CD bands at the same position with an almost matching magnitude but of opposite signs. In general, the intensity of the signals decreases with decreasing temperature, as summarized in Table S4 (ESI⁺). The occurrence of CD bands can be attributed to the selective reflection wavelengths of circularly polarized light by the helical structure of the phase. The appearance of a less intense peak can be ascribed to the presence of phenyl rings.²⁹ So, chiroptical measurement in the N* phase by CD formally indicates its optically active (helical) supramolecular macroscopic organization in which intermolecular interactions between electronic transitions occur. It can be pointed out here that the observation of an intense positive CD signal in the N* phase of odd-membered dimer DSB-4,4 indicates a right-handed screw sense of the helical structure.^{4,29a} Needless to say, the parity of the spacer appears to dictate the handedness of the N* phase formed by LC dimers.

V. Conclusion

Four series of nonsymmetric, optically active dimeric liquid crystalline compounds, in which cholesterol and Schiff base mesogen are interlinked *via* an ω -oxyalkanoyl flexible spacer, have been synthesized and characterized using optical microscopy and differential scanning calorimetry. With the purpose of gaining insight into the parameters governing the structureproperty relations, the lengths of the central ω -oxyalkanoyl spacers and those of the terminal alkoxy chains have been varied. All the twenty dimers belonging to four series exhibit enantiotropic liquid crystal behavior. The study especially revealed that the transitional properties of these LC dimers depend not only on the length and parity of the flexible spacer



Fig. 13 Temperature dependent CD spectra of the N* phase obtained while cooling the dimers DSB-3,4, DSB-4,4, DSB-5,4, and DSB-7,4, from their isotropic phase (a–d). LD (red trace) and CD (black trace) spectra recorded, respectively, in the N* phase and isotropic phase of the samples (e–h); notice that, as expected, in these spectra the CD signals are not seen; the insets show that there is no LD activity.

but also on the lengths of the terminal tails. The dimers with odd-parity spacer show considerably lower N*-I (clearing) transition (isotropization) temperature as compared to their evenmembered counterparts; within the series the isotropization temperature generally decreases with the increase in terminal tail length. The even-members commonly show SmA and N* phases; some of them, depending upon the lengths of the spacer and terminal chain, display TGB, SmC* and TGBC* phases additionally. Remarkably, some of these dimers stabilize highly frustrated LC phases such as TGB and TGBC* over a wide thermal width. On the other hand, the dimers with an oddnumbered spacer commonly show the blue phase (BPI/II/III) and N* phases, while some of the dimers (higher members) also stabilize an unfamiliar tilted smectic phase; this observation is in accordance with the general important finding that BPs are stabilized by optically active, non-symmetric dimers comprising an odd-membered spacer, and not by their counterpart dimeric liquid crystals possessing an even spacer. Chiroptical properties of the chiral nematic phase of the samples were investigated by CD measurements; this study reveals that the handedness of cholesteric superstructure depends on the parity of the spacer. In essence, the study clearly illustrates the complex interplay of the different molecular sub-units of the dimers in stabilizing mesophases such as blue, chiral nematic, twist grain boundary, smectic A and chiral smectic C phases. Thus, the cholesterolbased dimers described here are early examples of what could be a vast family of materials that may secure a vital position in both basic and applied research.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

CVY sincerely thanks the Department of Science and Technology (DST), New Delhi, Govt. of India, for financial support through SERB project No. EMR/2017/S1/000153.

References

 (a) C. T. Imrie and P. A. Henderson, *Curr. Opin. Colloid Interface Sci.*, 2002, 7, 298–311; (b) I. M. Saez and J. W. Goodby, *J. Mater. Chem.*, 2005, 15, 26–40; (c) T. Kato, N. Mizoshita and K. Kishimoto, *Angew. Chem., Int. Ed.*, 2006, 45, 38–68; (d) C. T. Imrie and P. A. Henderson, *Chem. Soc. Rev.*, 2007, 36, 2096–2124; (e) J. W. Goodby, I. M. Saez, S. J. Cowling, V. Gortz, M. Draper, A. W. Hall, S. Sia, G. Cosquer, S.-E. Lee and E. P. Raynes, *Angew. Chem., Int. Ed.*, 2008, 47, 2754–2787; (f) A. Yoshizawa, *J. Mater. Chem.*, 2008, 18, 2877–2889; (g) J. W. Goodby, I. M. Saez, S. J. Cowling, J. S. Gasowska, R. A. MacDonald, S. Sia, P. Watson, K. J. Toyne, M. Hird, R. A. Lewis, S. E. Lee and V. Vaschenko, *Liq. Cryst.*, 2009, 36, 567–605; (h) A. S. Achalkumar, U. S. Hiremath, D. S. Shankar Rao and C. V. Yelamaggad, *Liq. Cryst.*, 2011, **38**, 1563–1589; (*i*) Handbook of Liquid Crystals; Volume 5: Non-Conventional Liquid Crystals, ed. J. W. Goodby, P. J. Collings, T. Kato, C. Tschierske, H. Gleeson and P. Peter Raynes, Wiley-VCH, Weinheim, 2nd edn, 2014.

- 2 R. J. Mandle, Soft Matter, 2016, 12, 7883-7901.
- 3 (a) C. T. Imrie, in *Structure and Bonding Liquid crystals, II*, ed. D. M. P. Mingos, Springer-Verlag, 1999, p. 149; (b) C. T. Imrie and G. R. Luckhurst, in *Handbook of liquid crystals*, ed. D. Demus, J. W. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Weiley-VCH, Germany, 1998, vol. 2B, part III, p. 799; (c) S. K. Pal and S. Kumar, *Liquid Crystal Dimers*, Cambridge University Press, UK, 2017.
- 4 C. V. Yelamaggad, G. Shanker, U. S. Hiremath and S. K. Prasad, J. Mater. Chem., 2008, 18, 2927–2949.
- 5 (a) Chirality in Liquid Crystals, ed. H.-S. Kitzerow and C. Bahr, Springer-Verlag, New York, 2001; (b) Materials Chiralty: Volume 24 of Topics in Stereochemistry, ed. M. M. Green, R. J. M. Nolte and E. W. Meijer, John Wiley & Sons Inc., New Jersey, 2003; (c) I. Dierking, Symmetry, 2014, 6, 444–472.
- 6 F. Hardouin, M. F. Achard, J.-I. Jin, J.-W. Shin and Y.-K. Yun, *J. Phys. II*, 1994, 4, 627–643.
- 7 (a) F. Hardouin, M. F. Achard, J.-I. Jin and Y. K. Yun, J. Phys. II, 1995, 5, 927–935; (b) F. Hardouin, M. F. Achard, J.-I. Jin, Y. K. Yun and S.-J. Chung, Eur. Phys. J. B, 1998, 1, 47–56; (c) C. V. Yelamaggad, A. Srikrishna, D. S. Shankar Rao and S. K. Prasad, Liq. Cryst., 1999, 26, 1547–1554; (d) J.-W. Lee, Y. Park, J.-I. Jin, M. F. Achard and F. Hardouin, J. Mater. Chem., 2003, 13, 1367–1372; (e) Y. Tian, X. Xu, Y. Zhao, X. Tang and T. Li, Liq. Cryst., 1997, 22, 87–96; (f) K. C. Majumdar, P. K. Shyam, D. S. Shankar Rao and S. K. Prasad, J. Mater. Chem., 2011, 21, 556–561.
- 8 (a) C. V. Yelamaggad, Uma S. Hiremath and D. S. Shankar Rao, *Liq. Cryst.*, 2001, 28, 351–355; (b) C. V. Yelamaggad, U. S. Hiremath, S. Anitha Nagamani, D. S. Shankar Rao and S. K. Pasad, *Liq. Cryst.*, 2003, 30, 681–690; (c) K. C. Majumdar and P. K. Shyam, *Mol. Cryst. Liq. Cryst.*, 2010, 528, 3–9; (d) K. C. Majumdar, P. K. Shyam, D. S. Shankar Rao and S. K. Prasad, *Liq. Cryst.*, 2012, 39, 1117–1123; (e) D. D. Sarkar, R. Deb, N. Chakraborty, G. Mohiuddin, R. Kanti Nath and N. V. S. Rao, *Liq. Cryst.*, 2013, 40, 468–481; (f) M. Kumar, T. Padmini and K. Ponnuvel, *J. Saudi Chem. Soc.*, 2017, 21, S322–S328.
- 9 T.-N. Chan, Z. Lu, W.-S. Yam, G.-Y. Yeap and C. T. Imrie, *Liq. Cryst.*, 2012, **39**, 393–402.
- 10 C. V. Yelamaggad, M. Mathews, U. S. Hiremath, D. S. S. Rao and S. K. Prasad, *Tetrahedron Lett.*, 2005, 46, 2623–2626.
- (a) N. Tamaoki, Y. Aoki, M. Moriyama and M. Kidowaki, *Chem. Mater.*, 2003, **15**, 719–726; (b) V. Ajay Mallia and N. Tamaoki, *J. Mater. Chem.*, 2003, **13**, 219–224; (c) V. Ajay Mallia and N. Tamaoki, *Chem. Mater.*, 2003, **15**, 3237–3239; (d) V. Ajay Mallia and N. Tamaoki, *Chem. Commun.*, 2004, 2538–2539; (e) K.-N. Kim, E.-D. Do, Y.-W. Kwon and J.-I. Jin, *Liq. Cryst.*, 2005, **32**, 229–237; (f) W.-K. Lee, K.-N. Kim, M. F. Achard and J.-I. Jin, *J. Mater. Chem.*, 2006, **16**, 2289–2297; (g) C. Wu, *Mater. Lett.*, 2007, **61**, 1380–1383;

(*h*) Y. Kim and N. Tamaoki, *ACS Appl. Mater. Interfaces*, 2016, **8**, 4918–4926.

- 12 (a) C. V. Yelamaggad, I. Shashikala, G. Liao, D. S. Shankar Rao, S. Krishna Prasad, Q. Li and A. Jakli, *Chem. Mater.*, 2006, 18, 6100–6102; (b) G. Liao, I. Shashikala, C. V. Yelamaggad, D. S. Shankar Rao, S. Krishna Prasad and A. Jakli, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2006, 73, 051701.
- 13 G. Shanker and C. V. Yelamaggad, *New J. Chem.*, 2012, 36, 918–926.
- 14 (*a*) C. V. Yelamaggad, A. S. Achalkumar, N. L. Bonde and A. K. Prajapati, *Chem. Mater.*, 2006, **18**, 1076–1078; (*b*) C. V. Yelamaggad, N. L. Bonde, A. S. Achalkumar, D. S. Shankar Rao, S. Krishna Prasad and A. K. Prajapati, *Chem. Mater.*, 2007, **19**, 2463–2472.
- 15 K. C. Majumdar, S. Mondal and R. K. Sinha, *New J. Chem.*, 2010, **34**, 1255–1260.
- 16 (a) A. T. M. Marcelis, A. Koudijs and E. J. R. Sudholter, *Recl. Trav. Chim. Pays-Bas*, 1994, 113, 524–526; (b) V. Surendranath, *Mol. Cryst. Liq. Cryst.*, 1999, 332, 135–140; (c) A. T. M. Marcelis, A. Koudijs and E. J. R. Sudholter, *Liq. Cryst.*, 2000, 27, 1515–1523; (d) A. T. M. Marcelis, A. Koudijs, E. A. Klop and E. J. R. Sudholter, *Liq. Cryst.*, 2001, 28, 881–887; (e) C. V. Yelamaggad, S. A. Nagamani, U. S. Hiremath and G. G. Nair, *Liq. Cryst.*, 2001, 28, 1009–1015; (f) C. V. Yelamaggad and M. Mathews, *Liq. Cryst.*, 2001, 28, 1009–1015; (g) A. T. M. Marcelis, A. Koudijs and E. J. R. Sudholter, *Mol. Cryst. Liq. Cryst.*, 2004, 411, 193–200.
- 17 S. Abraham, V. Ajay Mallia, K. V. Ratheesh, N. Tamaoki and S. Das, J. Am. Chem. Soc., 2006, **128**, 7692–7698.
- 18 (a) C. V. Yelamaggad, Mol. Cryst. Liq. Cryst., 1999, 326, 149–153;
 (b) S. W. Cha, J.-I. Jin, M. Laguerre, M. F. Achard and F. Hardouin, Liq. Cryst., 1999, 26, 1325–1337; (c) D. S. Shankar Rao, S. Krishna Prasad, V. N. Raja, C. V. Yelamaggad and S. A. Nagamani, *Phys. Rev. Lett.*, 2001, 87, 085504; (d) C. V. Yelamaggad, I. Shashikala, U. S. Hiremath, D. S. Shankar Rao and S. K. Prasad, *Liq. Cryst.*, 2007, 34, 153–167.

- B. Pradhan, N. Chakraborty, R. K. Gupta, G. Shanker and A. S. Achalkumar, *New J. Chem.*, 2017, 41, 879–888.
- 20 M. Gupta and S. K. Pal, Liq. Cryst., 2015, 42, 1250-1256.
- 21 (a) D. J. Byron, D. A. Keating, M. T. O'Neill, R. C. Wilson, J. W. Goodby and G. W. Gray, *Mol. Cryst. Liq. Cryst.*, 1980, 58, 179–192; (b) S.-T. Ha and T.-L. Lee, *ISRN Mater. Sci.*, 2014, 904657, 1–7.
- 22 I. W. Hamley, V. Castelletto, P. Parras, Z. B. Lu, C. T. Imrie and T. Itoh, *Soft Matter*, 2005, 1, 355–363.
- 23 I. Dierking, *Textures of Liquid Crystals*, Wiley-VCH Verlag GmBH & KGaA, Weinheim, 2003.
- 24 S. Aya, A. Zep, K. Aihara, K. Ema, D. Pociecha, E. Gorecka, F. Araoka, K. Ishikawa and H. Takezoe, *Opt. Mater. Express*, 2014, 4, 662–671.
- 25 A. E. Blatch, I. D. Fletcher and G. R. Luckhurst, *J. Mater. Chem.*, 1997, 7, 9–17.
- 26 V. Padmini, P. N. Babu, G. G. Nair, D. S. Shankar Rao and C. V. Yelamaggad, *Chem. – Asian J.*, 2016, **11**, 2897–2910 and references cited therein.
- 27 (a) B. N. Veerabhadraswamy, D. S. Shankar Rao, S. Krishna Prasad and C. V. Yelamaggad, *New J. Chem.*, 2015, 39, 2011–2027; (b) B. N. Veerabhadraswamy, D. S. Shankar Rao and C. V. Yelamaggad, *J. Phys. Chem. B*, 2015, 119, 4539–4551; (c) B. N. Veerabhadraswamy, D. S. Shankar Rao and C. V. Yelamaggad, *Chem. – Asian J.*, 2018, 13, 1012–1023.
- 28 Circular Dichroism: Principles and Applications, ed. N. Berova, K. Nakanishi and R. Woody, Wiley-VCH, Weinheim, 2nd edn, 2000.
- 29 (a) G. Shanker and C. V. Yelamaggad, *Liq. Cryst.*, 2007, 34, 799–809; (b) F. D. Saeva and J. J. Wysocki, *J. Am. Chem. Soc.*, 1971, 93, 5928–5929; (c) F. D. Saeva and G. R. Olin, *J. Am. Chem. Soc.*, 1973, 95, 7882–7884; (d) H. Toriumi and I. Uematsu, *Mol. Cryst. Liq. Cryst.*, 1984, 116, 21–33; (e) M. Sisido and R. Kishi, *Macromolecules*, 1991, 24, 4110–4114; (f) D. K. Rout, S. P. Barman, S. K. Pulapura and R. A. Gross, *Macromolecules*, 1994, 27, 2945.