Liquid Crystal Trimers Composed of Banana-Shaped and Rodlike Anisometric Segments: Synthesis and Characterization

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In this article, we report the first examples of mesomorphic linear trimers consisting of bent-core and rodlike anisotropic segments, primarily conceived to explore the possibility of stabilizing optically biaxial mesophase(s), and we briefly review the work carried out in the area of dimers composed of bent-core mesogen(s). Specifically, four C_2 symmetric trimers, which are formed by covalently tethering nematogenic cyanobiphenyls axially at the peripheral ends of a strongly shape-biaxial bent-core mesogen through two identical polymethylene spacers of varying length and parity, have been probed for their phase behavior and compared with those of the closely related oligomesogens. Four alkylene spacers, namely, hexamethylene, heptamethylene, octamethylene, and decamethylene, have been employed with the sole purpose of learning about the correlation between the resulting molecular conformation (shape) and mesomorphism. The optical and calorimetric studies revealed that all of the trimers, contrary to our prediction, display an enantiotropic uniaxial nematic phase over a wide thermal range (>50 °C), whereas the compound possessing a heptamethylene (odd-parity) spacer displays a metastable smectic phase, additionally. The nematic phase seems to have an inclination for the homogeneous alignment. The nematic–isotropic transition temperatures and associated enthalpies display a moderate odd–even effect; the even members show relatively higher values in a manner reminiscent of trimers made of conventional rodlike anisometric segments.

Introduction

Currently, banana-shaped liquid crystals (LCs) have been attracting a great deal of attention[1] because they show spontaneous polarization (*Ps*) through chiral induction in self-organizing systems such as smectic (SmCP/B_2)[2] or two-dimensional ($\mathrm{Col_r}$/B_1)[3] LC phases and also form superhelical (B_7) structures,[4] though the molecules themselves do not possess molecular chirality. These peculiar properties of the materials have been attributed to their bent or bow (twisted) anisometric molecular shape possessing C_{2v} symmetry, leading to a directed packing and tilt of the constituent molecules, which results in polar order and chirality in these fluid structures.[1,5] In recent times, some significant advances have been made in the field; the research has begun to focus on the design and synthesis of linear dimers incorporating bent-core mesogen(s).[6–10] Specifically, a variety of dimers have been reported, wherein either two bent-core segments are tied axially[6,9,10] or one bent-core segment is tethered to an achiral/chiral rodlike mesogen[7,8] through a flexible spacer. In fact, Tschierske et al.[6a] were the first to synthesize LC dimers comprising two bent-core entities separated by a dimethylsiloxane unit; this study showed that the number of dimethylsiloxane units of the spacer determines the ferroelectric or antiferroelectric nature of the SmCP phase. Later, our group reported the first occurrence of the biaxial nematic

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(N_b)−biaxial smectic A (SmA_b) phase transition in a nonsymmetric dimer formed by covalently linking a banana-shaped molecule to a rodlike mesogen through a hexamethylene spacer; however, the analogous dimer with a pentamethylene spacer was found to be nonmesomorphic.[7a] In a continuation of this project, we have recently prepared a variety of such dimeric systems and found that they display interesting thermal behavior.[7e] In subsequent studies, we showed that, by covalently joining a bent-core mesogen to cholesterol through a flexible spacer, structurally frustrated mesophases can be obtained over a wide thermal interval.[7b–d] In addition, some of these dimeric designs lead to polar smectic fluids and new phase sequences originating from the interplay between the shape anisotropy of the two mesogenic units as well as the parity and length of the flexible spacer.[7b]

Later on, Weissflog et al. reported their studies on both nonsymmetric[8] and symmetric[9] dimers almost simultaneously. It was revealed that the occurrence of columnar (Col/B_1) and/or nematic (N) phase behavior of nonsymmetric dimers, which are formed by joining a five-ring bent-core moiety with different calamitic units through a flexible spacer, depends on the size and structure of the rodlike segment as well as the length and polarity of the spacer. Interestingly, some unusual electrooptical effects of the nematic phase differing from those of the calamitic nematic phase were also disclosed.[8b] On the other hand, the thermal behavior of symmetric dimers, comprising two bent-core mesogens, was shown to depend critically on the chemical nature of the spacer they possess.[9] For example, the dimers consisting of a highly flexible dimethylsiloxane spacer display a ferroelectric SmCP phase, while the members with a tetraethylene glycol spacer show Col phase behavior. By contrast, the twins with a decamethylene spacer did not show mesomorphism. They, however, observed that the general trend of the thermal behavior remains unaltered even when the structural changes are made in bent-core segments, viz., increasing the number of aromatic rings, inserting lateral polar groups, and inverting the direction of one of the connecting groups between the aromatic rings. It was also noted that the ground-state structure of the SmCP phase can be changed on going from a monomeric to a dimeric system.[9] Almost concomitantly, Sadashiva and co-workers[10a] reported the synthesis of several mesogenic twins composed of bent-core molecules possessing an alkylene spacer of varying parity; all of them, unlike others,[9] were evidenced to show mesomorphism; especially, the occurrence of a ferroelectrically switchable (polar) oblique columnar phase ($Col_{ob}P_F$) was established for these dimers. Notably, the results of this work have shown that the change in the parity of the spacer does not alter the phase behavior; this is in contrast to the dramatic odd–even effect observed as the parity of the spacer is varied for several series of dimers derived from rodlike mesogenic segments. In the mean time, Tschierske and co-workers[6a] reported the synthesis and characterization of two series of bent-core dimers possessing a carbosilane spacer; this particular spacer was found to lower the transition temperatures of the mesogens and facilitate the easy switching characteristics from antiferroelectric to surface-stabilized ferroelectric states of the SmCP phase. Recently, Sadashiva et al., in a continuation of their previous work,[10a] have synthesized and investigated three series of dimers consisting of two identical bent-shaped molecules separated by an alkylene spacer. Between the terminal and spacer lengths, keeping either one fixed and varying the other had no influence on the phase behavior; all of the dimers exhibited a $Col_{ob}P_F$ phase.[10b] Thus, these accumulated results indicate that the dimers made of bent-core mesogens themselves are of significant interest in their own right because their phase behavior, originating from the complex interplay among the different molecular fragments, seems to deviate, to an extent, from the monomeric systems. However, the clear understanding of the correlation between the overall molecular structure and thermal properties of these dimers is seemingly still very much in its infancy; the task seems to be highly tedious because several structural factors are involved. Thus, there is considerable scope in the design and synthesis of such molecular systems to reveal their general thermal behavior. As is often the case in calamitic systems, the studies focusing on the design and synthesis of higher oligomesogens would shed light on the structure–property correlation of dimers containing bent-core unit(s). However, it may be pointed out here that several kinds of nonlinear oligomesogens incorporating bent-core molecules have also been investigated in recent times,[11] although they are not discussed in this article.

Mesomorphic linear trimers[12–25] (also called trimesogens or triplet LCs), in which three achiral/chiral mesogenic segments are tethered by two flexible spacers in an end-to-end manner, have also attracted considerable attention owing

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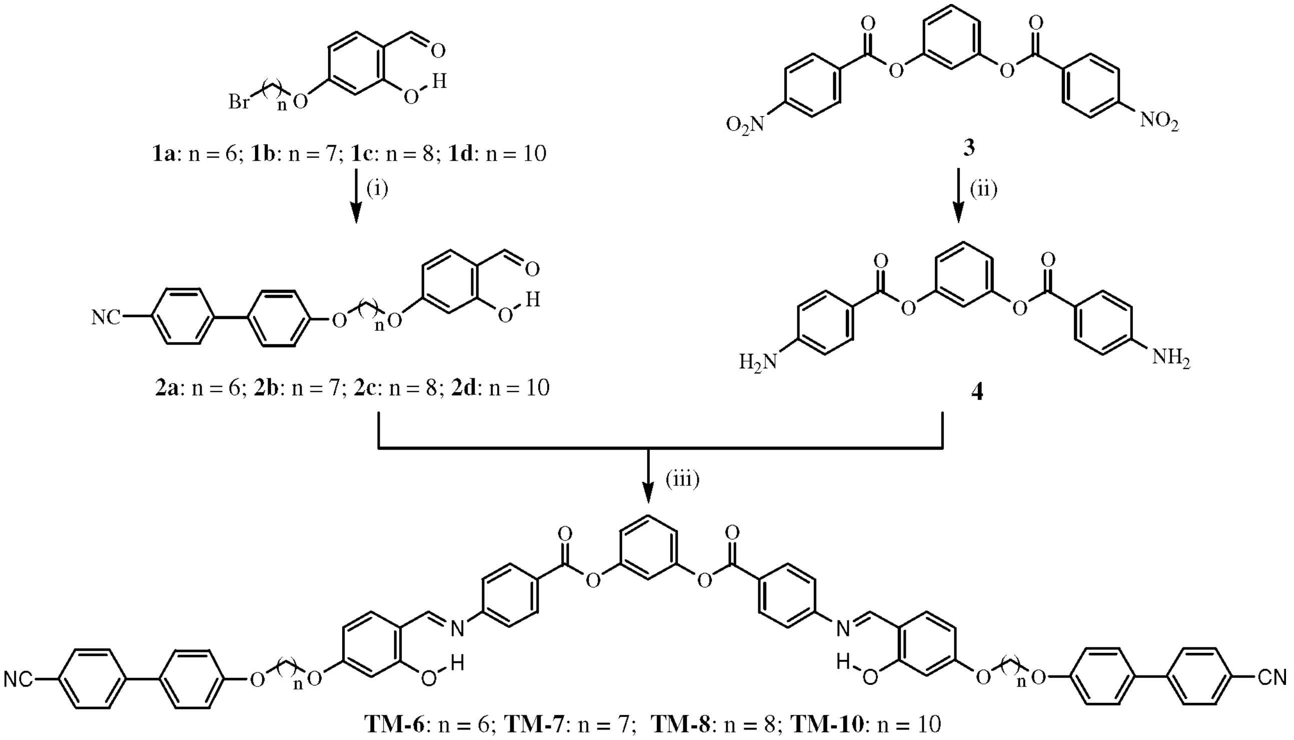
Scheme 1. Synthesis of LC Bent-Rod Trimers[a]



[a] Reagents and conditions: (i) 4-hydroxy-4-biphenylcarbonitrile, $NaHCO_3$, acetone, reflux, 48 h; (ii) H_2/PdC (10%), 15 psi, EtOAc, 6 h; (iii) AcOH (catalytic), EtOH, reflux, 2 h.

to the demonstration that a flexible-backbone-based virtual trimer model successfully accounts for the transitional properties of side-chain liquid-crystalline polymers.[26] In essence, the trimers facilitate our understanding of the origin of the thermal behavior from dimers to the polymers.[12] Of primary importance, they exhibit interesting phase-transitional properties; it is especially remarkable in the case of chiral trimers.[18,21,22] Trimers, depending upon the chemical nature of the mesogenic segments they possess, can be broadly classified into three groups: (i) symmetric, in which all of the mesogenic units are identical, (ii) mixed, in which two of the mesogens are identical, and (iii) nonsymmetric, in which none of the mesogenic units are identical. Hitherto, conventional mesogenic segments, viz., rodlike or disklike cores, have been employed to realize linear trimers. Despite the fact that bent-core mesogens and their dimeric counterparts possess a range of very exciting mesomorphic properties, to the best of our knowledge, they have not been incorporated in linear trimeric molecular architecture of any kind up until now.

Inspired by these observations and in a continuation of our quest for molecular systems capable of exhibiting biaxial mesophase(s), we intended to prepare trimers involving a banana-shaped molecule. As a first step in this direction, we aimed to covalently tie two cyanobiphenyls at the terminal ends of a five-ring banana-shaped mesogen through two alkylene spacers. Interest in devising this specific molecular design primarily stemmed from two of our earlier findings: (i) as discussed above, we have recently shown that optically biaxial LC phases can be stabilized upon covalent linking of a cyanobiphenyl to a salicylaldimine-based five-ring bent-core molecule through an even-parity flexible spacer;[7a] (ii) subsequently, we noted that, by terminally linking an electron-deficient cyanobiphenyl core with an electron donor salicylaldimine core via an odd-parity spacer, the SmA_b phase can be stabilized.[27] We thus sought to join the above-mentioned anisometric segments into trimers to further study their effects. Here we report the preparation and characterization of the first examples of LC trimers (**TM-*n*** series) comprising a bent-core and two rodlike anisometric segments separated by two alkylene spacers. Four methylene spacers (***n***), viz., hexamethylene, heptamethylene, octamethylene, and decamethylene, were employed to form trimers **TM-6**, **TM-7**, **TM-8**, and **TM-10** respectively.

Results and Discussion

Synthesis and Molecular Structural Characterization. The desired molecules and their precursors were synthesized by the reaction pathways shown in Scheme 1. The key intermediates **2a**−**d**, 4′-[*n*-(4-formyl-3-hydroxyphenoxy)alkoxy]biphenyl-4-carbonitriles, were accomplished by O-alkylating 4′-hydroxy-4-biphenylcarbonitriles with

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Table 1. Phase-Transition Temperatures (°C)[a] and Associated Enthalpies [kJ mol^{-1}] of Trimers (TM-*n* Series)

	phase sequence	
trimers	heating	cooling
TM-6	Cr 135.1 [31.8] Cr$_1$ 183.5 [51.9] N 261.1 [6.6] I	I 259 [5.8] N[b]
TM-7	Cr 167.9 [67.4] N 216.5 [2.5] I	I 211.7 [2.2] N 157.4 [0.9] M 139.3 [42.1] Cr
TM-8	Cr 137.4 [3] Cr$_1$ 164.8 [41.4] N 234.1 [7.2] I	I 232.6 [7.1] N 121.1 [22.3] Cr
TM-10	Cr 91 [12.1] Cr$_1$ 157 [46.5] N 208.7 [7.7] I	I 206.5 [7.5] N 123.8 [22.1] Cr

[a] Peak temperatures in the DSC thermograms obtained during the first heating and cooling cycles at a rate of 5 °C/min. [b] The transition to crystallization does not occur; instead, the N phase vitrifies at about 60 °C, and this glass transition is too weak to be recognized by DSC. I = isotropic liquid state. N = nematic phase. M = unknown smectic phase. Cr, Cr$_1$ = crystal.

appropriate 4-(ω-bromoalkoxy)-2-hydroxybenzaldehydes (**1a**−**d**) in the presence of anhydrous $NaHCO_3$ in acetone;[7a,27] in turn, the latter compounds **1a**−**d** were prepared by the reaction of 2,4-dihydroxybenzaldehyde with appropriate α,ω-dibromoalkanes.[7a,27] The diamine compound **4**, namely, 3-[4-(aminobenzoyl)oxy]phenyl 4-aminobenzoate, was synthesized in almost quantitative yield by the catalytic hydrogenation of 3-[4-(nitrobenzoyl)oxy]phenyl 4-nitrobenzoate (**3**), which, in turn, was obtained by treating resorcinol with 4-nitrobenzoyl chloride in the presence of a mild base.[28] Finally, the acid-catalyzed condensation of diamine **4** with appropriate aldehydes **2a**−**d** furnished the target **TM-*n*** series of molecules in good yields. All of the trimers were found be readily soluble in most of the common organic solvents, and therefore they were purified satisfactorily by repeated recrystallization using a mixture of ethanol and dichloromethane (9:1). This is noteworthy given the fact that higher oligomesogens are known to exhibit poor solubility in organic solvents.[20,29] The ^{1}H and ^{13}C NMR spectra obtained were found to be in complete consonance with the predicted structure; fast atom bombardment (FAB) mass and microanalytical data further confirmed the molecular structure of the trimers (see the Experimental Section for details).

General Information. The solvents used for the reactions were purified and dried as per the standard protocols. The chemicals obtained, from either local companies or Aldrich, were used without any further purification. Thin-layer chromatography was performed on aluminum sheets precoated with silica gel (Merck, Kieselgel 60, F254). ^{1}H NMR spectra were recorded using either a Bruker AMX-400 (400 MHz) or a Bruker Avance series DPX-200 (200 MHz) spectrometer. For ^{1}H NMR spectra, the chemical shifts are reported in ppm relative to $SiMe_4$ (TMS) as an internal standard and coupling constants are presented in hertz. IR spectra were recorded on a Perkin-Elmer Spectrum 1000 FTIR spectrometer; the spectral positions (absorption maxima) are given in wave numbers (cm^{-1}). Microanalyses were performed using a Eurovector model EA3000 CHNS elemental analyzer. Mass spectra were determined on a JEOL JMS-600H spectrometer in FAB$^+$ mode using 3-nitrobenzyl alcohol as a liquid matrix. The initial phase transitions and corresponding temperatures for the compounds were determined by a polarizing optical microscope (Leitz DMRXP or Leica DMLP) equipped with a programmable hot stage (Melter FP90 or FP82HT). The preliminary optical textural observations were performed using untreated clean glass slides. For confirmation of assignments, two differently surface-coated slides, one treated for homogeneous alignment and the other for homeotropic alignment, were used. The phase-transition temperatures and associated enthalpies were determined from thermograms recorded at a scanning rate of 5 °C/min on a differential scanning calorimeter (DSC; Perkin-Elmer DSC-7 with the PC system operating on *Pyris* software) apriorically calibrated using pure indium as a standard. The energy-minimized space-filling molecular structures of trimers were obtained using MM2 computations of the CS *ChemDraw3D* (version 5) program.

Evaluation of the Phase-Transition Behavior. Phase sequences, transition temperatures, and associated enthalpies of all of the four trimers, determined by a combination of POM and DSC measurements, are summarized in Table 1. From these accumulated results, it can be seen that all of the compounds exhibit enantiotropic nematic mesomorphism, while the trimer **TM-7** comprising an odd-parity spacer exhibits a highly metastable mesophase, hereafter referred to as the M phase, additionally. The occurrence of the nematic phase was evidenced by observation of characteristic, but interesting, optical textures, which we describe as follows.

The isotropic liquid of trimers was placed between clean glass slides and viewed under POM on slow cooling (2 °C/min); the occurrence of the N phase with striking nematic droplets (with director fluctuations; flickering) emanating from the dark background was noted. Indeed, the texture flashed when the top glass substrate was pressed gently. On cooling further, the nematic droplets coalesce to give a texture consisting of schlieren, threaded, and marbled patterns. Notably, at the edges of the slide, schlieren texture with mostly four-brush disclinations (strength $S = 1$) was persistent. As a representative case, the microphotographs of the nematic droplets, a texture comprising schlieren−threaded−marbled patterns, and an exclusive schlieren textural pattern obtained for the compound **TM-7** are shown in parts a−c of Figure 1, respectively. The usage of slides treated for different surface anchoring conditions seemed to have no effect on the configuration of the molecules; that is, the nematic phase displayed identical optical textures (as described above) when the samples were examined in the slides treated for homogeneous or homeotropic alignment. Therefore, it appears that these oligomesogens possess a strong tendency of orienting along the substrate plane; this is remarkable given the fact that these systems with two terminal cyanobiphenyl segments should have shown an inclination to align perpendicularly to the substrates. In fact, our recent experimental results indicate that the dimers with cyanobiphenyl segments show an inclination for homeotropic alignment.[7a,27] The rigidity of the central banana-shaped

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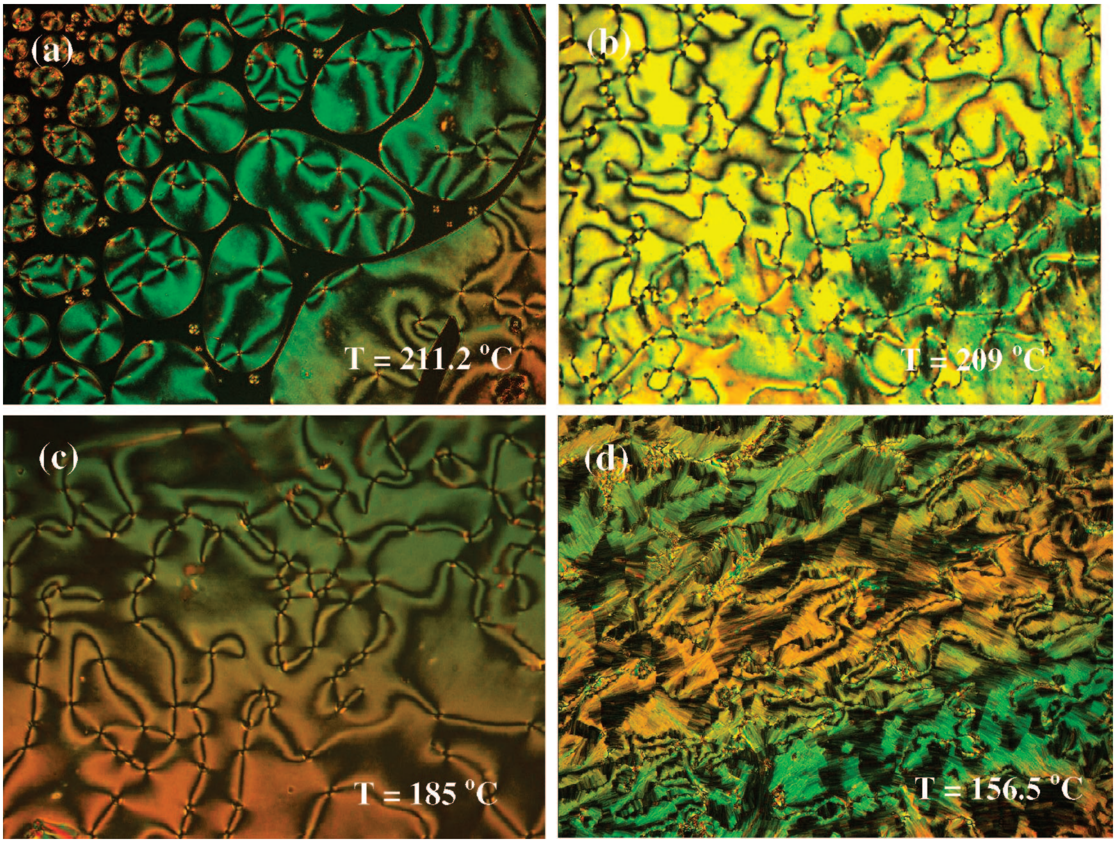

Figure 1. Photomicrographs of the optical textures of mesophases obtained for the trimer **TM-7**: (a) nematic droplets occurring just below the isotropic liquid phase; (b) a fully grown nematic phase (thick) exhibiting schlieren−threaded−marbled patterns; (c) a schlieren texture (with mostly four-brush disclamations) of the nematic phase (thin); (d) a paramorphotic focal-conic fan texture of the M phase occurring below the nematic phase (*T* = temperature).

segment, which is made of two salicylaldimine [*N*-(2-hydroxy-4-alkoxybenzylidene)aniline] cores featuring intramolecular hydrogen bonding between the H atom of the hydroxy group and the N atom of the imine functionality, may be one of the causes for the preferential homogeneous alignment of these compounds. Besides, this restricted conformational freedom at the central region of the molecules may also facilitate the tilting of molecules with respect to the plane of the substrate that perhaps accounts for the favored existence of four-brush disclinations in the nematic schlieren texture.[30]

On cooling further, the nematic phase transforms into a crystal phase in the case of trimers **TM-8** and **TM-10**, while the trimers **TM-6** and **TM-7** show a different behavior, which we describe as follows. In the optical study of compound **TM-6**, it was observed that the texture of the nematic phase once formed either by melting of the sample or on cooling from the isotropic phase remains unaltered. Indeed, the phase seems to lose its fluidity at about 60 °C. In the DSC traces of the first cooling (until ~30 °C) and subsequent heating/cooling cycles, no peaks, except for the signatures due to N−I or I−N phase transitions, were seen. These experimental results suggest that the nematic phase formed by trimer **TM-6** freezes into a glassy state. On the other hand, upon cooling of the sample **TM-7** further from the nematic phase, a transition to another mesophase (M) occurs sharply (at 157.4 °C), with a paramorphotic texture consisting of very tiny focal-conic fans, as shown in Figure 1d. In some regions of the slide, well-defined focal conics (Figure 2a) were seen and, therefore, the possibility that the M phase is a smectic A (SmA) phase cannot be ruled out. However, when the M phase was subjected to homeotropic boundary conditions, it failed to produce the pseudoisotropic texture, a diagnostic feature of the SmA phase. In essence, this mesophase exhibited identical optical textures irrespective of the types of substrates used. Owing to the metastable nature and short thermal range of the phase, it was not possible to characterize it by X-ray diffraction study; hence, it has been presently designated as an unknown smectic phase. The DSC thermograms obtained at a rate of 5 °C/min during the first heating and subsequent cooling cycles are shown in Figure 2b, where the signatures due to a dimesomorphic sequence, viz., I−N−M, can be seen.

Seemingly, a thorough comparison of the transitional behavior with respect to variation in the parity of the spacers constrained as only a system with odd-parity spacers, the trimer **TM-7**, has been realized. Nonetheless, some clues seem to be available in this context. It can be seen from Table 1 that the transitional behavior of these trimers displays some dependence on the length and parity of the two alkylene spacers (***n***) that connect central bent-core and terminal cyanobiphenyl mesogens linearly. As shown in Figure 3a, the N−I phase transition temperatures exhibit a moderate odd–even effect as the parity of the spacer is varied in which the even members **TM-6** and

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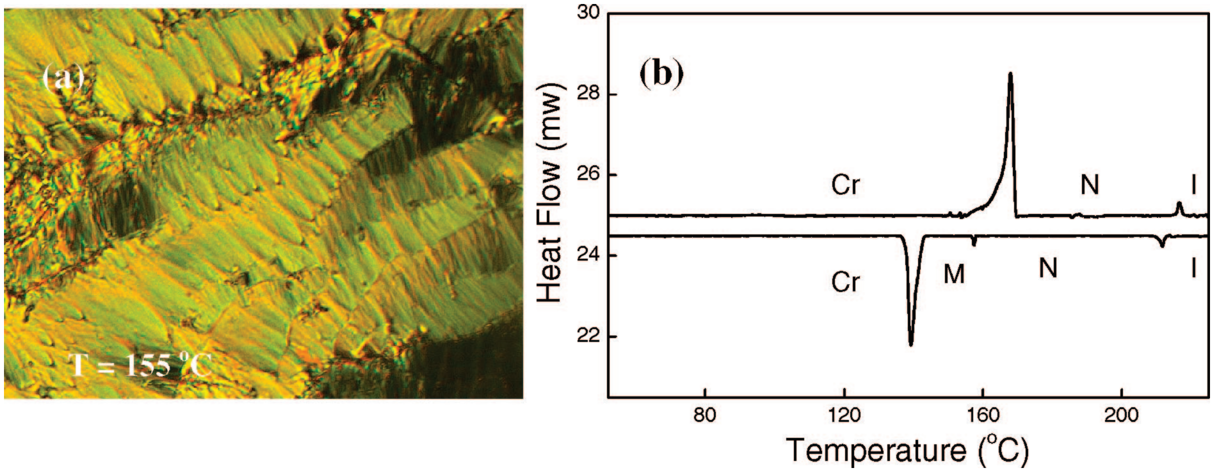


Figure 2. (a) Microphotograph of the paramorphotic texture of the M phase of trimer **TM-7**, where the occurrence of focal conics can be seen. (b) DSC traces obtained for the first heating and cooling cycles of trimer **TM-7** at a rate of 5 °C/min.

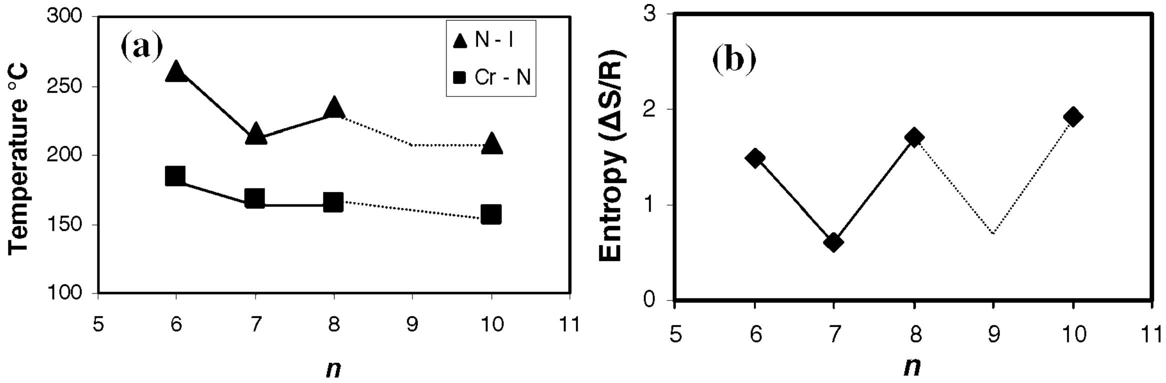


Figure 3. Dependence of the transition temperatures (a) and the entropy changes associated with the N−I (b) phase transition on the number of methylene units (*n*) in the flexible alkyl spacers for the **TM-*n*** series in the heating cycle. The dashed lines joining points are suggestive of the general trend; it may be noted that experimental data do not cover that for *n* = 9.

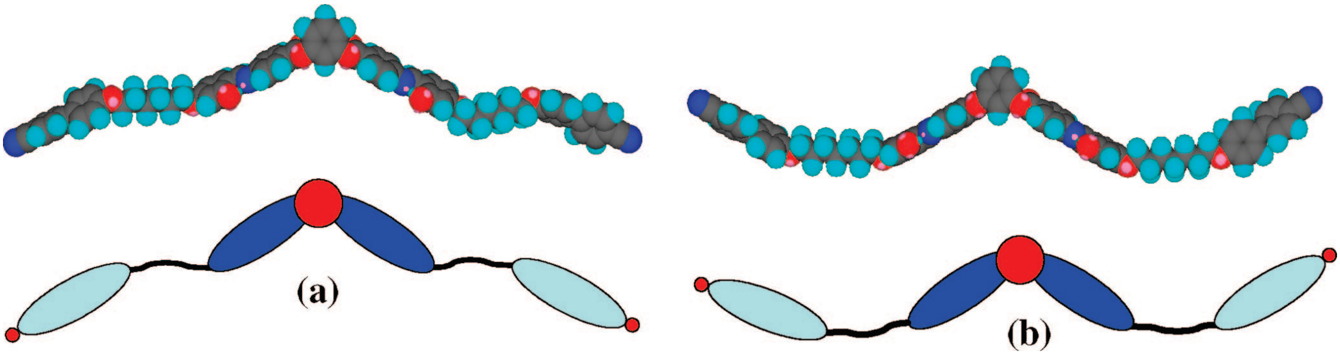
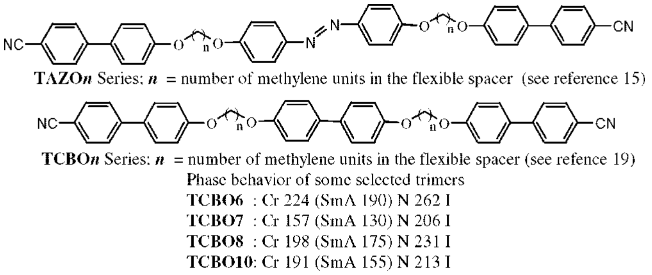


Figure 4. Space-filling models of energy-minimized molecular structures (top) and the corresponding schematic representations of trimers **TM-6** (a) and **TM-7** (b) (bottom).

TM-8, except for **TM-10**, exhibit the higher values. The trimer **TM-10** with decamethylene (***n*** = 10) spacers displays a lower N−I transition temperature even when compared to that of **TM-6**. In terms of entropy changes associated with the N−I transition, the trimer **TM-7** shows a much lower value when compared to those obtained for the even members of the series. This behavior can be attributed to the overall molecular shape of the trimers primarily evolving from the geometry and flexibility of the spacers they possess. Parts a and b of Figure 4 show the space-filling models of energy-minimized molecular structures of trimers **TM-6** and **TM-7**, respectively; for clarity, the cartoons of these two trimers are also shown below their respective models.

Apparently, the trimer **TM-6** possesses an “elongated bent shape”, whereas the compound **TM-7** bears a resemblance to a “well-stretched W shape” or it looks like a double bent-shape core. This implies, therefore, that the conformation of trimer **TM-6** (or **TM-8** or **TM-10**) is more compatible with the molecular association found in the nematic phase than that for the compound **TM-7**, which enhances the orientation order of the phase, resulting in a greater N−I transition entropy.[12] In other words, the lower N−I transition



TAZO*n* Series: ***n*** = number of methylene units in the flexible spacer (see reference 15)

TCBO*n* Series: ***n*** = number of methylene units in the flexible spacer (see refence 19)

Phase behavior of some selected trimers

TCBO6 : Cr 224 (SmA 190) N 262 I

TCBO7 : Cr 157 (SmA 130) N 206 I

TCBO8 : Cr 198 (SmA 175) N 231 I

TCBO10: Cr 191 (SmA 155) N 213 I

Figure 5. Molecular structures of the two known series of trimers, the analogues of the present series of oligomesogens.

temperature and associated entropy observed for the compound **TM-7** can be attributed to its reduced-shape anisotropy. These observations persuaded us to envision the different kinds of molecular organization (packing) in the nematic phase formed by trimers **TM-6** and **TM-7**, and accordingly we suggest speculative models. In all probability, owing to the elongated banana shape of the trimer **TM-6**, two molecules having a common bent direction pair up and these pairs self-assemble to form nematic phase, where the bent direction of the neighboring or nearby molecular pair is mostly antiparallel, whereas such a thorough molecular packing may not occur in the nematic phase of the compound **TM-7** because it possesses a stretched W shape. Further, it is also worth noting that, upon an increase in the length of the even-parity spacers, the N−I phase transition temperature decreases; this can be perhaps ascribed to the higher degree of conformational freedom of the molecules.

The exclusive and wide thermal range enantiotropic occurrence of the nematic phase in these trimers, except for the trimer **TM-7**, which stabilizes a metastable smectic phase additionally, appears to be rather fascinating. This is because the analogous trimers (which we hereafter refer to as the **TAZO*n*** series of compounds; see Figure 5 for a general molecular structure), formed by interlinking two electron-deficient moieties, the cyanobiphenyls, to a central electron-rich azobenzene core through two flexible spacers of varying length and parity, are known to display smectic mesomorphism exclusively.[16] This is analogous to the occurrence of smectic phase(s) in nonsymmetrical dimers made of electron-rich and -poor anisometric segments, where specific intermolecular interaction between these unlike mesogenic cores plays a vital role.[27,31] Likewise, the preferential formation of smectic phase(s) by the trimers of the **TAZO*n*** series must be originating from the specific interaction between azobenzene and cyanobiphenyl mesogenic cores. Notably, such a behavior of oligomesogens has been considered to be evolving from the electrostatic quadrupolar interactions between the dissimilar anisometric segments with quadrupole moments that are opposite in sign.[32] Therefore, it is reasonable to expect that the trimers of the present study should have favored the smectic mesomorphism because they are made of more electron-rich salicylaldimine[27] (like azobenzene) and electron-deficient cyanobiphenyl entities. Contrary to the presumption, as illustrated above, they are nematics, indicating that their behavior is comparable to a novel series of trimers (**TCBO*n*** series; see Figure 5 for a general molecular structure) reported by Imrie and Luckhurst.[20] Specifically, the phase sequence and transition temperatures of the heating cycle evidenced for the trimers **TM-6**, **TM-7**, **TM-8**, and **TM-10** (see Table 1) are comparable to those of analogous trimers of the **TCBO*n*** series, namely, **TCBO6**, **TCBO7**, **TCBO8**, and **TCBO10** (see Figure 5). However, the notable difference is the occurrence of a metastable SmA phase in the case of trimers **TCBO6**, **TCBO8**, and **TCBO10**. Furthermore, the values of the entropy change associated with the N−I transitions for the trimers **TM-*n*** are seemingly lower than those reported for the trimers of the **TCBO*n*** series; this suggests that the latter series of trimers are more compatible with the molecular assembly in the nematic structure than the former ones. Thus, the nematic behavior of the **TM-*n*** series of trimers appears rather interesting. Needless to say, further intensive investigations are required to establish the structure–property correlation; such events are presently underway in our laboratories.

In conclusion, in an exploratory attempt to realize molecules capable of stabilizing optically biaxial mesophases, LC trimers, which are formed by covalently linking a banana-shaped and two rodlike mesogenic segments via two flexible spacers of varying length and parity, the first of their kind, have been prepared and their phase behavior investigated. Contrary to expectation, all of the trimers, irrespective of the variations in the length and parity of the spacer they possess, exhibit an enantiotropic nematic phase possessing uniaxial symmetry. The novelty of these compounds originates from the fact that the central banana-shaped segment, which is made of two salicylaldimine [*N*-(2-hydroxy-4-alkoxybenzylidene)aniline] cores featuring intramolecular hydrogen bonding between the H atom of the hydroxy group and the N atom of the imine functionality, induces special features to the molecules. Indeed, the parity of the spacer determines the phase sequence, phase-transition temperatures, and associated enthalpy values; a metastable smectic phase with a relatively lower transition temperature was observed for the trimer comprising odd-parity (heptamethylene) spacers. The structure of the trimers featuring even-parity spacers looks to be more compatible with the molecular association found in the nematic phase than that of an odd-member analogue. Further investigations are essential to assess these observations. This initial study provides insight into what could be a vast family of materials that are interesting from both fundamental research and application viewpoints.

Experimental Section

General Procedure for the Preparation of Bent-Rod Trimers for the TM-*n* Series of Compounds. A mixture of freshly prepared 3-[4-(aminobenzoyl)oxy]phenyl 4-aminobenzoate (**4**; 2.5 mmol, 1 equiv), aldehyde **2a−d** (5.25 mmol, 2.1 equiv), absolute ethanol (30 mL), and 2 drops of acetic acid was refluxed until the yellow solid precipitated out (2 h). The hot reaction mixture was filtered to collect the crude product; it was repeatedly washed with hot ethanol, and the yellow product obtained was further purified by repeated recrystallization in a mixture of ethanol and CH_2Cl_2 (9:1).

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(32) Blatch, A. E.; Fletcher, I. D.; Luckhurst, G. R. *Liq. Cryst.* **1995**, *18*, 801.

TM-6: a yellow solid; IR (KBr pellet) ν_{max} 2944, 2867, 2224, 1732, 1591 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 13.35 (s, 2H, 1 × OH), 8.58 (s, 2H, CH=N), 8.24 (d, J = 8.5 Hz, 4H, Ar), 7.69 (d, J = 8.4 Hz, 4H, Ar), 7.64 (d, J = 8.3 Hz, 4H, Ar), 7.53 (d, J = 8.6 Hz, 4H, Ar), 7.49 (d, J = 8 Hz, 1H, Ar), 7.33 (d, J = 8.5 Hz, 4H, Ar), 7.31 (t, J = 9.2 Hz, 2H, Ar), 7.25–7.18 (m, 3H, Ar), 6.99 (d, J = 8.7 Hz, 4H, Ar), 6.52–6.5 (m, 4H, Ar), 4.06–4.02 (m, 8H, 4 × OCH$_2$), 1.88–1.85 (m, 8H, 4 × CH$_2$), 1.58–1.57 (m, 8H, 4 × CH$_2$). MS (FAB$^+$). Calcd (M + 1) for $C_{72}H_{63}N_4O_{10}$: m/z 1143.5. Found: m/z 1143.6. Anal. Calcd for $C_{72}H_{62}N_4O_{10}$: C, 75.64; H, 5.47; N, 4.9. Found: C, 75.9; H, 5.6; N, 4.8.

TM-7: a yellow solid; IR (KBr pellet) ν_{max} 2934, 2859, 2224, 1736, 1591 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 13.35 (s, 2H, 1 × OH), 8.57 (s, 2H, CH=N), 8.24 (d, J = 8.4 Hz, 4H, Ar), 7.69 (d, J = 8.4 Hz, 4H, Ar), 7.64 (d, J = 8.8 Hz, 4H, Ar), 7.53 (d, J = 8.8 Hz, 4H, Ar), 7.48 (d, J = 8.6 Hz, 1H, Ar), 7.35 (d, J = 8.5 Hz, 4H, Ar), 7.29 (t, J = 9.2 Hz, 2H, Ar), 7.22–7.18 (m, 3H, Ar), 6.99 (d, J = 8.7 Hz, 4H, Ar), 6.52–6.50 (m, 4H, Ar), 4.04–4 (m, 8H, 4 × OCH$_2$), 1.85–1.82 (m, 8H, 4 × CH$_2$), 1.55–1.53 (m, 12H, 6 × CH$_2$); ^{13}C (100 MHz, CDCl$_3$) δ 164.25, 164.08, 162.98, 159.62, 153.18, 151.32, 145.13, 133.92, 132.44, 131.61, 131.17, 129.78, 128.21, 126.95, 126.64, 121.14, 119.15, 119.01, 115.74, 114.94, 109.89, 107.97, 101.4, 68.1, 67.91, 29.15, 29.1, 26. MS (FAB$^+$). Calcd (M + 1) for $C_{74}H_{67}N_4O_{10}$: m/z 1171.5. Found: m/z 1172.3. Anal. Calcd for $C_{74}H_{66}N_4O_{10}$: C, 75.88; H, 5.68; N, 4.78. Found: C, 75.9; H, 5.7; N, 4.8.

TM-8: a yellow solid; IR (KBr pellet) ν_{max} 2934, 2859, 2224, 1736, 1591 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 13.35 (s, 2H, 1 × OH), 8.57 (s, 2H, CH=N), 8.24 (d, J = 8.5 Hz, 4H, Ar), 7.68 (d, J = 8.5 Hz, 4H, Ar), 7.63 (d, J = 8.5 Hz, 4H, Ar), 7.52 (d, J = 8.7 Hz, 4H, Ar), 7.48 (d, J = 8.0 Hz, 1H, Ar), 7.34 (d, J = 8.6 Hz, 4H, Ar), 7.29 (t, J = 9.2 Hz, 2H, Ar), 7.22–7.17 (m, 3H, Ar), 6.99 (d, J = 8.8 Hz, 4H, Ar), 6.52–6.50 (m, 4H, Ar), 4.03–4 (m, 8H, 4 × OCH$_2$), 1.85–1.79 (m, 8H, 4 × CH$_2$), 1.54–1.42 (m, 16H, 8 × CH$_2$); ^{13}C (100 MHz, CDCl$_3$) δ 164.33, 164.16, 163.1, 162.98, 159.9, 153.42, 151.57, 145.33, 134, 132.56, 131.73, 131.36, 129.9, 128.33, 127.1, 126.9, 121.25, 119.22, 119.1, 115.83, 115.17, 112.88, 110.16, 108.1, 101.66, 68.33, 68.18, 29.25, 29.05, 25.95. MS (FAB$^+$). Calcd for $C_{76}H_{70}N_4O_{10}$: m/z 1198.5. Found: m/z 1198.2. Anal. Calcd for $C_{76}H_{70}N_4O_{10}$: C, 76.11; H, 5.88; N, 4.67. Found: C, 76.3; H, 5.6; N, 4.8.

TM-10: a yellow solid; IR (KBr pellet) ν_{max} 2922, 2853, 2224, 1732, 1593 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 13.35 (s, 2H, 1 × OH), 8.58 (s, 2H, CH=N), 8.24 (d, J = 8.5 Hz, 4H, Ar), 7.69 (d, J = 8.4 Hz, 4H, Ar), 7.64 (d, J = 8.3 Hz, 4H, Ar), 7.53 (d, J = 8.6 Hz, 4H, Ar), 7.49 (d, J = 8.0 Hz, 1H, Ar), 7.33 (d, J = 8.5 Hz, 4H, Ar), 7.31 (t, J = 9.2 Hz, 2H, Ar), 7.25–7.18 (m, 3H, Ar), 6.99 (d, J = 8.7 Hz, 4H, Ar), 6.52–6.50 (m, 4H, Ar), 4.06–4.02 (m, 8H, 4 × OCH$_2$), 1.88–1.85 (m, 8H, 4 × CH$_2$), 1.58–1.57 (m, 24H, 12 × CH$_2$). Anal. Calcd for $C_{80}H_{78}N_4O_{10}$: C, 76.53; H, 6.26; N, 4.46. Found: C, 76.9; H, 5.9; N, 4.5.

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