

# Multiple nematic phases observed in chiral mesogenic dimers

Anna Zep, Satoshi Aya, Kenji Aihara, Kenji Ema, Damian Pocięcha, Karolina Madrak, Piotr Bernatowicz, Hideo Takezoe, Ewa Gorecka

## Experimental

The  $^1\text{H}$  NMR spectra were recorded at 500 MHz NMR Varian Unity Plus spectrometer. Proton chemical shifts are reported in ppm ( $\delta$ ) relative to the internal standard – tetramethylsilane (TMS  $\delta=0.00$  ppm). Data are presented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constant (Hz).

The variable temperature  $^{13}\text{C}$  NMR spectra were acquired at external magnetic field of 11.7 T, using Bruker AVANCE II 500 MHz spectrometer. The 4mm DVT MAS probehead was exploited. Temperature was calibrated using  $\text{Pb}(\text{NO}_3)_2$  sample (see P. A. Beckmann and C. Dybowski, *J. Magn. Reson.* 2000, 146, 379), while the  $^{13}\text{C}$  chemical shifts were referenced to the methyl group of external glycine sample, whose shift was assumed 43.3 ppm. TPPM15  $^1\text{H}$  decoupling was applied during acquisition with the RF field strength of 66 kHz. The delay between scans was set to 20 s. which is much longer than five longest  $^{13}\text{C}$  relaxation times in the sample, and the VT gas flow was set to 935 l/h. Such setting of the latter two parameters allowed for diminishing of sample heating effects occurring as a result of high  $^1\text{H}$  decoupling power. All the experiments were performed on non-spinning samples.

Low resolution calorimetric studies were performed with TA DSC Q200 machine, samples of mass 1-3 mg were sealed in aluminum pans and kept in nitrogen atmosphere during measurement, both heating and cooling scans with rate 5-10 deg/min were applied. In order to study the detailed thermal properties of the samples, we also carried out heat capacity investigation by using a home-built high-sensitivity differential scanning calorimeter (HS-DSC) [Y. Sasaki, Y. Setoguchi, H. Nagayama, H. Yao, H. Takezoe, K. Ema, *Physica E*, 2011, 43, 779.]. Two semiconducting thermoelectric modules were used to detect the temperature difference between a sample and a reference cell. The sample of 10-15 mg is loaded into a gold pan and hermetically sealed with a gold lid under a helium atmosphere. The temperature scan rates used in the present study were 0.10 or 0.05°C/min, for which the samples were close to the thermal equilibrium state.

The small angle X-ray diffraction (SAXRD) patterns for the powder as well as partially aligned samples were obtained with the Bruker Nanostar system. The  $\text{CuK}\alpha$  radiation was used, patterns were registered with an area detector VANTEC2000. The temperature of the sample was controlled with precision of 0.1 K. Samples were prepared either in thin-walled glass capillaries or as droplets on heated surface. Wide angle diffractograms were obtained with Bruker D8 GADDS system ( $\text{CuK}\alpha$  line, Goebel mirror, point beam collimator, Vantec2000 area detector).

The optical studies were performed using Zeiss Imager A2m

polarizing microscope equipped with Linkam heating stage. The birefringence of the samples was checked using CRI Abrio Imaging System integrated with microscope. For optical studies glass cells, provided by WAT, Linkam and EHC, having ITO and polymer aligning layer were used with various thickness 1.5 to 10 microns. The same glass cells were also used in electrooptic measurements and dielectric studies.

Dielectric constant as a function of frequency and temperature were measured with Solartron SI1260 Impedance Analyzer.

IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer. The sample was placed on ZnSe plate, aligned by shearing and heated with a Linkam heating stage. The IR polarizer was rotated with respect to the rubbing direction in the sample to obtain variation of IR signal intensities.

## Organic synthesis

Following abbreviations are used:

TEA – triethylamine

DMF – dimethylformamide

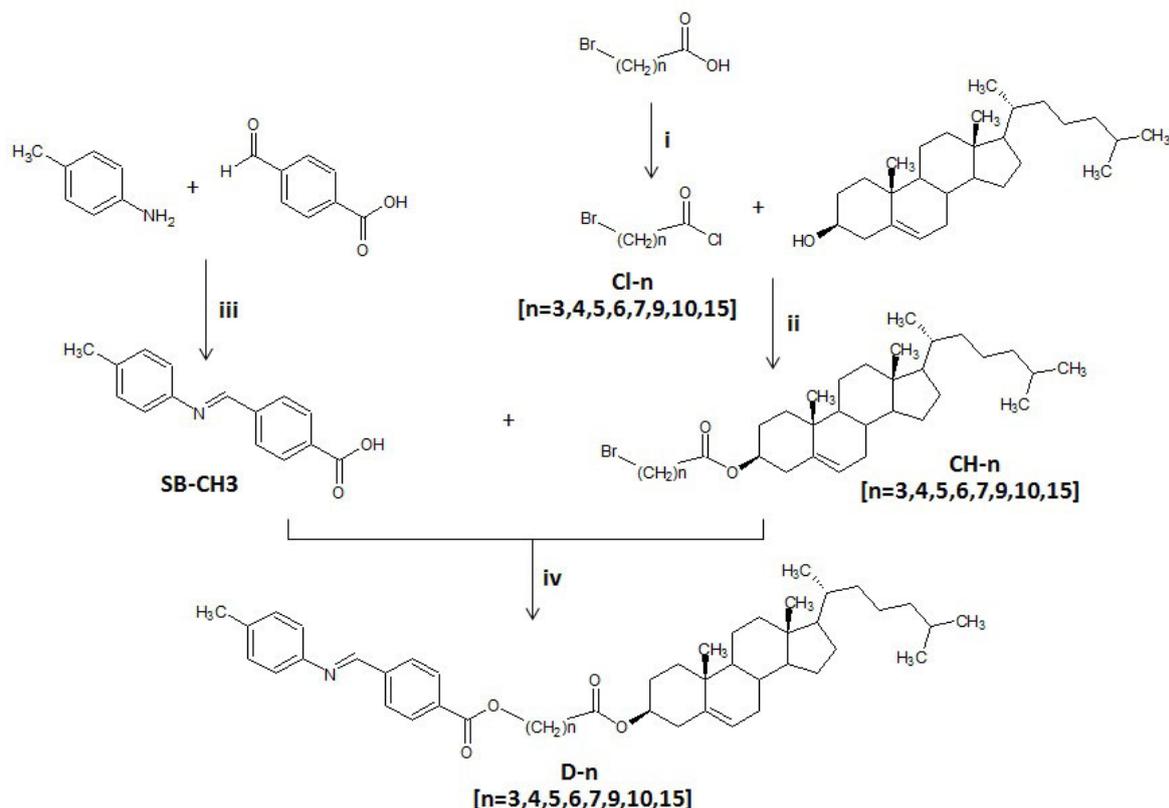
The general procedure for the synthesis of compounds **D-3** – **D-15** is presented in Scheme 1.

### Preparation of 16-bromohexadecanoil chloride (CI-15)

To the round bottom flask 16-bromohexadecanoic acid (5,0g; 0,0149 mol) and thionyl chloride (2,16 mL; 0,0293 mol) were added. This solution was stirred overnight at the room temperature. The thionyl chloride was removed from the mixture by the vacuum distillation to achieve 3,5 g (66% yield) of a transparent oil. The same procedure was applied to obtain homologues CI-3, CI-4; CI-5, CI-6; CI-7, CI-9; CI-10. Yield: 70%, 68%, 71%, 74%, 66%, 72%, 70%, respectively.

### Preparation of cholesteryl 16-bromohexadecanoate (CH-15)

To the solution of cholesterol (2,87 g; 0,0074 mol) in anhydrous toluene (75 mL) redistilled and dried triethylamine (1,0g; 0,01 mol) was added and the mixture was vigorously stirred whilst 16-bromohexadecanoyl chloride (3,5g; 0,01 mol) was added dropwise at the room temperature. The resultant pink-colored solution was stirred for a further 24 h and then the toluene was removed using rotary evaporator. Diethyl ether (200 mL) was added to the mixture along with water (150 mL), the layers were separated, and the organic phase was washed with two further portions of water (2 x 100 mL). The organic phase was evaporated to 30 mL in a rotary evaporator and mixed with 150 mL of methanol to precipitate product, which was then collected by filtration. After washing with methanol the resultant product



**Scheme 1** General procedure for the synthesis of compounds D-3 – D-15. Reagents and conditions: (i) SOCl<sub>2</sub>, room temperature; (ii) TEA, toluene, room temperature; (iii) methanol, room temperature; (iv) KI, K<sub>2</sub>CO<sub>3</sub>, DMF, 90°C

5 was dried and analyzed for purity by TLC. No further purification was needed. (Yield: 3,864 g, 73,95%). The same procedure was applied to obtain analogue compounds CH-3, CH-4; CH-5, CH-6; CH-7, CH-9; CH-10. Yield: 79%, 80%, 79%, 78%, 76%, 74%, 73%, respectively.

**Compound CH-15**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz) δ=0.68 (3H, s); 0.85-0.88 (6H, m); 0.91(3H, d, J=6.6Hz); 1.02(3H,s); 1.03-2.04 (50H, m); 2.26 (2H, t, J=7.6Hz); 2.28-2.33 (2H, m); 3.40 (2H, t, J=6.9Hz); 4.57-4.65 (H, m); 5.34-5.42 (H, m)

**Compound CH-10**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz) δ=0.68 (3H, s); 0.85-0.88 (6H, m); 0.91(3H, d, J=6.6Hz); 1.02(3H,s); 1.03-2.04 (40H, m); 2.26 (2H, t, J=7.6Hz); 2.28-2.33 (2H, m); 3.40 (2H, t, J=6.9Hz); 4.57-4.65 (H, m); 5.34-5.42 (H, m)

**Compound CH-9**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz) δ=0.68 (3H, s); 0.85-0.88 (6H, m); 0.91(3H, d, J=6.6Hz); 1.02(3H,s); 1.03-2.04 (38H, m); 2.26 (2H, t, J=7.6Hz); 2.28-2.33 (2H, m); 3.40 (2H, t, J=6.9Hz); 4.57-4.65 (H, m); 5.34-5.42 (H, m)

**Compound CH-7**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz) δ=0.68 (3H, s); 0.85-0.88 (6H, m); 0.91(3H, d, J=6.6Hz); 1.02(3H,s); 1.03-2.04 (34H, m); 2.26 (2H,

t, J=7.6Hz); 2.28-2.33 (2H, m); 3.40 (2H, t, J=6.9Hz); 4.57-4.65 (H, m); 5.34-5.42 (H, m)

**Compound CH-6**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz) δ=0.68 (3H, s); 0.85-0.88 (6H, m); 0.91(3H, d, J=6.6Hz); 1.02(3H,s); 1.03-2.04 (32H, m); 2.26 (2H, t, J=7.6Hz); 2.28-2.33 (2H, m); 3.40 (2H, t, J=6.9Hz); 4.57-4.65 (H, m); 5.34-5.42 (H, m)

**Compound CH-5**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz) δ=0.68 (3H, s); 0.85-0.88 (6H, m); 0.91(3H, d, J=6.6Hz); 1.02(3H,s); 1.03-2.04 (30H, m); 2.26 (2H, t, J=7.6Hz); 2.28-2.33 (2H, m); 3.40 (2H, t, J=6.9Hz); 4.57-4.65 (H, m); 5.34-5.42 (H, m)

**Compound CH-4**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz) δ=0.68 (3H, s); 0.85-0.88 (6H, m); 0.91(3H, d, J=6.6Hz); 1.02(3H,s); 1.03-2.04 (28H, m); 2.26 (2H, t, J=7.6Hz); 2.28-2.33 (2H, m); 3.40 (2H, t, J=6.9Hz); 4.57-4.65 (H, m); 5.34-5.42 (H, m)

**Compound CH-3**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz) δ=0.68 (3H, s); 0.85-0.88 (6H, m); 0.91(3H, d, J=6.6Hz); 1.02(3H,s); 1.03-2.04 (26H, m); 2.26 (2H, t, J=7.6Hz); 2.28-2.33 (2H, m); 3.40 (2H, t, J=6.9Hz); 4.57-4.65 (H, m); 5.34-5.42 (H, m)

### Preparation of 4-(p-tolylimino-methyl)-benzoic acid (SB-CH3)

A solution of p-toluidine (1,08 g; 0,01 mol) in 50 ml of methanol was added slowly to a stirred suspension of 4-carboxybenzaldehyde (1,56 g; 0,01 mol) in 100 ml of methanol. The reaction mixture was stirred at room temperature for 24 h and the obtained yellow precipitate was filtered out and washed with little amount of methanol to yield the desired Schiff base. (Yield: 1,65 g; 66,26 %)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz) δ=2.39 (3H, s); 7.18 (2H, d, J=8.2Hz); 7.23 (2H, d, J=8.2Hz); 8.00 (2H, d, J=8.2Hz); 8.19 (2H, d, J=8.2Hz); 8.55 (H, s)

### Preparation of cholesteryl 16-[4'-(4''-methylphenyliminomethyl)-benzoyloxy]-hexadecanoate (D-15)

To the Schiff base (SB-CH3) (0,239 g; 0,001 mol) dissolved in 40 mL of DMF in the ambient temperature was added K<sub>2</sub>CO<sub>3</sub> (0,552 g; 0,004 mol) and KI (0,664 g; 0,004 mol). Obtained mixture was stirred at the 50°C for 15 min and after this time the solution of cholesteryl 16-bromohexadecanoate (0.704 g; 0,001 mol) was added dropwise. The mixture was stirred at 90°C for 24 h. Next it was cooled down at the room temperature and added to 100 mL of distilled water. To the mixture was added diethyl ether (200 mL) and the layers were separated. The organic phase was washed with two further portions of water (2 x 100 mL). Then it was evaporated to 20 mL in a rotary evaporator and mixed with the 150 mL of methanol to precipitate crude product, which was then collected by filtration. After washing with methanol the resultant product was dried and analysed for purity by TLC. No further purification was needed. (Yield: 0,3237g; 37,54%). The same procedure was applied to obtain compounds D-3, D-4; D-5, D-6; D-7, D-9; D-10. Yield: 40%, 38%, 42%, 41%, 43%, 42%, 40%, respectively.

#### Compound D-15

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz) δ=0.68 (3H, s); 0.85-0.88 (6H, m); 0.91(3H, d, J=6.6Hz); 1.02(3H,s); 1.03-2.04 (50H, m); 2.26 (2H, t, J=7.6Hz); 2.28-2.33 (2H, m); 2.38 (3H, s); 4.34 (2H, t, J=6.7Hz); 4.57-4.65 (H, m); 5.34-5.42 (H, m); 7.17 (2H, d, J=8.3Hz); 7.22 (2H, d, J=8.3Hz); 7.96 (2H, d, J=8.3Hz); 8.12 (2H, d, J=8.3Hz); 8.52 (H, s)

#### Compound D-10

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz) δ=0.68 (3H, s); 0.85-0.88 (6H, m); 0.91(3H, d, J=6.6Hz); 1.02(3H,s); 1.03-2.04 (40H, m); 2.26 (2H, t, J=7.6Hz); 2.28-2.33 (2H, m); 2.38 (3H, s); 4.34 (2H, t, J=6.7Hz); 4.57-4.65 (H, m); 5.34-5.42 (H, m); 7.17 (2H, d, J=8.3Hz); 7.22 (2H, d, J=8.3Hz); 7.96 (2H, d, J=8.3Hz); 8.12 (2H, d, J=8.3Hz); 8.52 (H, s)

#### Compound D-9

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz) δ=0.68 (3H, s); 0.85-0.88 (6H, m); 0.91(3H, d, J=6.6Hz); 1.02(3H,s); 1.03-2.04 (38H, m); 2.26 (2H, t, J=7.6Hz); 2.28-2.33 (2H, m); 2.38 (3H, s); 4.34 (2H, t, J=6.7Hz); 4.57-4.65 (H, m); 5.34-5.42 (H, m); 7.17 (2H, d, J=8.3Hz); 7.22 (2H, d, J=8.3Hz); 7.96 (2H, d, J=8.3Hz); 8.12 (2H, d, J=8.3Hz); 8.52 (H, s)

#### Compound D-7

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz) δ=0.68 (3H, s); 0.85-0.88 (6H, m); 0.91(3H, d, J=6.6Hz); 1.02(3H,s); 1.03-2.04 (34H, m); 2.26 (2H, t, J=7.6Hz); 2.28-2.33 (2H, m); 2.38 (3H, s); 4.34 (2H, t, J=6.7Hz); 4.57-4.65 (H, m); 5.34-5.42 (H, m); 7.17 (2H, d, J=8.3Hz); 7.22 (2H, d, J=8.3Hz); 7.96 (2H, d, J=8.3Hz); 8.12 (2H, d, J=8.3Hz); 8.52 (H, s)

#### Compound D-6

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz) δ=0.68 (3H, s); 0.85-0.88 (6H, m); 0.91(3H, d, J=6.6Hz); 1.02(3H,s); 1.03-2.04 (32H, m); 2.26 (2H, t, J=7.6Hz); 2.28-2.33 (2H, m); 2.38 (3H, s); 4.34 (2H, t, J=6.7Hz); 4.57-4.65 (H, m); 5.34-5.42 (H, m); 7.17 (2H, d, J=8.3Hz); 7.22 (2H, d, J=8.3Hz); 7.96 (2H, d, J=8.3Hz); 8.12 (2H, d, J=8.3Hz); 8.52 (H, s)

#### Compound D-5

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz) δ=0.68 (3H, s); 0.85-0.88 (6H, m); 0.91(3H, d, J=6.6Hz); 1.02(3H,s); 1.03-2.04 (30H, m); 2.26 (2H, t, J=7.6Hz); 2.28-2.33 (2H, m); 2.38 (3H, s); 4.34 (2H, t, J=6.7Hz); 4.57-4.65 (H, m); 5.34-5.42 (H, m); 7.17 (2H, d, J=8.3Hz); 7.22 (2H, d, J=8.3Hz); 7.96 (2H, d, J=8.3Hz); 8.12 (2H, d, J=8.3Hz); 8.52 (H, s)

#### Compound D-4

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz) δ=0.68 (3H, s); 0.85-0.88 (6H, m); 0.91(3H, d, J=6.6Hz); 1.02(3H,s); 1.03-2.04 (28H, m); 2.26 (2H, t, J=7.6Hz); 2.28-2.33 (2H, m); 2.38 (3H, s); 4.34 (2H, t, J=6.7Hz); 4.57-4.65 (H, m); 5.34-5.42 (H, m); 7.17 (2H, d, J=8.3Hz); 7.22 (2H, d, J=8.3Hz); 7.96 (2H, d, J=8.3Hz); 8.12 (2H, d, J=8.3Hz); 8.52 (H, s)

#### Compound D-3

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz) δ=0.68 (3H, s); 0.85-0.88 (6H, m); 0.91(3H, d, J=6.6Hz); 1.02(3H,s); 1.03-2.04 (26H, m); 2.26 (2H, t, J=7.6Hz); 2.28-2.33 (2H, m); 2.38 (3H, s); 4.34 (2H, t, J=6.7Hz); 4.57-4.65 (H, m); 5.34-5.42 (H, m); 7.17 (2H, d, J=8.3Hz); 7.22 (2H, d, J=8.3Hz); 7.96 (2H, d, J=8.3Hz); 8.12 (2H, d, J=8.3Hz); 8.52 (H, s)

## Phase diagram

Based on the DSC studies the phase diagram was constructed (Fig. SI-1). The miscibility studies were performed with compound having similar chemical structure to the dimer  $n=9$  but showing only conventional twisted nematic phase.

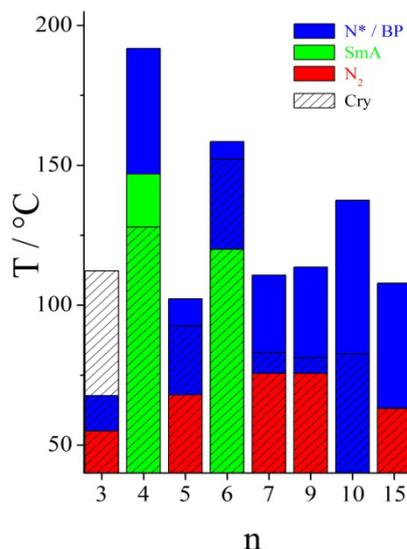


Fig. SI1 Phase sequences and temperature ranges for studied compounds.

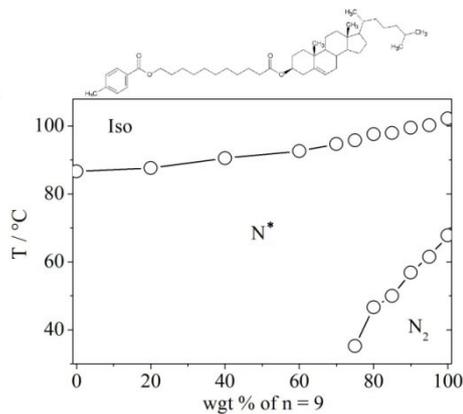


Fig. SI2 Binary phase diagram obtained for mixtures of dimer  $n=9$  with reference compound showing only  $N^*$  phase. Only upper temperature nematic phase of studied dimer  $n=9$  is miscible with conventional twisted nematic phase. Molecular structure of reference compound is given.

## Polarizing optical microscope studies

All materials were carefully checked for their optical textures. Polarizing microscopic studies revealed some transitional changes between  $N_2$  and  $N^*$  phases, that might correspond to the intermediate phases detected in HR DSC studies.

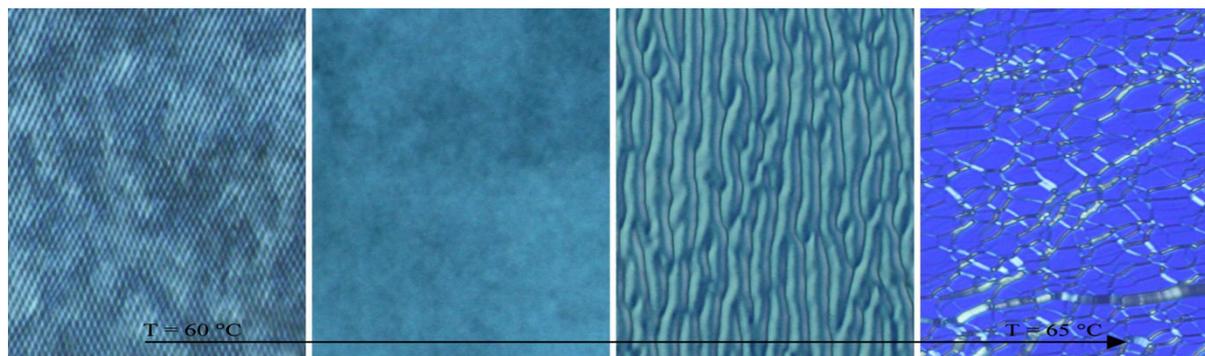


Fig. SI3 Texture changes observed in a planar cell of 3 micron thickness for dimer  $n=15$  between crossed polarizers on heating, showing sequential transitions from  $N_2$  phase (60C) to  $N^*$  (cholesteric) phase at 65C.

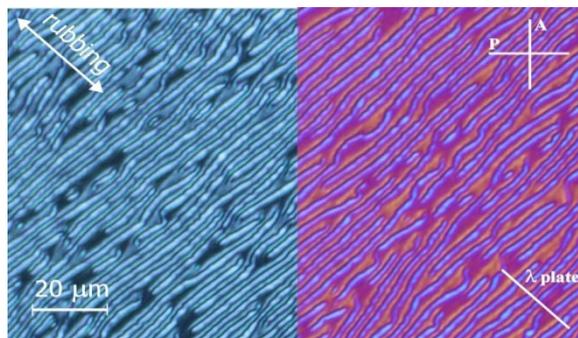
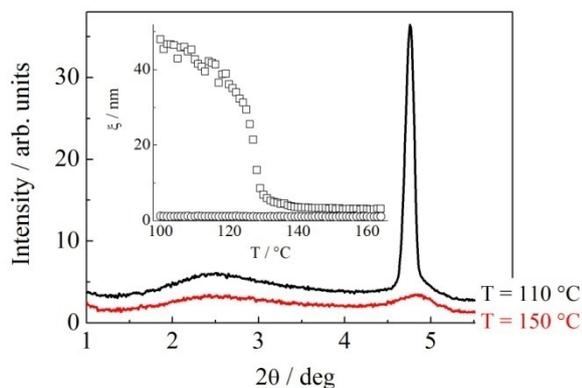


Fig. SI4 Texture of  $N_2$  phase in 1.6 micron cell for dimer  $n=15$  between crossed polarizers - left picture and with  $\lambda$  plate inserted in the optical path - right picture (bar denotes the 'slow' axis direction), registered few degrees below cholesteric to  $N_2$  phase transition temperature. In right picture the areas with blue/orange color have optical axis oriented perpendicular/parallel to rubbing direction. With lowering temperature areas with optical axis parallel to rubbing direction grow and finally cover all sample area.

## X-ray studies

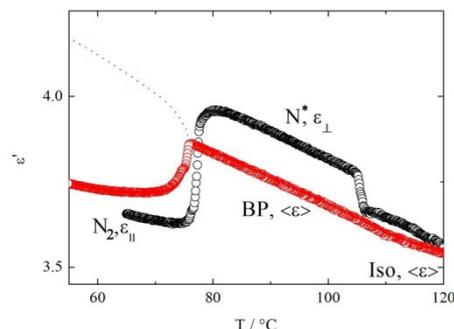
For all studied homologues in the nematic phase two short range density modulation waves exist, with periodicities close to whole and half molecular length. In case of odd homologues exhibiting the smectic A phase below the nematic phase on cooling only the fluctuations with wavelength corresponding to  $L/2$  condense, as seen by critical narrowing of corresponding xrd signal, to form long range ordered structure of intercalated smectic phase.



**Fig. SI5** Intensity of x-ray signal vs diffraction angle  $2\theta$  in the nematic (150 °C) and smectic A (110 °C) phases for dimer  $n=4$ . In the nematic phase two broad signals in a low angle region are seen (red curve) reflecting two short-range fluctuations with different periodicities, while in the smectic phase one of the signals become Bragg-type due to development of long-range positional order. In the inset temperature evolution of correlation length for positional order evaluated from the xrd signal width, for signals corresponding to full (circles) and half molecular length (squares).

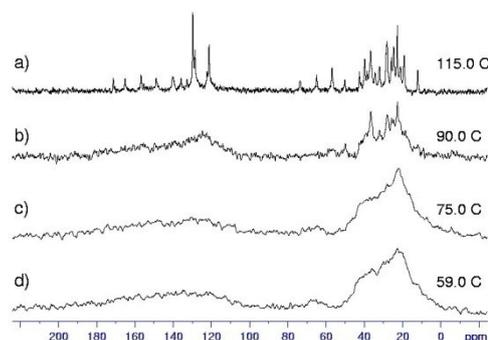
## Dielectric studies

Temperature dependence of dielectric constant measured in cooling and heating runs confirmed different phase sequence on heating and cooling for even homologues, namely isotropic – blue phase – nematic  $N_2$  on cooling and nematic  $N_2$  – cholesteric  $N^*$  – blue phase – isotropic phase on heating. In cooling scan there is no change in dielectric constant at isotropic – blue phase transition; in blue phase having cubic symmetry, similarly as in isotropic phase, the mean dielectric constant is measured as molecules have all possible orientations with respect to measuring electric field. Upon entering the lower temperature nematic phase the dielectric response decreases. Optical studies indicated that in a 5 micron cell used for this studies, in the  $N_2$  phase molecules adopt mainly homeotropic alignment (despite planar anchoring), thus dielectric constant along director is measured. On heating, dielectric response abruptly increases at transition to cholesteric  $N^*$  phase, this correlates with texture change, helical structure with its axis along the electric field direction is formed and thus dielectric constant related to the short molecular axis is measured. Observed changes of measured value of dielectric constant indicate negative dielectric anisotropy of studied here materials.



**Fig. SI6** Dielectric constant vs. temperature for dimer  $n=7$ , measured on cooling isotropic phase (in red), or on heating from lower temperature nematic phase (in black). On cooling the isotropic phase the blue phase exists in temperature range from 108 °C to 78 °C while the cholesteric  $N^*$  phase is formed on heating in the same temperature window. Dotted line (component of  $\epsilon$  perpendicular to the director) in the  $N_2$  phase was calculated assuming that average  $\epsilon$  value is not altered by the phase transitions.

## NMR Studies



**Fig. SI7**  $^{13}\text{C}$  NMR spectra of the CH-5 sample at 115.0, 75.0 and 59.0 °C. The listed temperatures correspond to (a) isotropic, (b and c)  $N^*$  and (d)  $N_2$  phases.

The sample of CH-5 was heated up to 115.0 C. The spectrum acquired at this temperature reveals relatively narrow (ca. 30 Hz width-at-half-height) lines. The signals corresponding to carbonyl groups appear between 140 and 170 ppm, aromatic lines are between 120 and 140 ppm and signals coming from aliphatic linkage and cholesterol part appear between 10 and 80 ppm (see Fig. SI-7a). Such chemical shifts are typical for the mentioned types of atoms in isotropic phase, where traceless anisotropic parts of chemical shielding tensors are averaged out to zero. Under cooling the sample to the temperature of 90.0 °C, at which the  $N^*$  phase occurs, the spectrum features change dramatically (see Fig. SI-7b). Individual isotropic lines are no longer visible in the region between 100 and 200, while extremely broad band is observed instead. In the aliphatic region the resonances are significantly broadened at this temperature, but most of the individual lines are still visible and they retain their isotropic

chemical shifts. Such a picture corresponds to the situation where the global dynamics of the molecules is significantly hindered, while some residual mobility still occurs for cholesterol fragment. Moreover, many orientations of the anisotropic part of the shielding tensors with respect to the external magnetic field must be present within the sample. Cholesteric phase with the director not parallel to the external magnetic field fulfills the above listed conditions. Under further cooling to 75.0 C (still N\* phase) the local dynamics of the cholesterol fragment slows down, so that in the aliphatic region single broad band is observed. There are no significant changes in the  $^{13}\text{C}$  spectrum under further cooling; in particular the phase transition N\*-N<sub>2</sub> is not reflected in this type of NMR spectra.