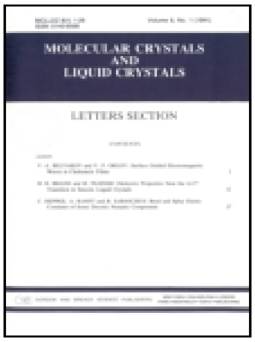

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Synthesis and Characterization of a Series of Cholesterol-Based Liquid Crystalline Dimers with a Chiral (-)- Menthyl Terminal Group

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A novel series of cholesterol-based liquid crystalline (LC) dimers with a menthyl terminal group in the biphenyl base side have been synthesized. The chemical structures and LC properties of this series of compounds are characterized by FT-IR, ^{1}H-NMR, elemental analysis, hot-stage coupled polarizing microscopy and differential scanning calorimetry. All the dimers exhibit enantiotropic mesophases. These dimesogenic compounds with a short spacer are chiral nematic LCs, while with long spacers, they are SmA and chiral nematic LCs. Some of these LC dimers exhibit iridescent colors in their chial nematic (N) states.*

Keywords Chiral nematic phase; cholesterol; dimesogenic; liquid crystalline dimer; menthyl

1. Introduction

LC dimers, also called dimesognic compounds, are molecules containing two identical (symmetric) or nonidentical mesogenic moieties (unsymmetric) connected by a flexible spacer. LC dimers have been attracted intensive attention not only because they are regarded as model compounds for LC polymers but also due to their inherently interesting LC properties [1–6]. Due to the great structural variety of unsymmetric compounds, the quantity of unsymmetric LC dimers is much more than that of symmetric LC dimers. In particular, unsymmetric cholesterol-based LC dimers which containing one cholesteryl moiety and another substituted aromatic mesogenic unit such as benzoate ester, Schiff's base, azobenzene, or biphenyl are especially interesting [7–25]. This is because the chiral cholesteryl moiety entitles many unique optical properties such as selective reflection, circular dichroism, and thermo-optical effects besides the properties of conventional rigid aromatic LC dimers. In this aspect, they could be applied in optical storage, optical switching, nonlinear optics, and liquid crystal display device [14–18].

(-)- Menthol is another natural chiral compound; it has three chiral carbon atoms in its molecule. Introduce the menthyl group to the LC compounds or polymers also can

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produce N*, blue or chiral smectic phases [26,20]. To reveal the properties of the LC dimers containing cholesteryl moiety and a chiral (-)- menthyl terminal group, a novel series of cholesterol-based LC dimers with menthyl terminal group in the biphenyl base side have been synthesized, also their LC properties are also studied.

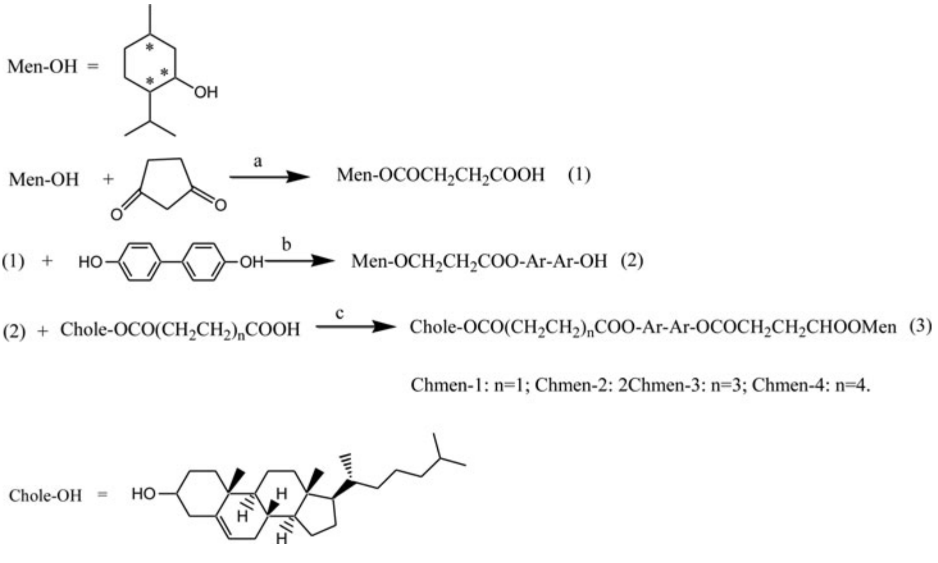
2. Experimental

2.1. *Materials*

(-)- Menthol (98%) was obtained from Aladdin chemical. Cholesterol was obtained from Tianjin Yingbo Biochemical Reagent Company (Tianjin, P.R. China). N, N-dicylcohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) were used as received (Arcos). Dichloromethane (DCM) was dried with CaH_2. Tetrahydrofuran (THF) was distilled from sodium-benzophenone. Other solvents and reagents were AR or CP grade and used without further purification.

2.2. *Synthesis*

The synthetic route used to prepare this series of LC dimers is shown in the Scheme 1. Dicarboxylic acid monocholesteryl esters were synthesized according to a reported procedure [20, 21].



Scheme 1. Synthetic route of the cholesterol-based LC dimers containing (-) menthyl terminal groups. Regents and conditions: (a) THF, DMAP, refluxing 12 hr; (b) DCC/DMAP/DCM, 24 hr, room temperature; and (c) DCC/DMAP/DCM, 24 hr, room temperature.

2.2.1. Synthesis of (-)-monomenthyl succinate (1). (-)- Monomenthyl succinate was synthesized using the common method esterification of (-)-methanol and succinic anhydride in THF with the catalyst DMAP. Yield: 78.6%. M.p. 61–63°C.

FR-IR (KBr, cm^{-1}): 2917–3440, 1727, 1710, 1388, 1285, 1224, 1177, 1037, 1011.

^{1}HNMR ($CDCl_3$, ppm): .4.67–4.74 (m, 1H), 2.67–2.72 9 (t, 2H), 2.58–2.63 (t, 2H), 0.72–2.01 (broad, 18H).

2.2.2. Synthesis of (4′-hydroxybiphenyl) 4-menthyloxycarboxyl propionate (2). Ten millimole compound (1) and 32 mmol 4, 4-biphenyl were dissolved in 40 mL dry THF, 10 mmol DCC, and 2 mmol DMAP were added with stirring at room temperature for 24 hr. The dicyclohexylurea formed as precipitation was removed by filtration and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (200–300 mesh) using a mixture of petroleum ether (60–90°C) and ethyl acetate (4/1, v/v) as eluent, white solid powder was obtained. Yield: 51.4%. mp. 135.5–137°C.

FR-IR (KBr, cm^{-1}): 3475, 2956, 1751, 1731, 1611, 1530, 1408, 1368, 1267, 1207, 1153, 969, 891, 824. ^{1}HNMR ($CDCl_3$, ppm): 7.74–7.49 (d, 2H), 7.37–7.40 (d, 2H), 7.09–7.12 (d, 2H), 6.82–6.95 (d, 2H), 5.29 (s, 1H), 4.70–4.79 (m, 1H), 2.89–2.93 (t, 4H), 2.73–2.77 (t, 4H), 0.74–2.02 (broad, 18H).

2.2.3. Synthetic of the cholesterol-based LC dimers containing (-) menthyl terminal groups (3) (chmen-1, chmen-2, chmen-3, and chmen-4). Four millimole compound (2) and 4 mmol corresponding dicarboxylic acid monocholesteryl ester were dissolved in 40 mL dry DCM. Four millimole DCC and 0.6 mmol DMAP were added with stirring at room temperature for 24 hr. The dicyclohexylurea formed as precipitation was removed by filtration and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (200–300 mesh) using a mixture of petroleum ether (60–90°C) and ethyl acetate (4/1, v/v) as eluent, then recrystallized from petroleum ether (60–90°C), white solid powder was obtained.

Chmen-1, Yield: 53.8%. FT-IR (KBr,cm^{-1}): 2955, 1760, 1731, 1622, 1493, 1313, 1198, 1166, 1136. ^{1}H-NMR ($CDCl_3$, ppm): 7.52–7.55 (d, 4H), 7.14–7.17 (dd, 4H), 5.38 (s,1H), 4.70–4.78 (m, 2H), 2.89–2.91 (t, 4H), 2.71–2.75 (t, 4H), 0.73–2.35 (broad, 61H). Element analysis for $C_{57}H_{80}O_8$; calculated C 76.64%, H 9.03%; found C 76.58%, H 9.27%.

Chmen-2, Yield: 50.1%. FT-IR (KBr,cm^{-1}): 2936, 1760, 1731, 1628, 1495, 1413, 1254, 1202, 1167, 1136. ^{1}H-NMR ($CDCl_3$, ppm): 7.53–7.55 (d, 4H), 7.13–7.7 (dd, 4H), 5.37 (s,1H), 4.59–4.78 (m, 2H), 2.88–2.92 (t, 2H), 2.72–2.76 (t, 2H), 2.61–2.63 (t, 2H), 2.31–2.38 (t, 4H), 0.67–2.02 (broad, 63H). Element analysis for $C_{59}H_{84}O_8$; calculated C 76.92%, H 9.19%; found C 77.00%, H 9.49%.

Chmen-3, Yield: 52.5%. FT-IR(KBr,cm^{-1}) : 2936, 1760, 1732, 1601, 1495, 1414, 1253, 1202, 1168, 1136. ^{1}H-NMR ($CDCl_3$, ppm): 7.53–7.56 (d, 4H), 7.12–7.17 (dd, 4H), 5.38 (s,1H), 4.60–4.78 (m, 2H), 2.88–2.92 (t, 2H), 2.72–2.76 (t, 2H), 2.55–2.60 (t, 2H), 2.27–2.32 (t, 4H), 0.67–2.02 (broad, 67H). Element analysis for $C_{61}H_{88}O_8$; calculated C 77.17%, H 9.34%; found C 77.18%, H 9.30%.

Chmen-4, Yield: 63.7%. FT-IR (KBr,cm^{-1}): 2933, 1760, 1733, 1628, 1495, 1367, 1254, 1202, 1168, 1136. ^{1}H-NMR ($CDCl_3$, ppm): 7.53–7.56 (d, 4H), 7.12–7.7 (dd, 4H), 5.38 (s,1H), 4.60–4.78 (m, 2H), 2.88–2.92 (t, 2H), 2.72–2.76 (t, 2H), 2.54–2.59 (t, 2H), 2.26–2.32 (dd, 4H), 0.67–2.02 (broad, 71H). Element analysis for $C_{63}H_{92}O_8$; calculated C 77.42%, H 9.49%; found C 77.29%, H 9.46%.

2.3. Characterization

Chemical structures of the intermediates and LC dimers were characterized with FT-IR by using Bruker Tensor 37 spectrometer and ^{1}H-NMR spectrum by using Bruker 300 MHz spectrometer with tetramethylsilane as an internal standard. Elemental analyses were carried out on a Germany Elementary Vario EL III instrument. The phase transitions of the LC dimers were determined by means of Nikon Eclipse E200 polarized optical microscope (POM) equipped with an Instec STC200 hot stage. A differential scanning calorimeter (DSC) (Netzsch DSC204) was used to measure the transformation temperature and transformation enthalpy at the heating and cooling rate of 5°C/min.

3. Results and Discussions

In this work, a series of Cholesterol-based LC dimers have been synthesized, the two nonidentical mesogenic moieties cholesteryl and biphenyl are linked through dicarboxylic ester bonds, the spacer lengths are 2, 4, 6, 8 methylenes, on the other side of biphenyl containing another chiral (-)-menthyl terminal group, they are depicted as chmen-1, chmen-2, chmen-3, and chmen-4. In the previous studies of unsymmetric cholesterol-based LC dimers, mostly, they had only one chiral moiety in their molecular structure, another mesogenic group such as benzoate ester, Schiff's base, azobenzene, or biphenyl did not catch a chiral tail [7–25]. Only a few researches reported the tolane mesogenic moiety was attached chiral tails such as 2S-chloro-3S-methylpentanoyloxy or 1, 3-dioxalane on the unsymmetric cholesterol-based LC dimers [26].

Menthyl is a well-known chial group which can introduce chiral nematic phase when it is incorporated in the LC molecules or polymers [27–31]. To the best to our knowledge, there is no report about the LC dimers containing chiral cholesteryl and (-)-menthyl groups together. So the aim of this study to reveal the structure-property relationships of novel Cholesterol-based dimeogenic compounds containing (-)-menthyl group.

Figures 1 and 2 show the DSC thermograms of LC dimers (Chmen-1, Chmen-2, Chmen-3, and Chmen-4) in the heating and cooling process, respectively. In the heating process of Chmen-1, there are two peaks appeared at 114.4 and 162.3°C. Very similar to Chmen-2, Chmen-3, and Chmen-4, there are three peaks appeared in heating, but the transition temperatures are decreased in turn. In the cooling processes, one peak appeared at 159.9°C for Chmen-1, two peaks appeared at 146.5 and 141.2°C for Chmen-2, but three peaks appeared in the Chmen-3 and Chmen-4 DSC curves.

In the POM observation coupled with hot stage, when Chmen-1 was heated to 115°C, the broken fan-shaped texture appeared (Fig. 3(a)), the oily-streak texture formed when the sample was slightly sheared (Fig. 3(b)). The LC phase transited to isotropic phase until hated to 163°C. When Chmen-1 was cooled from isotropic phase at 160°C, fan-shaped texture (also can changed to oily-streak texture after sheared) appeared again, but it could not crystallized even cooled down to room temperature. Therefore, the LC phase formed of Chmen-1 during and cooling is N* phase. In the POM observation of Chmen-2, when it was hated to 123°C, a typical focal-conic fan SmA texture was found (Fig. 4(a)), after it is heated to 143°C, the texture changed to oily-streak texture of N* phase until isotropic at 148°C (Fig. 4(b)). In the cooling process of Chmen-2, the isotropic to N* phase transition taken place at 146°C, and the N* phase transmitted to SmA phase at 141 °C, then the SmA phase retained at room temperature. The LC behavior of Chmen-3 and Chmen-4 are very similar to that of Chmen-2, but Chmen-3 and Chmen-4 could crystallized at low temperature 34°Cand 40°C, respectively.

Therefore, from combination of the results of DSC studies and POM observation, we can summarize the LC properties of LC dimers in Table 1.

From the above results of their LC properties, we could conclude, with the alkylene spacer lengths increased in the LC dimers, Chmen-1 appeared only one chiral nematic

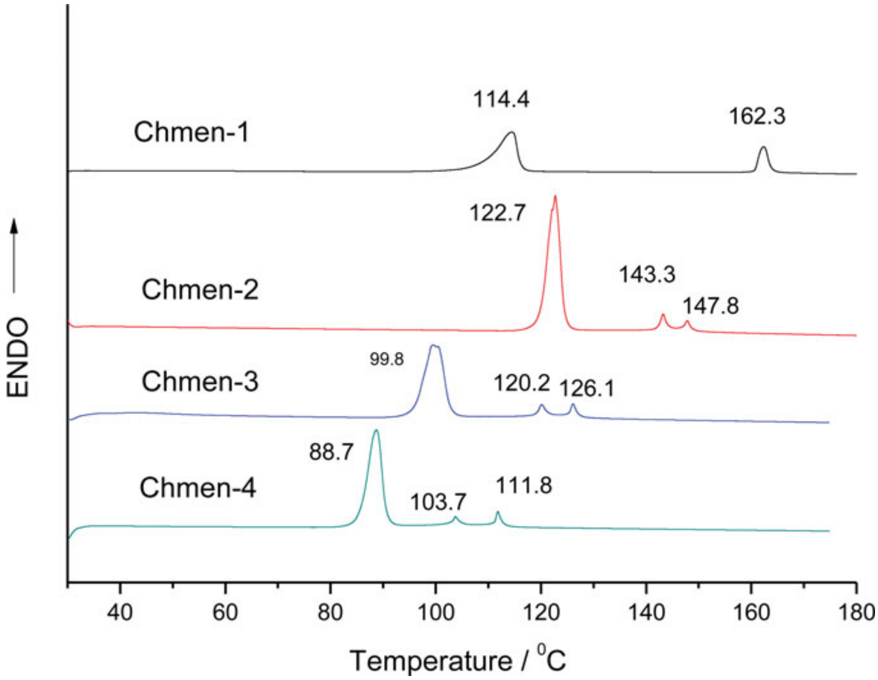


Figure 1. DSC traces for the LC dimers in the heating process.

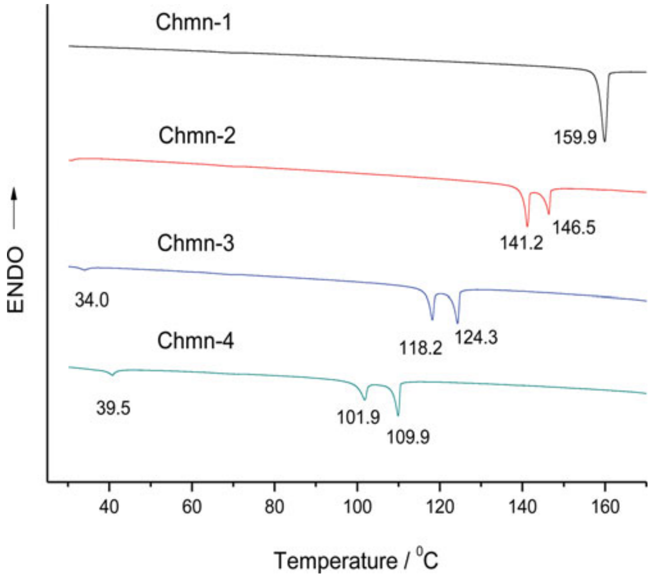
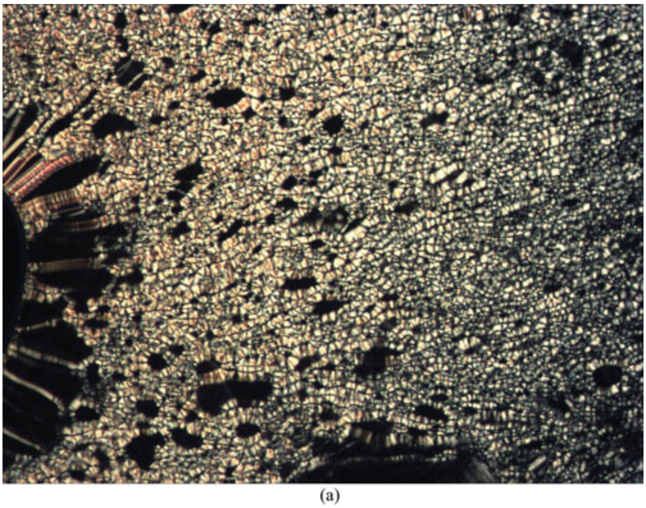
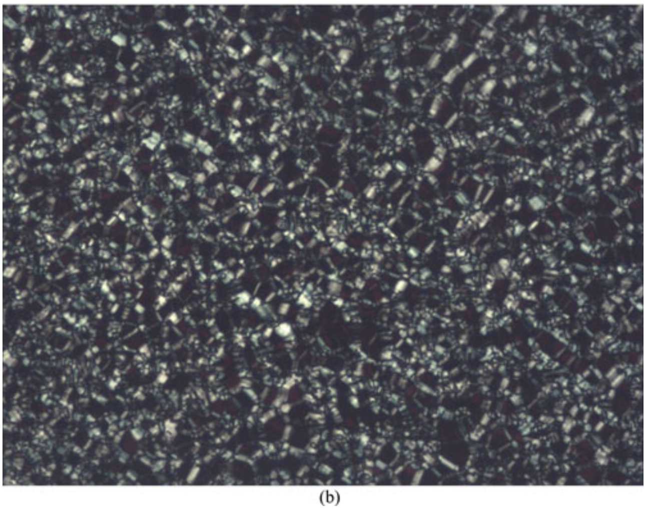


Figure 2. DSC traces for the LC dimers in the cooling process.

phase, but Chmen-2, Chmen-3, and Chmen-4 exhibited SmA and chiral nematic phases. The temperatures of N* to isotropic phase transition, isotropic phase to N* phase and N* to SmA phase transitions decreased as alkylene spacer lengths increased, this indicated that



(a)



(b)

Figure 3. Optical polarizing micrographs of Chmen-1 in heating process: (a) fan-shaped texture at 130°C and (b) oily-streak texture formed after sheared.

the longer of alkylene spacer length, the more flexible the dimesogenic compound was, so that the LC phase appeared at lower temperature as the alkylene spacer lengths increased.

Except Chmen-1, both in the heating and cooling processes of the LC dimers Chmen-2, Chmen-3, and Chmn-4, the iridescent colors appeared in their N* LC states. This property of N* phase is due to the presence of helical superstructure. The variation of temperature results in the change of the pitch of helical structure of the N* phase, this effect leads to the color changes at different temperature on the different observation angles [32]. unfortunately, the N* phases temperature ranges of these LC dimers are rather low, about 4.5°C–8.1°C, we roughly describe the phenomena as blow: Chmen-2 shows red to green color change during in the heating 143°C–148°C, the inverse color change of N* state takes

Table 1. Thermal transition temperatures of cholesterol-based LC dimers

Compound	Heating	Cooling
Chmen-1	Cr114.4 N*162.3I	I159.9 N*
Chmen-2	Cr 122.7SmA143.3 N* 147.8I	I146.5 N*141.2SmA
Chmen-3	Cr 99.8SmA120.2 N*126.1I	I124.3 N*118.2SmA34.0Cr
Chmen-4	Cr88.7SmA103.7 N*111.8I	I109.9 N*101.9SmA39.5Cr

N* = chiral nematic and I = isotropic, the temperature was taken at DSC curves peaks value.

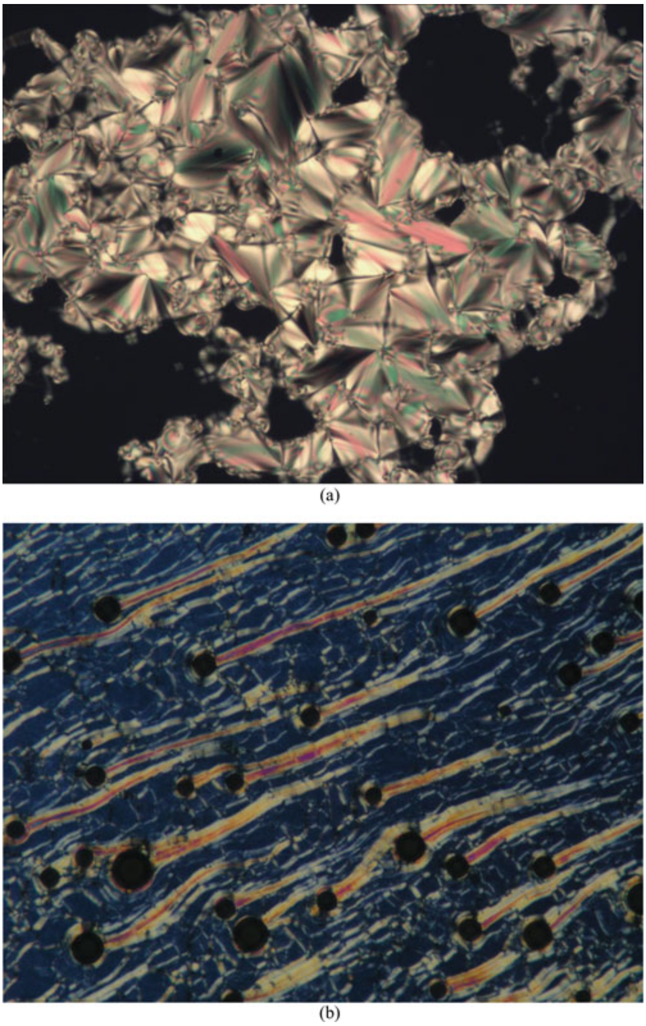


Figure 4. Optical polarizing micrographs of Chmen-2 in heating process: (a) fan-shaped texture at 130°C and (b) oily-streak texture formed at 145°C.

place in the cooling process. Chmen-3 and Chmen-4 mainly appear red and yellow color in the N* phase.

4. Conclusion

In this work, we have synthesized a series of Cholesterol-based LC dimers combining of biphenyl mesogen with (-)-menthyl terminal group, the two mesogenic moieties are linked through dicarboxylic ester bonds; the alkylenen spacers lengths are 2,4,6,8 mehylenes. The LC dimer with a short flexible spacer is N* phase while longer flexible spacer is SmA and N* phase. The phase transition temperatures are lower as the flexible spacers are longer in general. Except Chmen-1, other dimeogenic compounds exhibit iridescent colors in the N* states both in heating and cooling process.

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