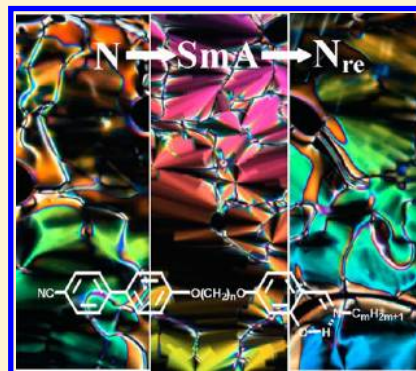


# Reentrant Nematic Phenomenon in a New Class of Low Molar Mass, Single-Component Liquid Crystals

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**ABSTRACT:** We report the observation of reentrant nematic behavior in a relatively new class of compounds, namely, dimerlike mesogens that are made by covalently linking nematogenic cyanobiphenyl and nonmesogenic *N*-(*n*-alkyl)salicylalimine segments through a central flexible spacer of varying length and parity. The existence of reentrant phenomenon in this class of mesogens, evidenced indubitably by means of several complementary studies, appears to be crucially dependent on the length of the terminal alkyl tail and parity of the spacer.



## I. INTRODUCTION

Ever since their accidental discovery by Reinitzer in 1888,<sup>1</sup> shape-anisotropic organic molecules exhibiting liquid crystal (LC) behavior (mesomorphism) upon heating, called thermotropic mesogens, continue to attract enormous attention of researchers.<sup>2,3</sup> This is because they have not only spawned intense excitement in fundamental science but also serve as an imperative media in display devices persistently.<sup>3,4</sup> One of the most fascinating aspects of these mesogens, in the context of basic research, is the occurrence of reentrant phenomenon where a LC phase characterized by higher symmetry reappears in the sequence of phases of otherwise decreasing symmetry.<sup>2,5</sup> In other words, it involves the transformation of an ordered LC state into a relatively disordered state as the temperature is lowered. This special feature of the mesogens has given rise to various atypical LC phase sequences when temperature, pressure, and concentrations are altered. In general, such sequences have been understood to be originating from different mechanisms involving factors such as structural packing frustration, complex molecular geometrical aspects, and competing fluctuations. Nonetheless, when compared to the richness and frequency of other phase transitions reported hitherto, reentrant phases occur relatively rarely in mixtures<sup>6</sup> or single-component systems<sup>7–10</sup> composed of monomers, such as calamitics and discotics,<sup>6,7</sup> oligomers<sup>8</sup> and polymers.<sup>9</sup> Recently, metallomesogens,<sup>10</sup> supramolecular complexes<sup>11</sup> banana-shaped LCs,<sup>12</sup> have also been demonstrated to exhibit such a behavior. Among these systems, the probability and the incidence of finding reentrant behavior appear to be rather more in mixture of compounds derived from the known concepts.<sup>6</sup> In fact, the reentrant behavior, in a phase sequence involving transition from nematic (N) to smectic A (SmA) to reentrant nematic ( $N_{re}$ ) phase, was first reported by Cladis in mixtures of cyano compounds.<sup>6a</sup> However, exploring the

possibility of finding single (pure) component low molar mass LCs capable of exhibiting reentrant phenomenon under normal atmospheric (pressure) conditions continues to be one of the important objectives of synthetic chemists.

The significance of yet another interesting class of low molar mass LCs, called “dimerlike LCs”, has been rationally illustrated by Henderson and Imrie only recently,<sup>13a</sup> although they are known since early 1970s.<sup>14</sup> They comprise an archetypal mesogenic (two-ring) core and a bulky nonmesogenic segment, such as aliphatic/aromatic (one-ring cores), interlinked through a flexible spacer of varying length and parity. This implies that they can be readily converted into LC dimers by replacing the nonmesogenic unit with mesogenic entity. Most importantly, their phase transitional behavior, especially the dependence of clearing temperature on the parity of the spacer, has generated a considerable amount of interest<sup>14,15</sup> as this property is similar to that of LC dimers.<sup>13</sup> Thus, in view of their close resemblance in the context of both molecular structural feature and thermal properties,<sup>13a,14,15</sup> they can be regarded as the bridging motifs between LC monomers<sup>2</sup> and dimers.<sup>13</sup>

The experimental results clearly indicate the dependence of their thermal behavior on the nature of both mesogenic and nonmesogenic units, besides the length and parity of the spacer.<sup>13a,14,15</sup> The selection of nonmesogenic unit appears to be especially crucial as it not only aids in modifying the intermolecular associations and thus the structures of the phases,<sup>13,15g–k</sup> but is also known to dictate the mesomorphic behavior of the compounds.<sup>13,14e–g,15a–d</sup> We have been working on such mesogens for quite some time now to understand structure–property correlations.<sup>16</sup> We are especially

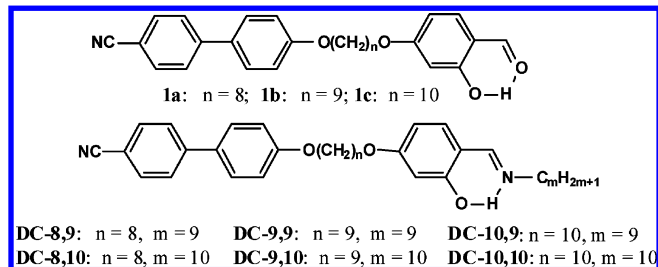
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focusing on the design and synthesis of dimerlike mesogens capable of promoting thermodynamically stable mesophases. In continuation of our work on this subject, we have prepared several dimerlike mesogens where a polar, promesogenic cyanobiphenyl core is covalently joined to a thermally and hydrolytically stable, nonmesogenic *N*-(*n*-decyl)salicylaldimine core through an oxy(oligomethylene)oxy spacer. Figure 1



**Figure 1.** Molecular structures of the dimerlike liquid crystals and their intermediates.

illustrates the general molecular structure of the six compounds synthesized by condensing salicylaldehydes **1a–c** with *n*-nonylamine/*n*-decylamine. Four compounds, **DC-8,9**, **DC-8,10**, **DC-10,9**, and **DC-10,10**, are even members possessing either oxyoctyloxy or oxydecyloxy spacers, while the other two materials, **DC-9,9** and **DC-9,10** are odd homologues. Remarkably, some of these, especially those with even-parity spacer and *n*-nonylamine terminal tail (**DC-8,9**, **DC-10,9**) exhibit reentrant liquid crystal behavior, which we describe as follows.

## II. RESULTS AND DISCUSSION

**II.a. Optical and Calorimetric Studies.** The mesomorphism of the prepared compounds was ascertained mainly by optical and calorimetric techniques. The results derived from these two complementary studies are compiled in Table 1. Compound **DC-8,9**, placed between a clean glass slide and a coverslip, when examined under polarizing optical microscope (POM), exhibits striking droplets (with director fluctuations; flickering) of the nematic phase (Figure 2a) on cooling from

**Table 1.** Phase Transition Temperatures ( $^{\circ}\text{C}$ )<sup>a</sup> and Associated Enthalpies (J/g) of Dimerlike Compounds<sup>b</sup>

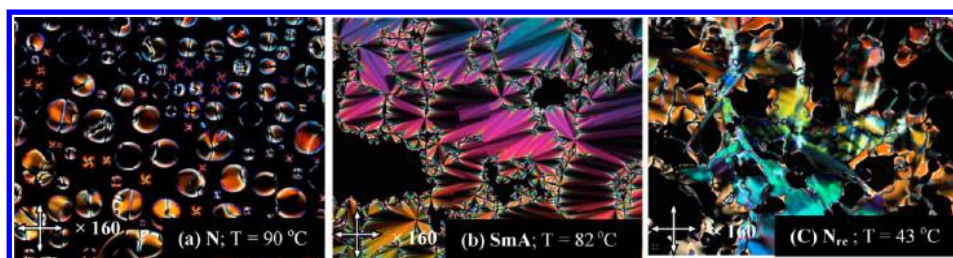
mesogens	phase sequence: heating; cooling
DC-8,9	Cr 69.2 (19.7) Cr <sub>1</sub> 77.5 (60) SmA 99.1 N 99.4 (7) <sup>c</sup> I; I 98.2 (6.9) <sup>c</sup> N 97.8 SmA 60.1 N <sub>re</sub> 25.4 (11.7) Cr
DC-8,10	Cr 67.3 (52.3) SmA 97.4 (6.9) I; I 95.8 (6.8) SmA 41 (47) Cr
DC-9,9	Cr 76.3 (33.4) I; I 66.7 N 66 (26.8) <sup>d</sup> Cr
DC-9,10	Cr 78.8 (40.6) I; I 64.5 N 63.9 (26.8) <sup>d</sup> Cr
DC-10,9	Cr 89 (62) SmA 91.9 N 92.7 (7) <sup>c</sup> I; I 91.4 (8.1) <sup>c</sup> N 90.5 SmA 74.5 N <sub>re</sub> 57.3 (58.4) Cr
DC-10,10	Cr 73.9 (51) SmA 91.5 (6) I; I 90.1 (5.9) SmA 30.7 (31.3) Cr

<sup>a</sup>Peak temperatures in the DSC traces recorded during the first heating–cooling cycles at 5  $^{\circ}\text{C}/\text{min}$ . <sup>b</sup>Cr/Cr<sub>1</sub> = crystal; SmA = smectic A; N = nematic; N<sub>re</sub> = reentrant nematic; I = isotropic liquid. <sup>c</sup>The SmA–N transition was observed under the microscope, but this was not resolved in the DSC scan and hence the  $\Delta H$  value represents the combined enthalpy for both SmA–N and N–I transitions. <sup>d</sup>The I–N transition was observed under the microscope, but this was not resolved in the DSC scan and hence the  $\Delta H$  value represents the combined enthalpy for both I–N and N–Cr transitions.

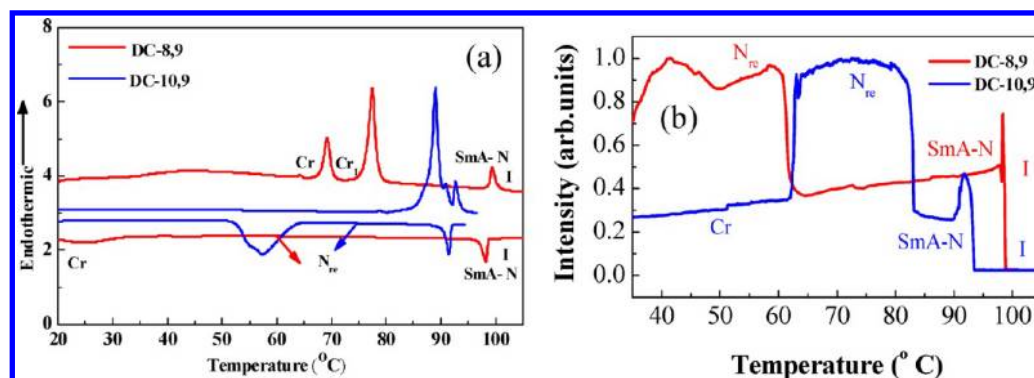
the isotropic (I) phase. On cooling further, the nematic droplets coalesce to give a texture comprising schlieren, threaded, and marble patterns. The schlieren texture, exhibiting strong director fluctuations, consisted of both two-brush (defect strength  $s = \pm 1/2$ ) and four-brush ( $s = \pm 1$ ) disclinations implying the heterogeneous planar orientation of molecules with their long molecular axis (director, *n*) remaining parallel to substrates but pointing in different directions. On further cooling from the N phase, the texture of the sample sharply changes at 97.8  $^{\circ}\text{C}$  to yield a pattern consisting of both focal-conic and pseudoisotropic textures (see Figure 2b). The presence of focal-conic fans suggests a layered structure, whereas the pseudoisotropic region indicates an orthogonal organization of the molecules with respect to the layer planes. If the sample is sheared gently the focal-conic pattern transforms into pseudoisotropic texture. These textural observations point to the presence of the SmA phase. On further cooling from the SmA phase, a transition to another mesophase phase occurs sharply at 60.1  $^{\circ}\text{C}$  exhibiting some interesting optical textural features which remains unaltered until crystallization at about 25  $^{\circ}\text{C}$ . As can be seen in Figure 2c, the texture consisted of schlieren, threaded, marble, and pseudoisotropic patterns; in some regions, especially at the edges, schlieren texture with two and four dark lines emanating from a point (i.e., two- and four-brush singularities) was observed prominently. Most importantly, the texture displayed flickering and flashed when subjected to mechanical stress. Thus, it is interesting to note that the optical textural patterns of the phase appearing below SmA phase are exactly identical to that of the nematic phase occurring above the SmA phase, confirming the reoccurrence of the nematic phase. That is, compound **DC-8,9** while cooling from its isotropic phase exhibits a trimesomorphic sequence involving nematic to smectic A to reentrant (N<sub>re</sub>) phase transitions.

An identical mesomorphic behavior was established for mesogen **DC-10,9**; that is, it displays N–SmA–N<sub>re</sub> phase sequence analogous to that of mesogen **DC-8,9**. In both the cases, the high-temperature N phase exists for a while as evidenced from the fact that its optical texture transforms into the SmA phase in the temperature range of 0.4–0.9  $^{\circ}\text{C}$  (see Table 1). As can be seen in Figure 3a, the DSC traces of the heating and cooling cycles of both compounds exhibit an endothermic and an exothermic peak due to SmA–N–I and I–N–SmA phase transitions, respectively. Further, the signature due to SmA–N<sub>re</sub> transition is not detectable in the thermogram indicating that the transition is of second order. DSC curves also supported the optical observation that the N<sub>re</sub> phase occurs for about 35 and 17  $^{\circ}\text{C}$  in compounds **DC-8,9** and **DC-10,9**, respectively. In fact, the aforementioned thermal range of the N<sub>re</sub> phase of the mesogens was found to be highly reproducible for any number of heating and cooling cycles. Optical transmission measurement carried out as a function of temperature for these two compounds contained in hybrid cells are shown in Figure 3b, where the variation in the optical intensity due to phase transitions can be visualized qualitatively.

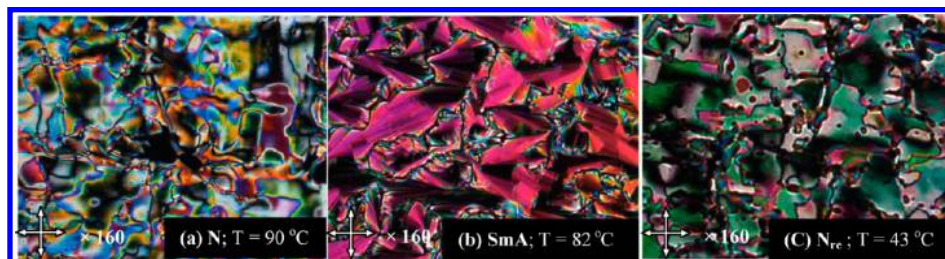
In order to confirm the N–SmA–N<sub>re</sub> phase sequence observed for these two compounds, glass substrates treated for either a polyimide solution for planar orientation or a silane solution for homeotropic alignment of the molecules were used. When a thin film of either compound **DC-8,9** or **DC-10,9** held between two glass plates pretreated for homogeneous geometry is slowly cooled from the isotropic phase, the mesophase sets in manifesting optically in the form of droplets



**Figure 2.** Microphotographs of the optical textures of three mesophases observed for compound DC-8,9 placed between untreated glass plates: (a) nematic droplets emanating from the dark background of isotropic liquid; (b) focal-conic pattern accompanied with pseudoisotropic texture of the SmA phase; (c) schlieren, threaded, marble, and pseudoisotropic patterns of the  $N_{re}$  phase.



**Figure 3.** (a) DSC traces of the second heating and first cooling cycles recorded at a rate of 5 °C for the compounds DC-8,9 (red traces) and DC-10,9 (blue traces). (b) The profiles of optical transmission obtained as a function of temperature for DC-8,9 (red trace) and DC-10,9 (blue trace).



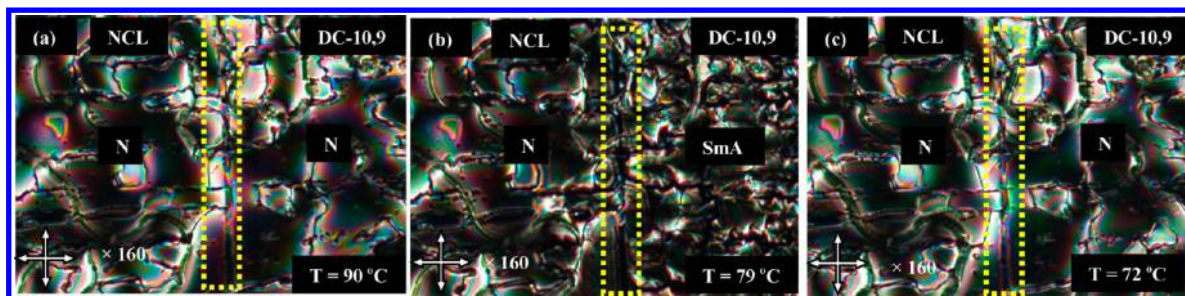
**Figure 4.** Photomicrographs of the three mesophases observed for planarly aligned DC-10,9: (a) coalescence of the nematic droplets into a texture consisting of schlieren, threaded, and marble patterns; (b) focal-conic texture of the SmA phase; and (c) marble texture of the reentrant N phase.

which on further cooling coalesce to give a characteristic nematic texture comprising schlieren, threaded, and marble patterns. Figure 4a depicts such a textural pattern observed for DC-10,9, as a representative case. On further lowering the sample temperature, as shown in Figure 4b, the SmA phase appears with characteristic focal-conic texture. In this planarly aligned SmA phase, the director  $\mathbf{n}$ , and thus the optic axis, lie in the plane of the substrate as in the case of the nematic phase. However, it may be noted here that, although the long molecular axis (director), in both N and SmA phases, is oriented in the plane of the substrate but the azimuthal angle is arbitrary as the substrates treated for homogeneous alignment are unrubbed. On further cooling from the SmA phase, a transition to nematic phase occurs with the marble textural pattern (Figure 4c) that exists until crystallization. Furthermore, the occurrence of these three phases in both the compounds was ascertained using glass substrates treated for homogeneous orientation and rubbed unidirectionally; in this uniform planar orientation, the long molecular axis remains in the plane of the glass substrate and also points toward a preferred azimuthal direction. On cooling the isotropic liquids of the samples, the nematic phase occurs with a striking planar

(uniform) texture where the optic axis lies in the plane of the substrate. On cooling further, sequential transitions to the SmA and N phases occur with textural patterns almost identical to that of the high-temperature nematic phase; however, unlike the SmA phase, both the nematic phases exhibited characteristic flickering which originate due to Brownian motion of the constituent molecules. On the other hand, these three phases, i.e., N, SmA, and  $N_{re}$ , showed pseudoisotropic textures when examined in substrates treated for homeotropic alignment; this is expected, given the fact that the optic axis of these phases remains parallel to direction of the light propagation. Of course, the pseudoisotropic textures of the N and  $N_{re}$  phases displayed characteristic flickering and flashed upon shearing gently. Thus, the textural studies, using ordinary slides or substrates treated for homogeneous and homeotropic alignments, unambiguously evidence the occurrence of N–SmA– $N_{re}$  phase sequence in DC-8,9 and DC-10,9.

**II.b. Miscibility Study.** Miscibility study by means of contact preparation was carried out to demonstrate the reoccurrence of the nematic phase in DC-10,9, as a representative case. For this purpose, room temperature (RT) nematic LC (NLC), a mixture of ZLI-2772 and ZLI-811

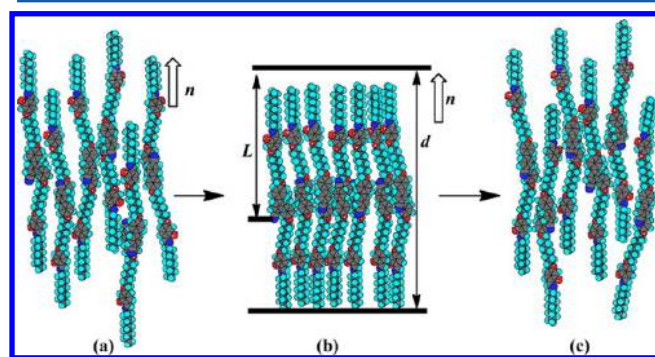




**Figure 5.** Microphotographs of the optical textures seen during the contact preparation (miscibility) study: (a) the pattern illustrating the miscibility at the contact region (yellow marking) of nematic phases of NLC and DC-10,9; (b) the texture showing the phase boundary (immiscibility) between the N and SmA phases of NLC and DC-10,9, respectively; and (c) the texture exhibiting the clear miscibility between the N phase of NLC and the  $N_{re}$  phase of DC-10,9.

(0.08%) from Merck, displaying the phase nematic phase from RT to 125 °C, was used as a standard LC sample. The isotropic liquid of NLC was filled between a clean glass slide and a coverslip by capillary action and cooled until about 95 °C; at this temperature, mesogen DC-10,9, was filled from the other side of cell also by capillary action. The phase boundary between the nematic phase of NLC and the dark pattern of isotropic liquid of DC-10,9 was observed. On further cooling, the N phase of DC-10,9 formed at 91.2 °C readily mixes with that of NLC (Figure 5a). Upon cooling the sample further, the SmA phase formed by DC-10,9 at about 90 °C separates out from the N phase of NLC (Figure 5b). On cooling further, the  $N_{re}$  phase of DC-10,9 appears (at about 74 °C) with a textural pattern analogous to that of the reference LC; as illustrated in Figure 5c, no phase boundary exists between the N phase of NLC and the  $N_{re}$  phase of DC-10,9. Thus, qualitative miscibility study also supported the N-SmA- $N_{re}$  sequence with the nematic phase exhibiting re-entrance.

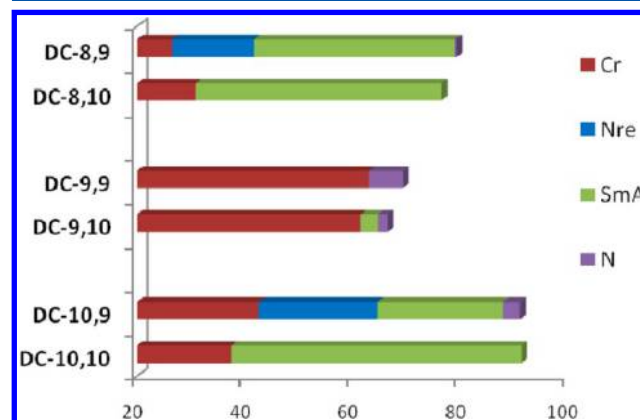
Figure 6a–c shows the schematic representation of molecular arrangement in the N, SmA, and  $N_{re}$  phases of mesogen DC-



**Figure 6.** Schematic representation showing the molecular organization in the nematic, N (a), partially bilayered smectic A,  $SmA_d$  (b), and re-entrant nematic,  $N_{re}$  (c) phases of dimerlike mesogen DC-8,9. Note that in all the mesophases there is an antiparallel pairing of molecules.

8,9 as a representative case. The occurrence of a reentrant nematic phase, especially in LCs having strong dipolar (cyano) group, is understood to be arising from the frustration of smectic order where dipolar forces play a vital role.<sup>6c</sup> Owing to their strong polar nature, the mesogens derived from cyanobiphenyl, like the present compounds, form antiparallel pairs (dimers) caused by intermolecular lateral association. Such an association is favored to minimize the dipolar energy contribution. The presence of this pairing results in the layer

thickness ( $d$ ) being greater than the molecular length  $L$ ; the smectic A phase with such a structure is referred to as a partial bilayer SmA ( $SmA_d$ ) phase (Figure 6b). The frustrated spin gas model<sup>17</sup> explains the occurrence of reentrant nematic phase in mesogens comprising terminal polar group by appealing to the relative domination of the ferroelectric or antiferroelectric interactions among a triplet of molecules. The frustration caused in the packing of the triplet molecules can give rise to two situations: (a) short-range dipolar interactions are strong resulting in stabilizing the smectic phase, and (b) the molecules are allowed to permeate or diffuse by arbitrary distances along the director ( $n$ ) direction yielding the nematic phase (Figure 6b). Obviously, the magnitude of frustration is a function of temperature giving rise to the occurrence of smectic A–reentrant nematic phase sequence. In this respect, it is quite remarkable and interesting to note that the next higher homologues DC-8,10 and DC-10,10 of compounds DC-8,9 and DC-10,9, respectively, exhibit SmA phase exclusively (Figure 7), although they differ in their molecular structure just



**Figure 7.** Bar graph showing the phase sequence observed during cooling cycle of the compounds with thermal range of mesophases such as N (violet bar), SmA (green bar), and  $N_{re}$  (blue bar) phases.

by a methylene unit in the terminal tail. This indicates the critical dependence of the occurrence of  $N_{re}$  phase on the length of terminal tail. The exclusive existence of SmA phase in mesogens DC-8,10 and DC-10,10 can be interpreted in terms of their strong lateral intermolecular attraction and an effective microphase segregation among the incompatible rigid cores and terminal tails. Besides, the parity of the spacer also appears to be crucial as the odd members DC-9,9 and DC-9,10 of the series display metastable nematic phase over very narrow

temperature range; such a behavior may be originating from their reduced shape anisotropy and very effective intermolecular terminal interactions. Overall, it is extremely difficult to point out the cause for the different behavior of these compounds, especially the origin of reentrant behavior in DC-8,9 and DC-10,9 exclusively, as they hardly differ in their structure when compared to other members of the series.

### III. EXPERIMENTAL SECTION

**III.a. General Information.** Analytical grade solvents obtained from local companies were further purified and dried as per the standard procedures. Chemicals procured from different companies were used without any purification. Thin layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck, Kieselgel 60, F254). Chromatography was performed using either silica gel (60–120, 100–200, and 230–400 mesh) or neutral aluminum oxide.  $^1\text{H}$  NMR spectra were recorded using a Bruker AMX-400 (400 MHz) spectrometer. For  $^1\text{H}$  NMR spectra, the chemical shifts are reported in ppm relative to  $\text{SiMe}_4$  (TMS) as an internal standard and coupling constants are expressed in hertz. Infrared spectra were recorded on a Perkin-Elmer Spectrum 1000 FTIR spectrometer. The spectral positions are given in wavenumber ( $\text{cm}^{-1}$ ) unit. Mass spectra were determined on a JEOL JMS-600H spectrometer in  $\text{FAB}^+$  mode where 3-nitrobenzyl alcohol was used as a liquid matrix. Microanalyses were performed using a Eurovector model EA3000 CHNS elemental analyzer. The initial phase transitions and corresponding temperatures for the compounds were determined by a polarizing optical microscope (POM) (Leitz DMRXP or Leica DMLP) equipped with a programmable hot stage (Mettler FP90 or FP82HT). The mesogenic compounds were investigated for their liquid crystalline behavior by employing an optical polarizing microscope equipped with a programmable hot stage. 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  $5\text{ }^\circ\text{C}/\text{min}$  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.

**III.b. General Procedure for the Synthesis of Dimerlike Compounds.** A round-bottom flask equipped with a magnetic stir bar, reflux condenser, and nitrogen gas inlet was charged with salicylaldehyde 1a–c (0.5 mmol, 1 equiv), *n*-nonylamine/*n*-decylamine (0.5 mmol, 1 equiv), absolute ethanol (10 mL), and traces of acetic acid. The resultant yellow solution was heated under reflux for 4 h. The reaction mixture was cooled to room temperature and the yellow-colored solid obtained was collected by filtration. The crude product was purified by repeated recrystallization in a mixture of dichloromethane–ethanol (1:9) until a constant isotropic phase transition temperature was obtained.

**DC-8,9:** 4'-(8-(3-Hydroxy-4-((nonylimino)methyl)phenoxy)octyloxy)biphenyl-4-carbonitrile. Yield: 80%; a yellow solid; IR(KBr pellet):  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$  2934, 2856, 2225, 1619, 1495, and 1181. UV–vis:  $\lambda_{\text{max}} = 295.06\text{ nm}$ ,  $\epsilon = 4.93 \times 10^3\text{ L mol}^{-1}\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.12 (s, 1H, 1  $\times$  OH), 8.08 (s, 1H, 1  $\times$  CH=N), 7.69 (d,  $J = 6.52\text{ Hz}$ , 2H, Ar), 7.64 (d,  $J = 6.64\text{ Hz}$ , 2H, Ar), 7.53 (d,  $J = 8.8\text{ Hz}$ , 2H,

Ar), 7.05 (d,  $J = 8.6\text{ Hz}$ , 1H, Ar), 7.00 (d,  $J = 6.76\text{ Hz}$ , 2H, Ar), 6.36 (d,  $J = 2.36\text{ Hz}$ , 1H Ar), 6.33 (dd,  $J_1 = 2.4\text{ Hz}$ ,  $J_2 = 8.56\text{ Hz}$ , 1H, Ar), 4.02 (t,  $J = 6.52\text{ Hz}$ , 2H, 1  $\times$   $\text{OCH}_2$ ), 3.97 (t,  $J = 6.56\text{ Hz}$ , 2H, 1  $\times$   $\text{OCH}_2$ ), 3.52 (t,  $J = 6.96\text{ Hz}$ , 2H, 1  $\times$   $\text{NCH}_2$ ), 1.86–1.28 (m, 26H, 13  $\times$   $\text{CH}_2$ ), and 0.89 (t,  $J = 6.76\text{ Hz}$ , 3H, 1  $\times$   $\text{CH}_3$ );  $^{13}\text{C}$  NMR(100 MHz): 167.6, 164.3, 159.8, 145.3, 135.6, 132.6, 131.3, 128.3, 127.1, 119.3, 115.2, 110.1, 101.9, 69.1, 68.2, 53.9, 31.8, 30.0, 29.1, 28.9, 26.9, 25.9, 25.8, 22.6 and 14.1; MS ( $\text{FAB}^+$ ):  $m/z$  calcd for  $\text{C}_{37}\text{H}_{48}\text{N}_2\text{O}_3$ : 568.3; found: 568.8. Anal. Calcd for  $\text{C}_{37}\text{H}_{48}\text{N}_2\text{O}_3$ : C, 78.13, H, 8.51, N, 4.93. Found: C, 78, H, 8.41, N, 5.69.

**DC-8,10:** 4'-(8-(4-((Decylimino)methyl)-3-hydroxyphenoxy)octyloxy)biphenyl-4-carbonitrile. Yield: 85%; a yellow solid; IR(KBr pellet):  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$  2934, 2856, 2225, 1619, 1495, and 1181. UV–vis:  $\lambda_{\text{max}} = 294.60\text{ nm}$ ,  $\epsilon = 6.74 \times 10^3\text{ L mol}^{-1}\text{ cm}^{-1}$ .  $^1\text{H}$  NMR(400 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.12 (s, 1H, 1  $\times$  OH), 8.08 (s, 1H, 1  $\times$  CH=N), 7.69 (d,  $J = 6.56\text{ Hz}$ , 2H, Ar), 7.64 (d,  $J = 6.72\text{ Hz}$ , 2H, Ar), 7.53 (d,  $J = 6.68\text{ Hz}$ , 2H, Ar), 7.05 (d,  $J = 8.6\text{ Hz}$ , 1H, Ar), 7.00 (d,  $J = 8.7\text{ Hz}$ , 2H, Ar), 6.36 (d,  $J = 2.32\text{ Hz}$ , 1H Ar), 6.33 (dd,  $J_1 = 2.36\text{ Hz}$ ,  $J_2 = 8.56\text{ Hz}$ , 1H, Ar), 4.02 (t,  $J = 6.52\text{ Hz}$ , 2H, 1  $\times$   $\text{OCH}_2$ ), 3.97 (t,  $J = 6.56\text{ Hz}$ , 2H, 1  $\times$   $\text{OCH}_2$ ), 3.52 (t,  $J = 6.7\text{ Hz}$ , 2H, 1  $\times$   $\text{NCH}_2$ ), 1.86–1.28 (m, 28H, 14  $\times$   $\text{CH}_2$ ), and 0.89 (t,  $J = 6.64\text{ Hz}$ , 3H, 1  $\times$   $\text{CH}_3$ ).  $^{13}\text{C}$  NMR(100 MHz): 167.6, 164.3, 159.8, 145.3, 135.6, 132.6, 131.3, 128.3, 127.1, 119.1, 115.1, 110.1, 101.9, 68.5, 68.1, 55.6, 31.9, 30.6, 29.5, 29.2, 28.9, 26.8, 25.9, 22.7, and 14.1. MS ( $\text{FAB}^+$ ):  $m/z$  calcd for  $\text{C}_{38}\text{H}_{50}\text{N}_2\text{O}_3$ : 582.3; found: 582.8; Anal. Calcd. for  $\text{C}_{38}\text{H}_{50}\text{N}_2\text{O}_3$ : C, 78.31, H, 8.65, N, 4.81. Found: C, 78.22, H, 8.44, N, 4.26.

**DC-9,9:** 4'-(9-(3-Hydroxy-4-((nonylimino)methyl)phenoxy)nonyloxy)biphenyl-4-carbonitrile. Yield: 83%; a yellow solid; IR(KBr pellet):  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$  2934, 2957, 2224, 1619, 1495, and 1181. UV–vis:  $\lambda_{\text{max}} = 295.06\text{ nm}$ ,  $\epsilon = 4.25 \times 10^3\text{ L mol}^{-1}\text{ cm}^{-1}$ .  $^1\text{H}$  NMR(400 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.12 (s, 1H, 1  $\times$  OH), 8.08 (s, 1H, 1  $\times$  CH=N), 7.69 (d,  $J = 6.56\text{ Hz}$ , 2H, Ar), 7.64 (d,  $J = 6.56\text{ Hz}$ , 2H, Ar), 7.53 (d,  $J = 6.7\text{ Hz}$ , 2H, Ar), 7.05 (d,  $J = 8.6\text{ Hz}$ , 1H, Ar), 7.00 (d,  $J = 6.7\text{ Hz}$ , 2H, Ar), 6.36 (d,  $J = 2.36\text{ Hz}$ , 1H Ar), 6.33 (dd,  $J_1 = 2.4\text{ Hz}$ ,  $J_2 = 8.56\text{ Hz}$ , 1H, Ar), 4.02 (t,  $J = 6.56\text{ Hz}$ , 2H, 1  $\times$   $\text{OCH}_2$ ), 3.97 (t,  $J = 6.56\text{ Hz}$ , 2H, 1  $\times$   $\text{OCH}_2$ ), 3.52 (t,  $J = 6.7\text{ Hz}$ , 2H, 1  $\times$   $\text{NCH}_2$ ), 1.84–1.31 (m, 28H, 14  $\times$   $\text{CH}_2$ ), and 0.89 (t,  $J = 6.8\text{ Hz}$ , 3H, 1  $\times$   $\text{CH}_3$ ).  $^{13}\text{C}$  NMR(100 MHz): 167.6, 164.5, 159.8, 145.3, 132.5, 131.3, 128.3, 127.1, 119.1, 115.1, 110.3, 101.8, 69.3, 68.2, 31.8, 29.8, 29.2, 29.0, 28.8, 26.5, 26.0, 25.8, 22.6, and 14.0. MS ( $\text{FAB}^+$ ):  $m/z$  calcd for  $\text{C}_{38}\text{H}_{50}\text{N}_2\text{O}_3$ : 582.3; found: 582.9; Anal. Calcd. for  $\text{C}_{38}\text{H}_{50}\text{N}_2\text{O}_3$ : C, 78.31, H, 8.65, N, 4.81. Found: C, 78.04, H, 8.42, N, 4.64.

**DC-9,10:** 4'-(9-(4-((Decylimino)methyl)-3-hydroxyphenoxy)nonyloxy)biphenyl-4-carbonitrile. Yield: 90%; a yellow solid; IR(KBr pellet):  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$  2934, 2868, 2232, 1628, 1495, and 1173. UV–vis:  $\lambda_{\text{max}} = 295.06\text{ nm}$ ,  $\epsilon = 4.25 \times 10^3\text{ L mol}^{-1}\text{ cm}^{-1}$ .  $^1\text{H}$  NMR(400 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.1 (s, 1H, 1  $\times$  OH), 8.08 (s, 1H, 1  $\times$  CH=N), 7.69 (d,  $J = 6.8\text{ Hz}$ , 2H, Ar), 7.64 (d,  $J = 6.8\text{ Hz}$ , 2H, Ar), 7.53 (d,  $J = 8.8\text{ Hz}$ , 2H, Ar), 7.05 (d,  $J = 8.8\text{ Hz}$ , 1H, Ar), 7.00 (d,  $J = 6.4\text{ Hz}$ , 2H, Ar), 6.36 (d,  $J = 2.4\text{ Hz}$ , 1H Ar), 6.33 (dd,  $J_1 = 2.4\text{ Hz}$ ,  $J_2 = 8.8\text{ Hz}$ , 1H, Ar), 4.02 (t,  $J = 6.8\text{ Hz}$ , 2H, 1  $\times$   $\text{OCH}_2$ ), 3.97 (t,  $J = 6.4\text{ Hz}$ , 2H, 1  $\times$   $\text{OCH}_2$ ), 3.52 (t,  $J = 6.8\text{ Hz}$ , 2H, 1  $\times$   $\text{NCH}_2$ ), 1.85–1.29 (m, 30H, 15  $\times$   $\text{CH}_2$ ), and 0.89 (t,  $J = 6.8\text{ Hz}$ , 3H, 1  $\times$   $\text{CH}_3$ ).  $^{13}\text{C}$  NMR(100 MHz): 167.6, 164.5, 159.8, 145.3, 132.5, 128.3, 127.1, 115.1, 111.6, 110.1, 101.9, 69.5, 68.2, 31.8, 29.7, 29.2, 28.8, 26.4, 26.0, 25.8, 22.6, and 14.10. MS ( $\text{FAB}^+$ ):  $m/z$  calcd for  $\text{C}_{39}\text{H}_{52}\text{N}_2\text{O}_3$ : 596.4; found: 596.8. Anal. Calcd.



for  $C_{39}H_{52}N_2O_3$ : C, 78.48, H, 8.78, N, 4.69. Found: C, 78.18, H, 8.76, N, 4.24.

**DC-10,9:** 4'-(10-(3-Hydroxy-4-((nonylimino)methyl)-phenoxy)decyloxy)biphenyl-4-carbonitrile. Yield: 78%; a yellow solid; IR(KBr pellet):  $\nu_{\max}$  in  $\text{cm}^{-1}$  2921, 2850, 2230, 1624, 1496, and 1173. UV-vis:  $\lambda_{\max} = 294.68 \text{ nm}$ ,  $\epsilon = 5.22 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ .  $^1\text{H}$  NMR(400 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.11 (s, 1H, 1  $\times$  OH), 8.08 (s, 1H, 1  $\times$  CH=N), 7.69 (d,  $J = 6.76 \text{ Hz}$ , 2H, Ar), 7.64 (d,  $J = 6.64 \text{ Hz}$ , 2H, Ar), 7.53 (d,  $J = 6.68 \text{ Hz}$ , 2H, Ar), 7.05 (d,  $J = 8.56 \text{ Hz}$ , 1H, Ar), 7.00 (d,  $J = 6.76 \text{ Hz}$ , 2H, Ar), 6.36 (d,  $J = 2.32 \text{ Hz}$ , 1H, Ar), 6.33 (dd,  $J_1 = 2.36 \text{ Hz}$ ,  $J_2 = 8.56 \text{ Hz}$ , 1H, Ar), 4.02 (t,  $J = 6.56 \text{ Hz}$ , 2H, 1  $\times$   $\text{OCH}_2$ ), 3.96 (t,  $J = 6.53 \text{ Hz}$ , 2H, 1  $\times$   $\text{OCH}_2$ ), 3.52 (t,  $J = 6.8 \text{ Hz}$ , 2H, 1  $\times$   $\text{NCH}_2$ ), 1.86–1.27 (m, 30H, 15  $\times$   $\text{CH}_2$ ), and 0.89 (t,  $J = 6.68 \text{ Hz}$ , 3H, 1  $\times$   $\text{CH}_3$ ).  $^{13}\text{C}$  NMR(100 MHz): 167.6, 164.2, 159.9, 145.3, 132.6, 131.3, 128.3, 127.1, 119.1, 115.2, 110.1, 108.3, 101.9, 69.0, 68.2, 54.2, 31.8, 30.1, 29.4, 29.2, 28.9, 26.6, 26.0, 25.9, 22.6, and 14.1. MS (FAB<sup>+</sup>):  $m/z$  calcd for  $C_{39}H_{52}N_2O_3$ : 596.4; found: 596.7. Anal. Calcd. for  $C_{39}H_{52}N_2O_3$ : C, 78.48, H, 8.78, N, 4.69. Found: C, 78.26, H, 8.57, N, 5.07.

**DC-10,10:** 4'-(10-(4-((Decylimino)methyl)-3-hydroxyphenoxy)decyloxy)biphenyl-4-carbonitrile. Yield: 85%; a yellow solid; IR(KBr pellet):  $\nu_{\max}$  in  $\text{cm}^{-1}$  2923, 2852, 2232, 1637, 1495, and 1184. UV-vis:  $\lambda_{\max} = 294.68 \text{ nm}$ ,  $\epsilon = 7.35 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ .  $^1\text{H}$  NMR(400 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.12 (s, 1H, 1  $\times$  OH), 8.08 (s, 1H, 1  $\times$  CH=N), 7.69 (d,  $J = 8.8 \text{ Hz}$ , 2H, Ar), 7.64 (d,  $J = 8.6 \text{ Hz}$ , 2H, Ar), 7.53 (d,  $J = 9.6 \text{ Hz}$ , 2H, Ar), 7.05 (d,  $J = 8.6 \text{ Hz}$ , 1H, Ar), 7.00 (d,  $J = 9.7 \text{ Hz}$ , 2H, Ar), 6.36 (d,  $J = 2.32 \text{ Hz}$ , 1H, Ar), 6.33 (dd,  $J_1 = 2.4 \text{ Hz}$ ,  $J_2 = 8.56 \text{ Hz}$ , 1H, Ar), 4.02 (t,  $J = 6.52 \text{ Hz}$ , 2H, 1  $\times$   $\text{OCH}_2$ ), 3.96 (t,  $J = 6.56 \text{ Hz}$ , 2H, 1  $\times$   $\text{OCH}_2$ ), 3.52 (t,  $J = 6.68 \text{ Hz}$ , 2H, 1  $\times$   $\text{NCH}_2$ ), 1.80–0.85 (m, 32H, 16  $\times$   $\text{CH}_2$ ), and 0.89 (t,  $J = 7.04 \text{ Hz}$ , 3H, 1  $\times$   $\text{CH}_3$ ).  $^{13}\text{C}$  NMR(100 MHz): 167.3, 164.3, 159.9, 145.3, 132.6, 131.3, 128.3, 127.1, 119.1, 115.2, 110.1, 108.3, 101.9, 69.0, 68.2, 54.1, 31.7, 30.1, 29.4, 29.3, 29.1, 28.9, 26.9, 26.6, 26.0, 25.9, 22.6, and 14.1. MS (FAB<sup>+</sup>):  $m/z$  calcd for  $C_{40}H_{54}N_2O_3$ : 610.8; found: 610.8. Anal. Calcd. for  $C_{40}H_{54}N_2O_3$ : C, 78.65, H, 8.91, N, 4.59. Found: C, 78.51, H, 8.37, N, 4.34.

#### IV. CONCLUSION

Summarizing, dimerlike liquid crystals comprising cyanobiphenyl and *N*-(*n*-alkyl)salicylalimine segments interlinked though via a flexible spacer of varying length and parity were synthesized and characterized thoroughly with the help of several complementary studies. Among the six synthesized LCs, two compounds with oxyoctyloxy–nonyloxy and oxydecyloxy–nonyloxy spacer-terminal chain combination exhibit N–SmA–N<sub>re</sub> sequence with the nematic phase exhibiting reentrance that can be perhaps attributed to originating from the packing frustrations (dipolar factors). In such compounds, the length of the terminal tail and parity of the spacer appear to be decisive structural factors in stabilizing reentrant nematic phase. Further investigations are necessary to know the molecular structural factors responsible for the generation of reentrant nematic phase.

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#### Notes

The authors declare no competing financial interest.

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