






Liquid crystal phases with unusual structures and physical properties formed by acute-angle bent core molecules

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Liquid crystals formed by acute-angle bent core (ABC) molecules with a 1,7 naphthalene central core show an intriguing phase behavior with the nematic phase accompanied by poorly understood additional phases. In this work, we characterize the physical properties of an ABC material, such as birefringence, dielectric permittivities, elastic constants, and surface alignment and present x-ray diffraction and transmission electron microscopy studies of their ordering. The ABC molecular shape resembling the letter λ yields a very small splay elastic constant in the uniaxial nematic phase and results in the formation of a tetragonal positionally ordered columnar phase consisting of alternating polar and apolar molecular columns with a uniform uniaxial director that can be bent but not splayed.

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I. INTRODUCTION

The molecular shape is a key factor responsible for physical properties of liquid crystals. The simplest rodlike molecules produce a uniaxial nematic (N), widely used in applications. Lately, there has been much interest in the so-called bent core molecules, formed by two rodlike segments attached to each other at some angle β . This kinked shape leads to fundamentally different properties and phases, as reviewed recently [1,2]. Nematics formed by molecules with $110^\circ \leq \beta \leq 170^\circ$ often exhibit a bend elastic constant that is smaller than the splay constant, $K_{33} < K_{11}$, [1–8], which is opposite to the trend $K_{33} > K_{11}$ found in conventional rodlike nematics. The tendency to bend might be so strong that the bent core materials exhibit alternative states, such as the twist-bend nematic [9–13] or a heliconical cholesteric [14]. Most of the studies so far focused on the obtuse-angle bent core (OBC) molecules, $\beta > 90^\circ$. Mesomorphism of the acute-angle bent core (ABC) molecules with $\beta < 90^\circ$ is poorly understood. Kang, Watanabe, and their colleagues [15–18] brought about interesting results for ABC molecules such as the one in Fig. 1. The molecule is formed by two arms attached in an asymmetric fashion to the central 1,7-naphthalene core. It produces a high-temperature uniaxial N and a low-temperature

phase, identified as a tetragonal packing of long cylinders. It is claimed [15–18] that each cylinder contains a double-twisted director field which is necessarily associated with a bend. The cylinders are of alternating chirality: a left-twisted cylinder has four close neighbors of right-twisted cylinders and vice versa.

Recent studies demonstrate that surprising new types of the nematic ordering can be formed even by seemingly simple rodlike molecules, such as 4-[(4-nitrophenoxy)carbonyl]phenyl-2,4-dimethoxybenzoate, abbreviated RM734. Mandle *et al.* found that these materials could exhibit a transition from a uniaxial nematic to some other nematic upon cooling [19,20]. In studies that followed, Mertelj and co-workers [21,22] suggested that the transition is to a splay nematic, in which the director \hat{n} experiences a periodic splay with a period 5–10 μm [23]. The spontaneous splay was attributed to the wedge shape of the molecules and by an ensuing smallness of K_{11} [21]. The situation is similar to the formation of a twist-bend nematic, which is heralded by a decrease of K_{33} [13,24,25]. The overall structure of the splay nematic was suggested to be of an antiferroelectric type [21]. Clark and co-workers [26] reexamined the electro-optical and textural properties of RM734 and concluded that the material is in fact a three-dimensional ferroelectric uniaxial nematic in which the large longitudinal dipole moments (about 11 D) are parallel to each other. A unidirectional ferroelectric order has also been announced by Kikuchi and co-workers in 2017 [27] for a different compound with dipole moments ~ 9.4 D.

Motivated by these recent advancements and by the need to establish a structure-property relationship for ABC compounds, in this work, we characterize mesomorphic properties of the liquid crystal 1,7-naphthylene bis(4-(3-chloro-4-(4-(hexyloxy)benzoyloxy)phenyliminomethyl) benzoate),

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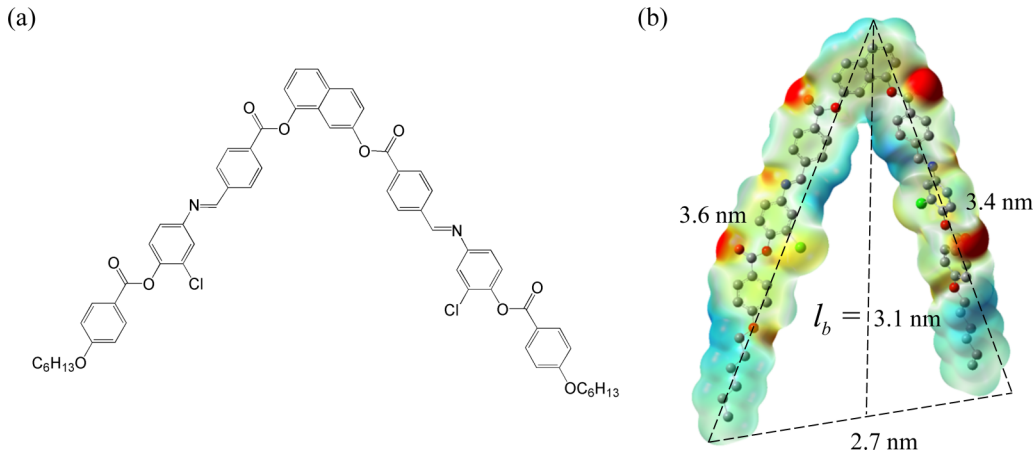


FIG. 1. (a) Molecular formula and (b) one of the conformations of the studied ABC material 1Cl-N(1,7)-O6. Panel (b) is obtained by numerical simulation using GAUSSIAN 09W software to find a minimum energy of a conformation based on density functional theory (DFT) at the B3LYP 6-31G(d) level.

abbreviated as 1Cl-N(1,7)-O6, Fig. 1; see the Supplemental Material [28] for the chemical synthesis details. The material shows a uniaxial N phase at high temperatures and transforms into a columnar Col_t phase of tetragonal symmetry at lower temperatures. K_{11} in the N phase is smaller than the twist elastic constant K_{22} by a factor of 2 and smaller than K_{33} by a factor of 6. We explain this anomalous elasticity by the alignment of the longitudinal axes of λ -shaped molecules parallel to the director. The splay is facilitated by flip-flops of the molecules. Using the x-ray diffraction data, we propose that the Col_t phase is formed by columnar aggregates of a diameter roughly equal to the distance between the legs of a single λ molecule. The columns are of two types, one polar and one apolar. In the polar columns, all λ molecules point along the same direction in a ferroelectric fashion, either upward or downward along the column. In the apolar aggregates, one half of the molecules points upward and the other half points downward. Each polar column is neighbored by four columns of opposite polarity, which yields a tetragonal lattice. The apolar columns fill gaps between the polar columns.

II. MATERIALS AND METHODS

The 1Cl-N(1,7)-O6 molecule in Fig. 1 is of a λ shape, with two legs being of slightly different length. Numerical simulations, Fig. 1(b), suggest that the legs tilt away from the naphthalene core plane, to minimize the conformation energy.

The optical and surface anchoring properties of the material 1Cl-N(1,7)-O6 are explored by polarizing optical microscopy (POM), PolScope observations, and by measurements of the birefringence. Dielectric properties are examined in the frequency range from 100 Hz to 1 MHz using an LCR meter (4284A, Hewlett-Packard) operated by the LABVIEW program. The temperature of the cells is controlled by an LTS350 hot stage and a TMS-94 controller (both from Linkam Scientific Instruments). The dielectric permittivity ϵ_{\parallel} parallel to the director is measured in a cell of thickness $15.5\mu\text{m}$ with substrates covered with a surfactant hexadecyltrimethylammonium bromide (HTAB). The overlapped area of two

square-patterned indium tin oxide (ITO) electrodes is $1\text{ cm} \times 1\text{ cm}$. The perpendicular component ϵ_{\perp} is measured using planar cells with SE-1211 coatings. The cells' gap is fixed by glass microspheres of calibrated diameter and measured by recording the light interference spectrum of an empty cell. The cells are filled by capillary action at $T = 190^\circ\text{C}$. K_{11} and K_{33} are measured in a planar cell of thickness $d = 5.8\mu\text{m}$ with the aligning polyimide SE-1211 layers. K_{11} is determined from the threshold voltage of the splay Frederiks transition and K_{33} is determined by fitting $C(U)$ well above the threshold, where splay is accompanied by bend [29]. To measure K_{22} , we add 2.8 wt % of a chiral dopant S-811 to 1Cl-N(1,7)-O6, and then use the electric field to unwind the resulting cholesteric helix in a homeotropic cell with SE-5661 alignment layers; the voltage at which the helix is unwound defines K_{22} [30].

Freeze-fracture (FF) transmission electron microscopy (TEM) and cryo-TEM of the samples follow the procedures described previously [31]. In FFTEM, the samples are heated into the N phase and equilibrated at 190°C . After that, they are slowly cooled down at a rate of $1^\circ\text{C}/\text{min}$ to the desired temperatures and equilibrated for 5 min. The sample is then plunge frozen in liquid nitrogen and fractured at -165°C . Replicas are prepared by depositing thin (4-nm) layers of Pt/C at a 45° angle, followed by 20-nm C film deposition at normal incidence. Unlike FFTEM, cryo-TEM produces direct images of ultrathin specimens. We use thin (up to 20-nm) films of the material supported by a holey carbon film. For cryo-TEM observation, the material supported by the carbon film is heated to the N phase and slowly cooled down to the desired temperature. The equilibrated samples are then rapidly frozen in liquid ethane and observed under the TEM.

X-ray experiments were performed at the 11-BM CMS beamline at National Synchrotron Light Source II, Brookhaven National Laboratory. The beamline was configured for a collimated x-ray beam with a beam size of cross section $0.2\text{ mm} \times 0.2\text{ mm}$ and divergence of $0.1\text{ mrad} \times 0.1\text{ mrad}$ with the x-ray energy of 17 keV. Two detectors, Pilatus 2M and Photon Science CCD, were placed at 3 m and 236 mm away from the samples, respectively, to collect

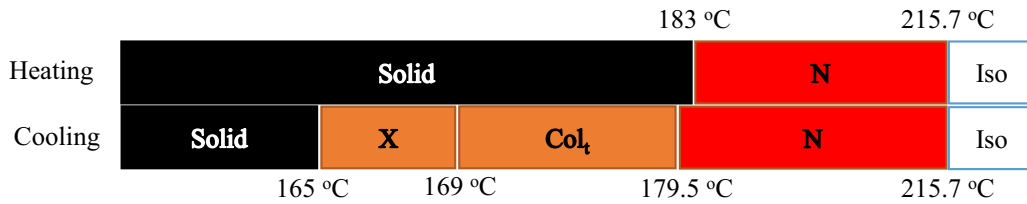


FIG. 2. Phase diagram of 1Cl-N(1,7)-O6. Heating rate is 1 °C/min for heating and cooling rate is 0.5 °C/min for cooling.

the small-angle x-ray scattering (SAXS) and wide-angle x-ray scattering (WAXS) signals. The sample-to-detector distances were calibrated by using a silver behenate standard. The experiments were performed with *in situ* thermal control by using an Instec HCS402 hot stage with a temperature deviation less than 0.1 °C. Two types of samples were studied. The first represents a quartz capillary with an inner diameter of 1 mm mounted into an aluminum cassette between two 1-T magnets. The second sample represents a flat cell formed by two glass plates with transparent ITO electrodes. Each glass substrate is 170 μm thick and the cell gap is also 170 μm. Using a waveform generator (Stanford Research Systems, Model DS345) and a power amplifier (Krohn-hite Corporation, Model 7602), we applied a sinusoidal voltage of the amplitude 100 V at the frequency 2 kHz, so that the director aligned along the field and perpendicular to the glass plates. The cell was mounted for transmission x-ray scattering with the incident beam normal to the plates, such that the director pointed along the beam.

III. EXPERIMENTAL RESULTS

A. Phase diagram

The phase diagram obtained by POM textural observations is shown in Fig. 2, which is consistent with the differential scanning calorimetry (DSC) data in Ref. [18]. The POM textures of different phases are shown in Figs. 3–6. On heating,

the material forms a uniaxial *N* phase between 183 °C and $T_{NI} = 215 °C$, where T_{NI} is the *N*-to-isotropic (*I*) transition point. On cooling, the *I*-*N* transition occurs through nucleation of spherical droplets, Fig. 3. Each droplet shows a texture of a Maltese cross with four dark brushes and a point defect in the center, Figs. 3(a)–3(c). Conventional POM with two crossed linear polarizers does not allow one to establish unequivocally whether the Maltese cross is caused by a radial configuration of the director or by a concentric configuration, since both these configurations would yield four dark brushes in the regions where the director is parallel to the polarizer (*P*) and analyzer (*A*). To establish the director orientation around the defect core we use a full-wavelength plate (FWP), also called a red-plate optical compensator. The FWP is a slab of a uniaxial crystal of positive birefringence that produces a 530-nm optical phase retardance. In POM observations, the FWP is placed between the crossed *P* and *A* with its optic axis along the angle bisector of quadrants I and III formed by *P* and *A*. In the absence of any birefringent sample, it produces the red-violet interference color, which separates the first- and second-order interference colors on the Michel-Lévy color interference chart. When a birefringent sample is present, the red-violet color remains in the region in which the sample’s optic axis (the director in our case) is along the *P* and *A* directions. Other orientations of the director produce either a blue-green or yellow-orange color, depending on whether the additional phase retardance adds to the phase retardance

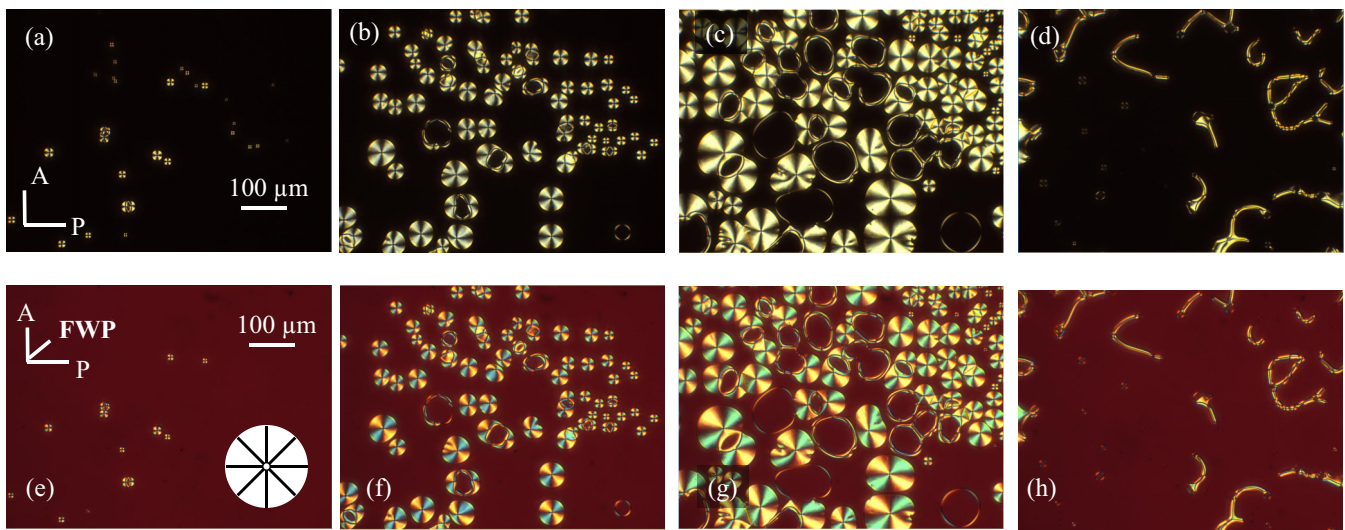


FIG. 3. POM of (a) nucleation and growth (b), (c) and (e), (f) of *N* droplets from the isotropic melt; director shows splay deformations; (c), (d) and (g), (h) nuclei that touch both glass plates adopt homeotropic alignment of the director. The slab is confined between two clean glasses with no alignment layers. Textures (a)–(d) are viewed between two crossed polarizers; textures (e)–(h) are viewed with a full-wavelength optical compensator of retardance 530 nm with the slow axis along the line “FWP.” The temperature is reduced from 214.7 °C in (a) to 213.5 °C in panel (d).

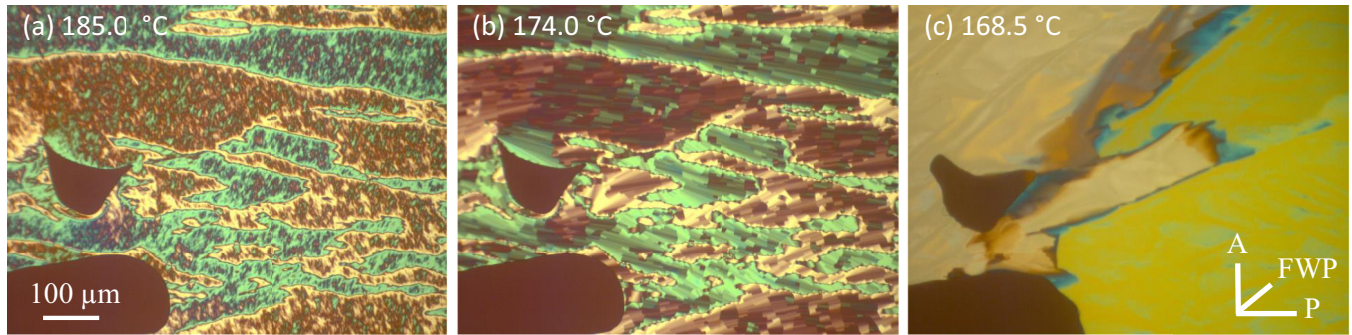


FIG. 4. Textural transition upon cooling from (a) the N phase; the cell with homeotropic alignment (polyimide PI-2555 coating) is sheared; (b) Col_l phase with a texture reminiscent of columnar phases texture; (c) X phase. POM observation with FWP.

of FWP or subtracts from it. This property is used either for the determination of the sign of optical birefringence of an optically anisotropic plate if the direction of the optic axis is known or for the determination of the direction of the optic axis if the optical sign is known [32]. As will be demonstrated in Sec. III D below, the optical birefringence of the liquid crystalline phases of the explored material is positive. Observation of the Maltese textures of the N droplets with the FWP shows that the I and III quadrants acquire a blue interference color, while the II and IV quadrants become yellow, Figs. 3(e)–3(g). Therefore, the director in the N droplets is perpendicular to the N - I interface and forms a radial point defect-hedgehog [33], Fig. 3(e), with predominantly splay deformation of the director. A radial director field in the N nuclei and homeotropic alignment at the N - I interface are unusual for thermotropic nematics, since the director orientation at the N - I interface in many of them is tilted, as is the case of cyanobiphenyls [34]. The nuclei grow and coalesce, Figs. 3(b) and 3(c). When they touch the top and bottom glass plates, the director realigns perpendicularly to the plates, Figs. 3(b)–3(d).

On cooling, the N phase exists down to $T_{NCol_l} = 179.5^\circ\text{C}$. Between T_{NCol_l} and the solidification temperature $T_S = 165^\circ\text{C}$, one observes two other phases, a higher-temperature Col_l and a lower-temperature X phase. Figure 4 demonstrates a textural transition from N to Col_l and then to X . The temperature T_{Col_lX} of the Col_l -to- X transition depends on the sample prehistory. If a fresh sample is cooled for the first time with a rate of $0.5^\circ\text{C}/\text{min}$, $T_{Col_lX} = 169^\circ\text{C}$. However, if the sample is kept for several hours at elevated temperatures, either in the N or in the Col_l phase, the material degrades irreversibly, and the temperatures of all transitions shift noticeably. Namely, T_{NI} and T_{NCol_l} decrease while T_{Col_lX} increases, approaching T_{NCol_l} by approximately 1°C per hour of sample stabilization at any temperature above 169°C .

B. Alignment

Table I lists the alignment effect of seven different materials on the N phase of 1CI-N(1,7)-O6 and a conventional rodlike nematic pentylcyanobiphenyl (5CB). The used alignment materials are four polyimides, PI 2555 (HD MicroSystems), SE 1211 (Nissan Chemicals), SE 5661 (Nissan Chemicals), SE 7511 (Nissan Chemicals); two surfactants from Sigma-Aldrich, hexadecyl trimethyl ammonium bromide (HTAB), dimethyloctadecyl [3-(trimethoxysilyl)propyl]

ammonium chloride (DMOAP); and clean glass. All but one produce homeotropic orientation of 1CI-N(1,7)-O6, with the director perpendicular to the bounding plates, $\hat{n} = (0, 0, 1)$. Rubbing the homeotropic substrates leads to the tilt of the nematic director by an angle $\sim 10^\circ - 15^\circ$. Homeotropic alignment is produced even by the polyimide PI2555, which is widely used for planar orientation of the conventional nematics such as 5CB. Homeotropic alignment by clean glass can be related to the hydrophilic nature of the substrate; many thermotropic nematics align similarly on clean glass [35]. The polyimide SE-1211 shows multiple regimes of alignment. If the nematic phase of 1CI-N(1,7)-O6 is obtained by cooling down from the I phase, SE-1211 imparts a homeotropic alignment, within about 1°C from the I - N transition point. At lower temperatures, the alignment becomes tilted, as evidenced by the defects of strength $+1$ and -1 , each with four extinction brushes, Fig. 5. Isolated semi-integer defects are prohibited at the tilted director alignment since the director projection onto the plates is a vector rather than a director; therefore, only integer strength defects could be observed [32]. If the material is filled into the cell in the N phase, the resulting alignment by SE-1211 is tangential, showing schlieren textures with isolated $+1/2$ and $-1/2$ disclinations. The reason is as follows. For strictly tangential boundary conditions, the surface orientations \hat{n} and $-\hat{n}$ are not distinguishable from each other. Therefore, not only integer but also semi-integer defects are topologically permissible [32]. If the director is even slightly tilted away from the surface, the tilts “up” and “down” are no longer indistinguishable: the up and down directors placed in the same point form a letter “x.” Therefore, if any semi-integer

TABLE I. Effect of different surface agents on the alignment of ABC nematic 1CI-N(1,7)-O6 and rodlike nematic pentylcyanobiphenyl (5CB).

Alignment agent	ABC nematic	5CB
PI 2555	Homeotropic	Tangential
SE 1211	Homeotropic, tangential or tilted	Homeotropic
SE 5661	Homeotropic	Homeotropic
SE 7511	Homeotropic	Homeotropic
HTAB	Homeotropic	Homeotropic
DMOAP	Homeotropic	Homeotropic
Clean glass	Homeotropic	Homeotropic

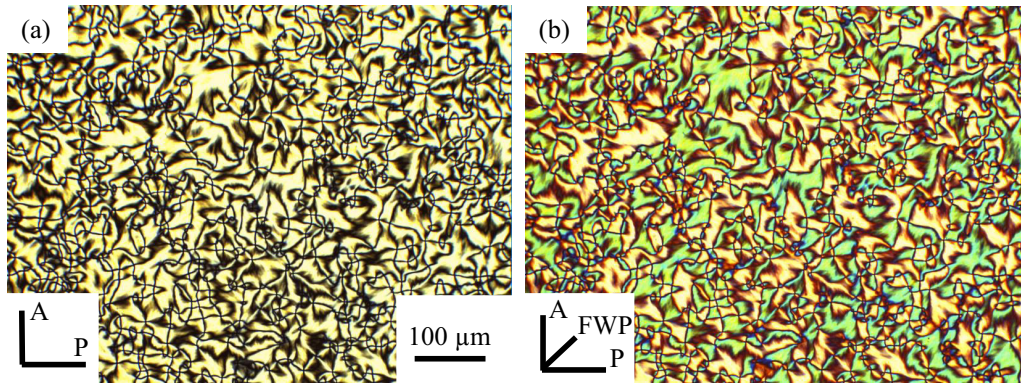


FIG. 5. Nematic schlieren texture ($T = 210^\circ\text{C}$) in a cell with SE1211 alignment layers, filled at the temperature $T = 220^\circ\text{C}$ in the I phase. Optical microscopy with two crossed polarizers without (a) and with (b) a full-wave plate. Note presence of defect centers with four dark brushes and absence of defect centers with two dark brushes. The feature is caused by the presence of integer-strength defects and absence of semi-integer defects, demonstrating a tilted conical alignment of the director at the bounding plates with SE1211 at this temperature.

defect existed before the tilt, it would give rise to a wall defect that starts at the defect core and provides a reorientation from the up to down state through a strictly tangential director. Such a wall is energetically unfavorable. This is why under strictly tangential anchoring one could observe semi-integer defects-disclinations, while under tilted conical boundary conditions the defects are of an integer strength, Fig. 5; these are typically surface point defects-boojums [33]. For more details and for illustration of this effect, see Ref. [32], pp. 395–396.

In freestanding films, prepared in the openings of the Cooper electron microscopy grids with $(40 \times 40) \mu\text{m}^2$ square openings, the N -air interface imposes tangential orientation, as evidenced by observations of pairs of $1/2$ defects, Fig. 6(a) [32,36–38]. The director field around the cores of the $1/2$ disclinations reveals two features: (1) there are no defect walls attached to the cores of the disclinations, which indicates that

the director is strictly parallel to the N -air interface; (2) the main in-plane director deformation is splay, signaling $K_{11} \ll K_{33}$. In contrast, the textures of the Col_t phase show bend rather than splay, which is a common feature of the columnar phases, Fig. 6(b).

C. Dielectric permittivity

Frequency dispersions for the parallel ϵ_{\parallel} and perpendicular ϵ_{\perp} components of the dielectric permittivity are shown in Fig. 7(a). The material is of a dual-frequency type, as $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp} > 0$ at low frequencies, $f < f_c$; and $\Delta\epsilon < 0$ at high frequencies, $f > f_c$, Fig. 7(b). The crossover frequency f_c is in the range $(10 - 60)$ kHz, depending on the temperature. The temperature dependencies $\epsilon_{\parallel}(T)$ and $\epsilon_{\perp}(T)$ measured at $f = 1$ kHz are relatively weak, Fig. 7(c). Both permittivities

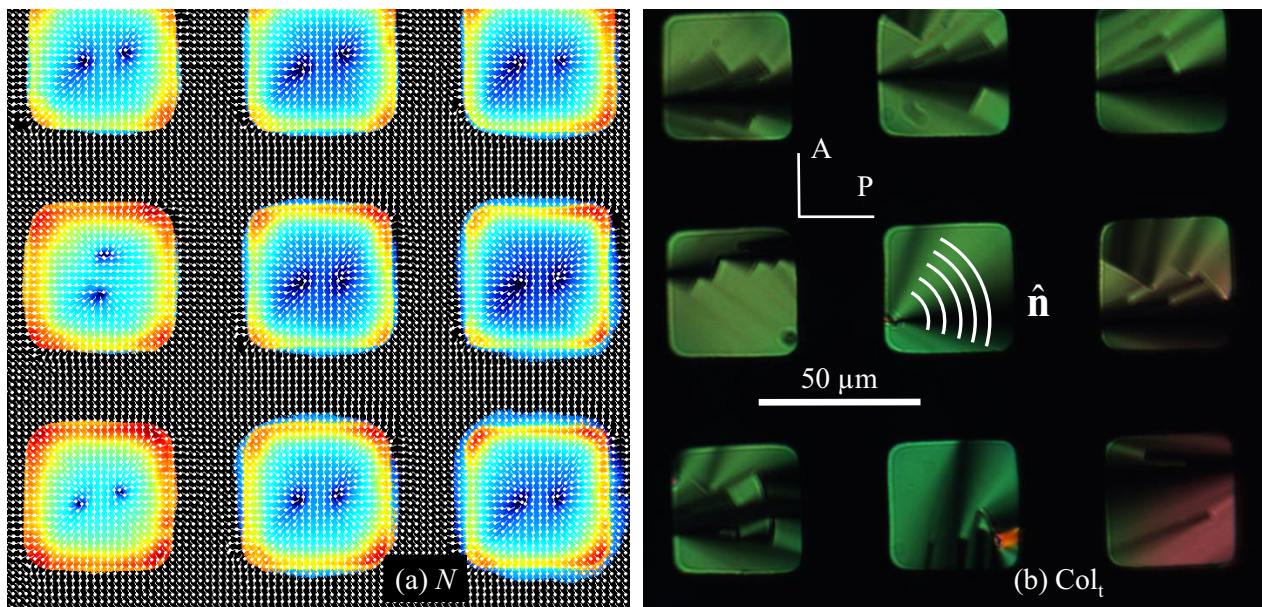


FIG. 6. Freely suspended films of 1CI-N(1,7)-O6. (a) PolScope texture of N phase with $1/2$ defects and predominant splay of the director; $T = 190^\circ\text{C}$; (b) POM texture of Col_t that reveals bend of the optic axis; one region of the bend is traced with arches in the central square. $T = 176^\circ\text{C}$.

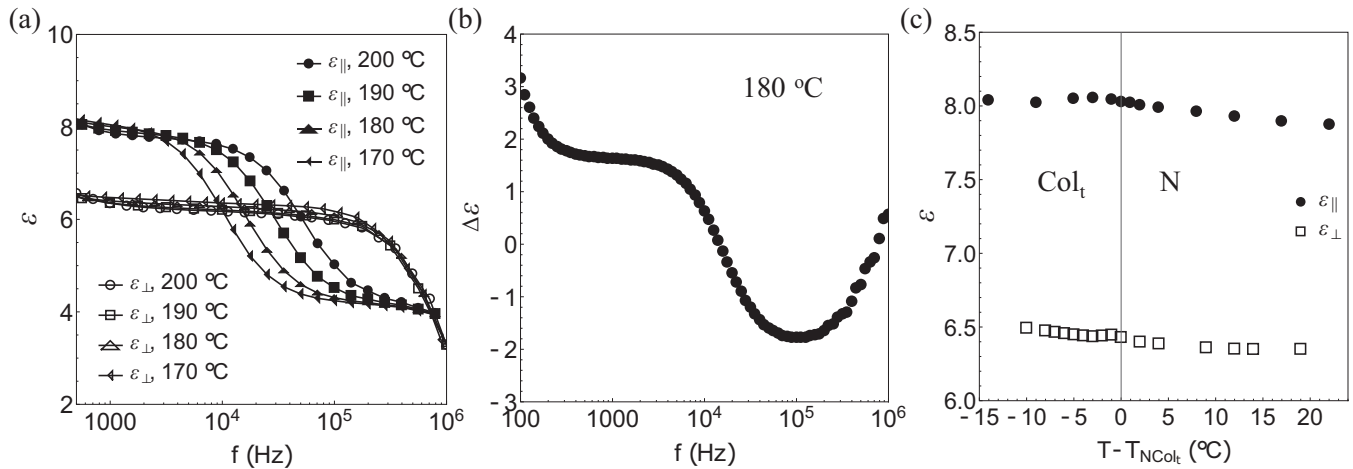


FIG. 7. (a) Frequency dispersion of parallel and perpendicular components of dielectric permittivity of 1Cl-N(1,7)-O6 at different temperatures. (b) Frequency dispersion of the dielectric anisotropy in the nematic phase at $T = 180\text{ }^\circ\text{C}$; (c) temperature dependencies $\epsilon_{||}(T)$ and $\epsilon_{\perp}(T)$ measured at $f = 1\text{ kHz}$ for 1Cl-N(1,7)-O6 in N and Col_t phases.

show a slight increase below the $N - \text{Col}_t$ transition, Fig. 7(c). The value of $\Delta\epsilon$ in the N phase is relatively small, which correlates with the apolar character of the N phase.

D. Birefringence

Optical conoscopy of homeotropic N cells with the director along the normal to the bounding plates, $\hat{\mathbf{n}} = (0, 0, 1)$, shows a Maltese cross with dark brushes oriented along the directions of crossed polarizers, Fig. 8(a), which means that the N phase is optically uniaxial. Conoscopic observation of the sample is performed by using a cone of converging rays of light. The homeotropic alignment of $\hat{\mathbf{n}} = (0, 0, 1)$ observed by a converging cone of rays appears as a radial configuration of the effective optical axis converging in the center of the

conoscopic pattern in Fig. 8(a). To establish the sign of birefringence, an FWP with 530 nm retardance is inserted with the optic axis along the angle bisector of the I and III quadrants formed by the polarizers P and A, Fig. 8(b). The POM texture in Fig. 8(b) shows that the I and the III quadrants acquire a blue interference color when the FWP is inserted. It implies that in these quadrants, the phase retardance of the sample adds to the phase retardance of the FWP, i.e., that the birefringence of the liquid crystal is positive. Accordingly, the quadrants II and IV become yellow, since the optical axes of the FWP and the liquid crystals are orthogonal to each other and the overall phase retardance is reduced. The texture in Fig. 8(b) thus establishes that the birefringence of the N phase is positive, $\Delta n = n_e - n_o > 0$, where n_e and n_o are the extraordinary and ordinary refractive indices, respectively. For an optically negative N , the I and III quadrants would be yellow, and the II and IV quadrants would be blue.

When the sample is cooled to the Col_t phase, the Maltese cross shifts towards the periphery of the field of view, Fig. 8(c), indicating that the optic axis tilts away from the normal to the bounding plates. The tilt angle is $\theta \approx 20^\circ$, as calculated from the relationship $NA \sin \theta = R/R_0$, where $NA = 0.65$ is the numerical aperture of the objective, R_0 is the radius of the circular conoscopy pattern, and R is the shift of the cross. In Fig. 8(c), $R/R_0 \approx 0.22$. Col_t is also of a positive birefringence, $\Delta n > 0$, as follows from the observations with the FWP, Fig. 8(d).

The temperature dependence of birefringence at the wavelength 546 nm was measured using PolScope and a planar cell of thickness $1.9\text{ }\mu\text{m}$ aligned by a unidirectionally rubbed SE-1211, Fig. 9. The measured values are close to those known for conventional nematics formed by rodlike molecules.

E. Frederiks transitions and elastic constants in the N phase

The temperature dependencies of the elastic constants are shown in Fig. 10(a). The most unusual result is that the splay elastic constant K_{11} is much smaller than the twist modulus K_{22} (by a factor $\sim 1/2$) and the bend modulus K_{33} (by a factor of $\sim 1/6$), Fig. 10(a). The result is also supported by a

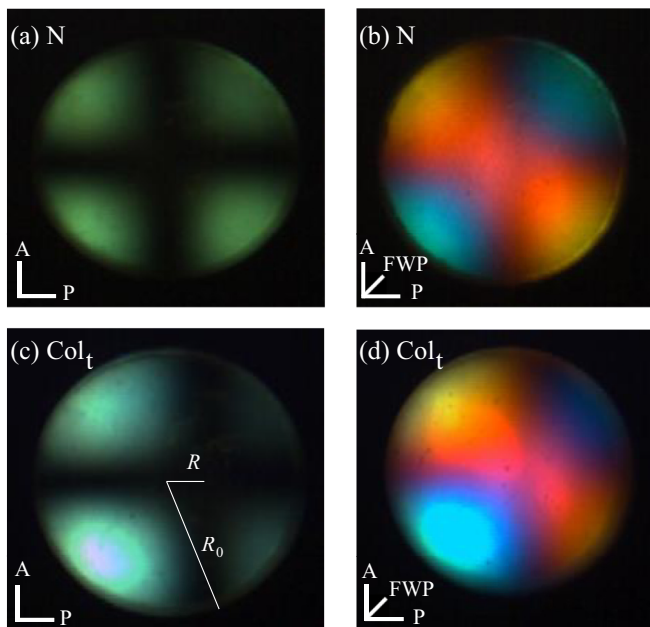


FIG. 8. Conoscopic patterns of the homeotropic cells with N (a), (b) and Col_t (c), (d) phases of 1Cl-N(1,7)-O6; observations with two crossed polarizers in (a), (c) and with an additional FWP in (b), (d).

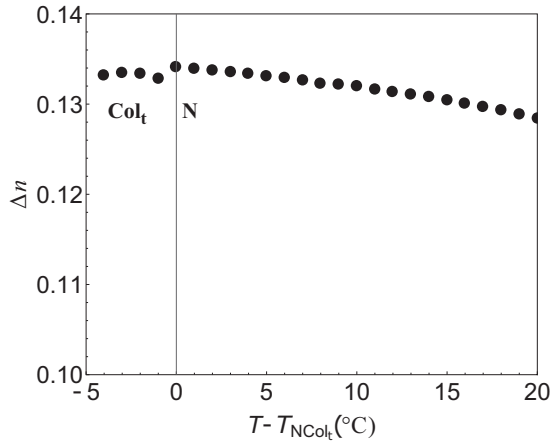


FIG. 9. Temperature dependence of birefringence at the wavelength 546 nm of 1Cl-N(1,7)-O6 in N and Col_t phases.

qualitative feature in Fig. 10(b): the schlieren N textures show a clear predominance of splay deformations over bend in the structure of $+1$ defects, which illustrates clearly that K_{11} is much smaller than K_{33} . This anomalously small splay elastic constant of ABC material can be related to the peculiar triangular shape of the molecules that could flip to accommodate splay deformations. Previously, Lee *et al.* [39] reported that ABC molecules, added in a weight proportion up to 10 wt %, decrease the splay constant of a rodlike nematic from 13 to 3 pN. A very small $K_{11} \approx 1$ pN is also reported for the uniaxial N phase of RM734 by Mertelj *et al.* [21].

The Frederiks effect in 1Cl-N(1,7)-O6 can be triggered by a magnetic field. For homeotropic cells of thickness $30 \mu\text{m}$, the threshold field is 0.26 T at 203°C , which yields $K_{33}/\Delta\chi = 4.8 \times 10^{-6}$ N, where $\Delta\chi = \chi_{\parallel} - \chi_{\perp} > 0$ is the diamagnetic anisotropy of 1Cl-N(1,7)-O6. At the same temperature, the electric Frederiks transition yields $K_{33} = 8$ pN; thus at 203°C , $\Delta\chi = 1.7 \times 10^{-6}$, which is comparable to the diamagnetic anisotropy of rodlike mesogens such as 5CB.

F. Frederiks transitions in Col_t phase

Planar to homeotropic transition. A high voltage $U > U_{\text{th}}$, where $U_{\text{th}} \approx 24$ V, of the frequency $f = 1$ kHz, at which

$\Delta\varepsilon > 0$, reorients the director from planar to homeotropic state in a planar $6.0\text{-}\mu\text{m}$ cell. Voltage dependence of optical retardance for the Col_t phase, Supplemental Fig. S1a, shows behavior reminiscent of the Frederiks transition in nematics, Supplemental Fig. S1b [28]. However, in the N phase, the threshold is much lower, $U_{\text{th}} \approx 1$ V. If one assumes that the threshold in Col_t depends on the splay modulus, $U_{\text{th}} = \pi \sqrt{K_{11}/\varepsilon_0 \Delta\varepsilon}$, then with the known $\Delta\varepsilon$ one obtains a very rough estimate, $K_{11} = \varepsilon_0 \Delta\varepsilon U_{\text{th}}^2 / \pi^2 \approx 10^3$ N, 500 times larger than in the N phase.

Homeotropic to planar transition. To stabilize the homeotropic Col_t state, the cell is cooled in the presence of an electric field with $f = 1$ kHz, at which $\Delta\varepsilon > 0$. The homeotropic state could be switched into a planar state by an electric field at $f = 200$ kHz, at which $\Delta\varepsilon < 0$. The reorientation involves nucleation of domains resembling developable domains of columnar phases [32], Fig. 11. The transition is of the first order (as evidenced by nucleation and by the sharp interface between the two states), i.e., dramatically different from the second-order Frederiks transitions in the N phase. The bent interface between the homeotropic and the deformed region, together with the POM and PolScope textures that show the director parallel to the interface, suggest that the deformation of the director is of a bend type.

The Frederiks transition in N can be of the first order only under very special circumstances, such as a strong difference in the values of splay and bend Frank constants and peculiar types of surface anchoring [40–42]. On the other hand, layered and columnar phases, in which either bend or splay deformations are prohibited by the requirement of equidistant positional order of layers or columns, routinely show the first-order Frederiks transitions with nucleation of domains such as focal conics [13,43,44].

G. Freeze fracture and cryo-TEM of the material in the Col_t phase

The freeze-fracture TEM textures, Fig. 12, and cryo-TEM textures, Fig. 13, prove periodic ordering of Col_t but do not establish the predominant period since it varies broadly from sample to sample and even within the same sample. The FFTEM texture of the Col_t phase quenched from 179°C in

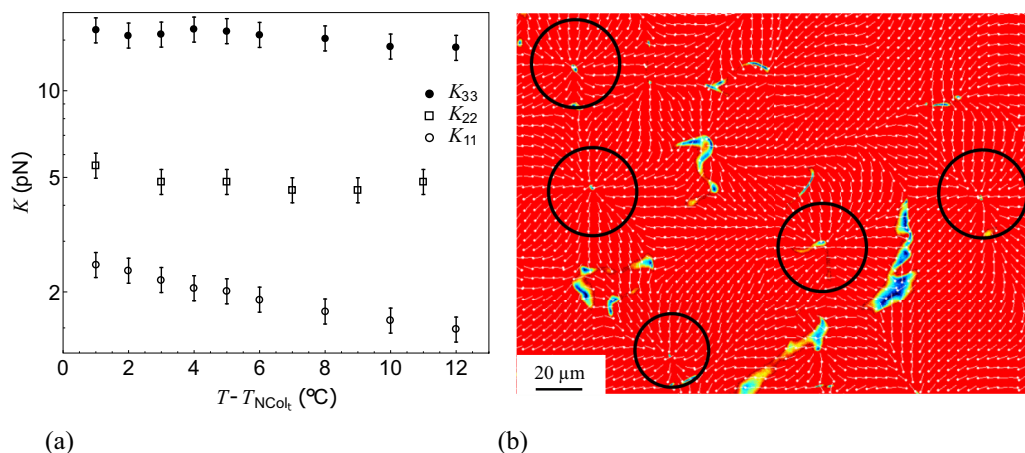


FIG. 10. (a) Temperature dependencies of the elastic constants in the N phase of 1Cl-N(1,7)-O6; (b) PolScope schlieren N texture of 1Cl-N(1,7)-O6 demonstrating prevalence of splay over bend around $+1$ defects of radial aster geometry marked by open circles.

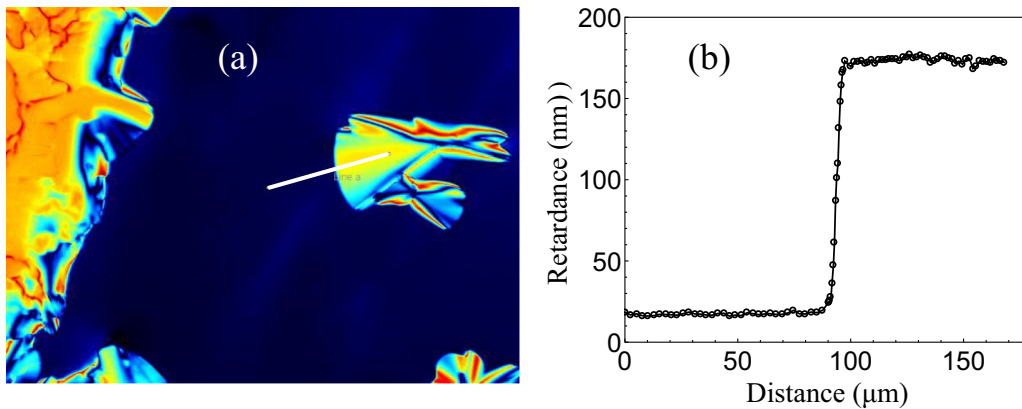


FIG. 11. (a) PolScope texture of the Frederiks transition in a homeotropic Col_t cell of 1Cl-N(1,7)-O6; $U = 24$ V; $f = 200$ kHz; (b) optical retardance across the interface between the realigned material and the homeotropic region along the white line in panel (a). Temperature $T = T_{N\text{Col}_t} - 4$ °C.

Fig. 12(a) exhibits linear periodic structures with a period P in the range (7–8) nm. Similar textures but with $P \approx 15$ –16 nm occur when the sample is quenched from the Col_t phase at 176 °C, Fig. 12(b). Another frequent texture is of wavy “ropes” that bend in space, revealing smooth terraces between them, Fig. 10(c). The thickness of the ropes varies from 3–4 nm to 5–6 nm.

Unlike FFTEM, cryo-TEM produces direct images of ultrathin (up to 20 nm) films of the material on a holey carbon substrate. In the area of carbon support, the structure shows periodic ordering with the period that varies broadly from 3.8 nm to 7–8 nm and even 12–15 nm, Fig. 13.

Periodic structures detected by TEM, combined with the optical observations of bend deformations, Fig. 6(b), demonstrate that the positional ordering of Col_t is of a columnar type. A layered smectic ordering is excluded since the optic axis in smectics experiences splay rather than bend. Broadly varying P and formation of smooth terraces in FFTEM and cryo-TEM suggest that the interactions between columns are weak.

H. X-ray studies

Wide-angle x-ray scattering (WAXS) and small-angle x-ray scattering (SAXS) characterization of 1Cl-N(1,7)-O6 was

performed for two types of samples: circular capillaries and flat cells aligned homeotropically by an ac electric field.

Capillary sample. The director is aligned perpendicularly to the incident x-ray beam by a magnetic field \mathbf{B} , Fig. 14. In both N and Col_t phases, WAXS spectra show a broad peak in the equatorial plane (along the direction perpendicular to \mathbf{B}) at the scattering vector $q = M_{\text{WAXS}} = 14.2 \text{ nm}^{-1}$ which corresponds to a spacing $d_{\text{WAXS}} = 2\pi/M_{\text{WAXS}} = 0.45 \text{ nm}$. The correlation length associated with this spacing is very small, roughly 0.3 nm, as can be estimated from the inverse of the half width at half maximum, which implies that there is no translational periodicity. Because of this, the lateral spacing of 0.45 nm should be associated with the typical separations of molecular legs and their thicknesses. These legs are seen by the probing beam at different orientations; note that the basic element of the structure, a benzene ring, has a diameter of 0.45 nm. SAXS spectra depend strongly on the temperature. In the N phase, $T = 204$ °C, there are broad meridional reflexes located along the line parallel to \mathbf{B} , at $M_1 = 1.73 \text{ nm}^{-1}$ ($d_1 = 3.63 \text{ nm}$). The distance $d_1 = 3.63 \text{ nm}$ is somewhat longer than the length $l_b \approx 3.0$ – 3.2 nm of the molecule measured along its bisector; it suggests that the molecules might associate into pairs with a slight shift along the director. As the temper-

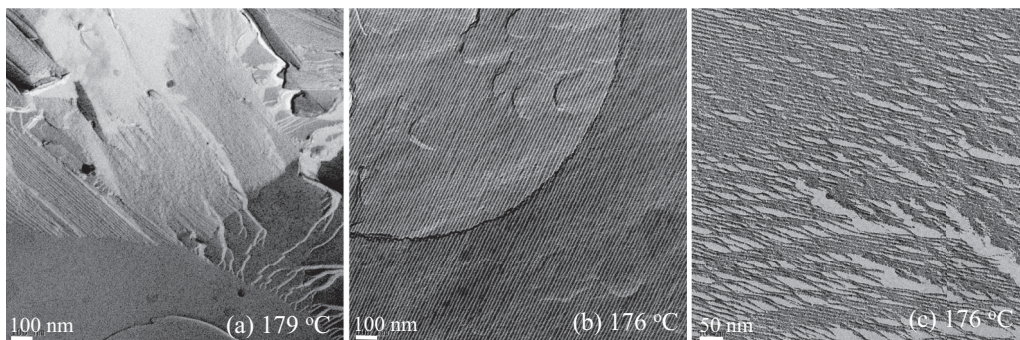


FIG. 12. Freeze-fracture TEM for the Col_t phase of 1Cl-N(1,7)-O6 obtained by quenching the samples from (a) $T = 179$ °C; (b), (c) $T = 176$ °C. The prevailing textures are linear periodic modulations (a), (b) and wavy textures of “ropes” with bend deformations (c). The period is 7–8 nm in (a) and 15–16 nm in (b).

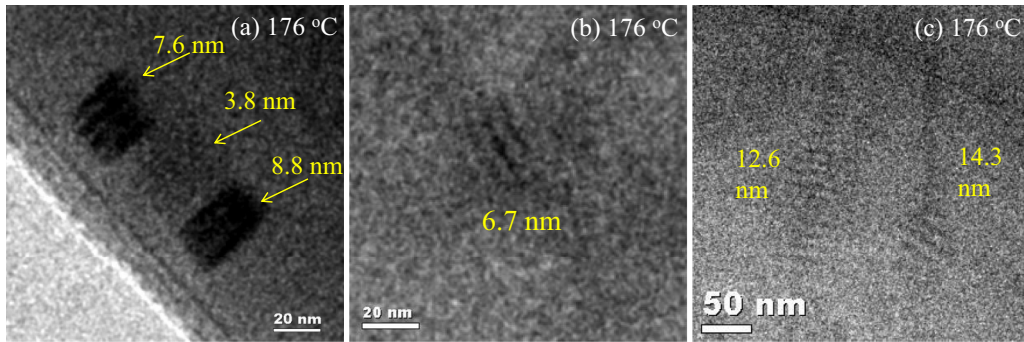


FIG. 13. Cryo-TEM textures of Col_l phase of 1Cl-N(1,7)-O6 obtained by quenching from $T = 176^\circ\text{C}$ with broadly varying period, from (a) 3.8 nm to (b) 6.7 nm and (c) 12–15 nm.

ature is lowered to $T = 180^\circ\text{C}$, the peaks slightly shift to $d_1 = 3.51$ nm.

The Col_l phase is associated with new sharp peaks at $M_2 = 1.08\text{ nm}^{-1}$ ($d_2 = 5.82$ nm) and $M_3 = 1.52\text{ nm}^{-1}$ ($d_3 = 4.1$ nm). The ratio $M_3/M_2 \approx 1.41 \approx \sqrt{2}$ signals tetragonal assembly, similarly to the results by Kang *et al.* [18].

The detail analysis of the SAXS pattern of the Col_l phase is presented in Fig. 15. The original SAXS pattern, Fig. 14(c), contains the grid lines, which are the dead zones between the segments of the detector. To eliminate the effect of the grid, we assume that the pattern possesses the inversion symmetry with respect to the beam center and substitute the dead zones with the pixels from the opposite side, Fig. 15(a). Both M_2 (5.8 nm) and M_3 (4.1 nm) reflexes exist at the direction perpendicular to the director, Fig. 15, which indicates an absence of positional order along the columns. However, the translational order of the columns themselves is strong, as indicated by the small widths of M_2 , Fig. 15(d), and M_3 , Fig. 15(f), reflexes in both radial and azimuthal directions. We estimate the correlation lengths to be 400 nm for M_2 and 300 nm for M_3 reflexes.

Field aligned homeotropic Col_l sample. In this case, the director is oriented along the incident x-ray beam. The WAXS peak at $M'_{\text{WAXS}} = 14.2\text{ nm}^{-1}$ ($2\pi/M'_{\text{WAXS}} = 0.45$ nm), Figs. 16(a) and 16(b), and the two SAXS peaks, $M'_2 = 1.08\text{ nm}^{-1}$ ($2\pi/M'_2 = 5.82$ nm) and $M'_3 = 1.52\text{ nm}^{-1}$ ($2\pi/M'_3 = 4.1$ nm), Figs. 16(c) and 16(d), are the same as the peaks observed in the capillary.

The azimuthal analysis of the SAXS reflexes from the homeotropic sample confirms the tetragonal packing of columns, Fig. 17. Both M'_2 (5.8 nm) and M'_3 (4.1 nm) reflexes appear as sets of four peaks separated by 90° , Figs. 17(b), 17(c), and 17(e); different sets correspond to the different domains, developed because of the in-plane tetragonal orientation degeneracy. The strongest intensity peaks appear at 19° for M'_2 and 64° for M'_3 , Figs. 17(c)–17(f), which means that there is an expected 45° difference between the two periodic arrangements. Note that the M'_2 reflex, Fig. 17(d), and the M'_3 reflex, Fig. 17(f), are more narrow than M_2 , Fig. 17(d), and M_3 , Fig. 17(f), revealing that under a homeotropic alignment, the correlation length of column packing is about $1\text{ }\mu\text{m}$.

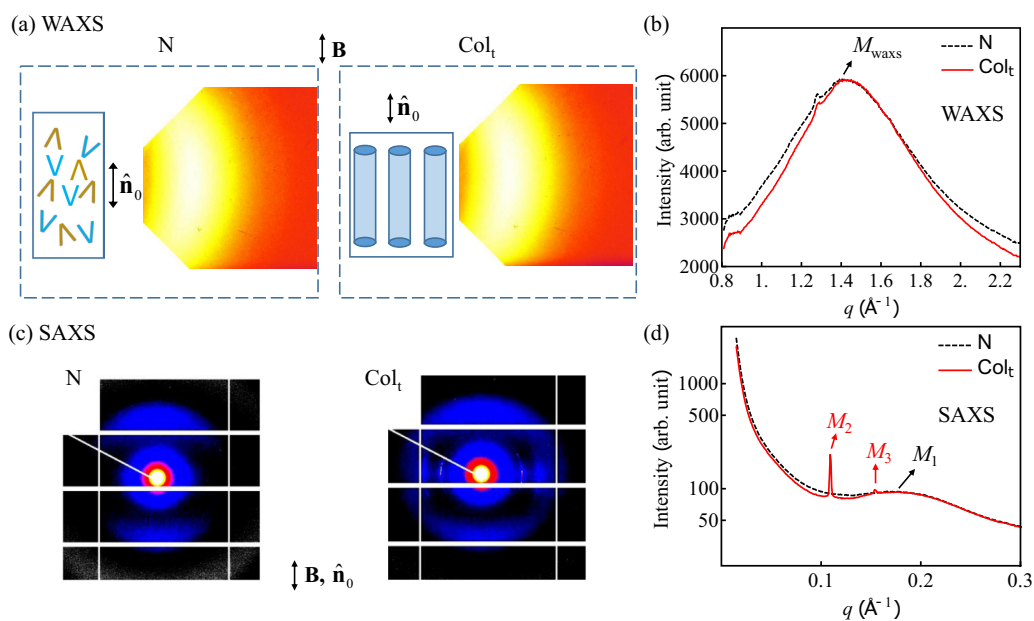


FIG. 14. X-ray diffraction data. (a) WAXS pattern of the N and Col_l phases; (b) WAXS intensity vs q in the N and Col_l phase; (c) SAXS pattern of the N and Col_l phases; (d) SAXS intensity vs q in the N and Col_l phases.

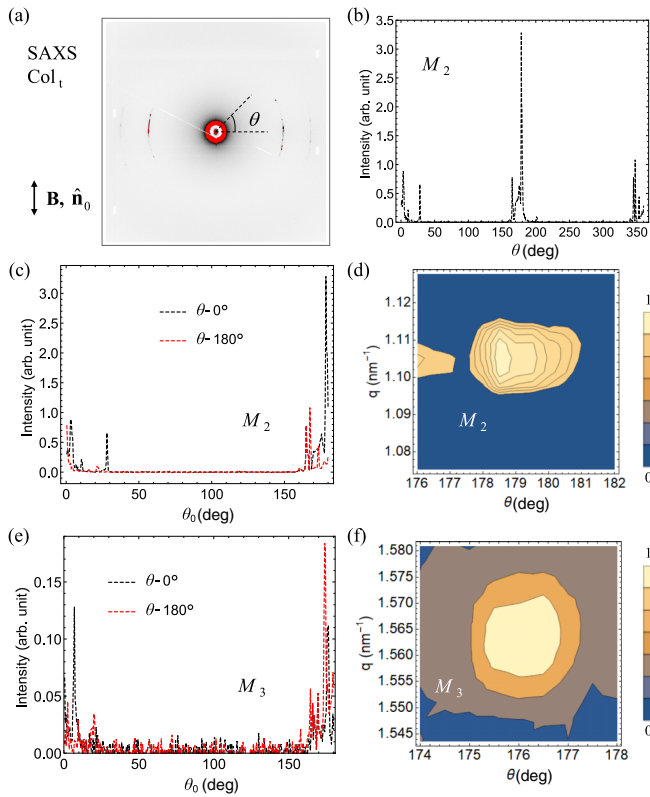


FIG. 15. Angular dependence of the SAXS signal in capillary: (a) diffraction pattern; (b) signal intensity vs the azimuthal angle θ for M_2 peak, where $2\pi/M_2 = 5.8$ nm; (c) intensity vs the angle θ_0 for the M_2 peak, where $\theta_0 = \theta - 0^\circ, 180^\circ$, respectively; (d) intensity map for M_2 peak; (e) intensity vs θ_0 for M_3 peak, where $2\pi/M_3 = 4.1$ nm; (f) intensity map for M_3 peak.

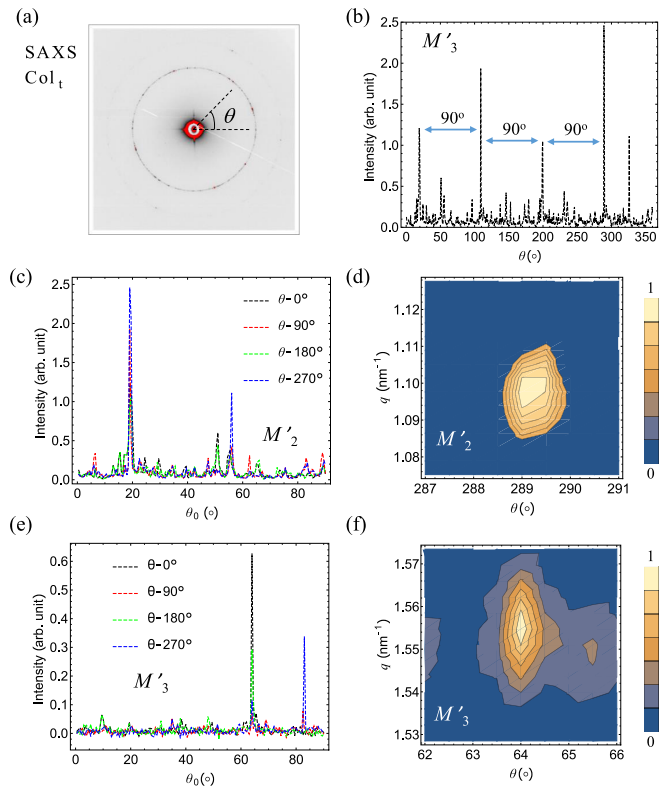


FIG. 17. Angular dependence of the SAXS signal: (a) diffraction pattern; (b) signal intensity vs the azimuthal angle θ for M'_2 peak, where $2\pi/M'_2 = 5.8$ nm; (c) intensity vs the angle θ_0 for the M'_2 peak, where $\theta_0 = \theta - 0^\circ, 90^\circ, 180^\circ, 270^\circ$, respectively; (d) intensity map for M'_2 peak; (e) intensity vs θ_0 for M'_3 peak, where $2\pi/M'_3 = 4.1$ nm; (f) intensity map for M'_3 peak.

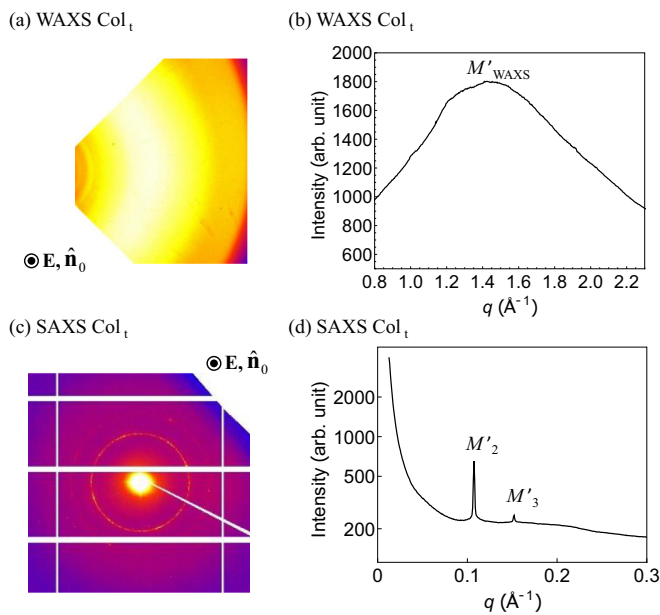


FIG. 16. X-ray diffraction at the sample aligned by the electric field at $T = 176^\circ\text{C}$ in the Col_t phase. (a) WAXS pattern; (b) WAXS intensity vs q ; (c) SAXS pattern; (d) SAXS intensity vs q .

Based on these results, we propose that the Col_t phase is a tetragonal packing of columns of two types, one polar and one apolar, Fig. 18. In the cross section of each column, one finds two ABC molecules, the λ planes of which are orthogonal to each other. These two molecules can point in the same direction, Figs. 18(a) and 18(b), or in the opposite directions, Fig. 18(c). A column formed by the pairs of the same orientation is polar, with the polarization vector either up [yellow columns in Fig. 18(d)] or down [blue columns in Fig. 18(d)]. Columns formed by stacks of the apolar pairs are apolar themselves, and marked as a combination of blue and yellow in Fig. 18(d). The polar columns form an antiferroelectric lattice, in which any up column is neighbored by four down columns and vice versa. The polar character of the columns is essential as it allows the system to avoid hexagonal packing and to form a square lattice instead. The cross section of each column is of a fourfold symmetry. The four arms of all polar columns are parallel to each other, while the four arms of the apolar columns are oriented by 45° with respect to the polar ones. The x-ray measured periodicity of 5.8 nm is associated with the distances between columns of the same polarity along the sides of a square lattice, while the 4.1-nm period is associated with the distances along the diagonal direction. The correlation lengths corresponding to M_2 and M_3 reflexes are both about 600 nm. Note that the columnar phase formed by ABC molecules is very different from the

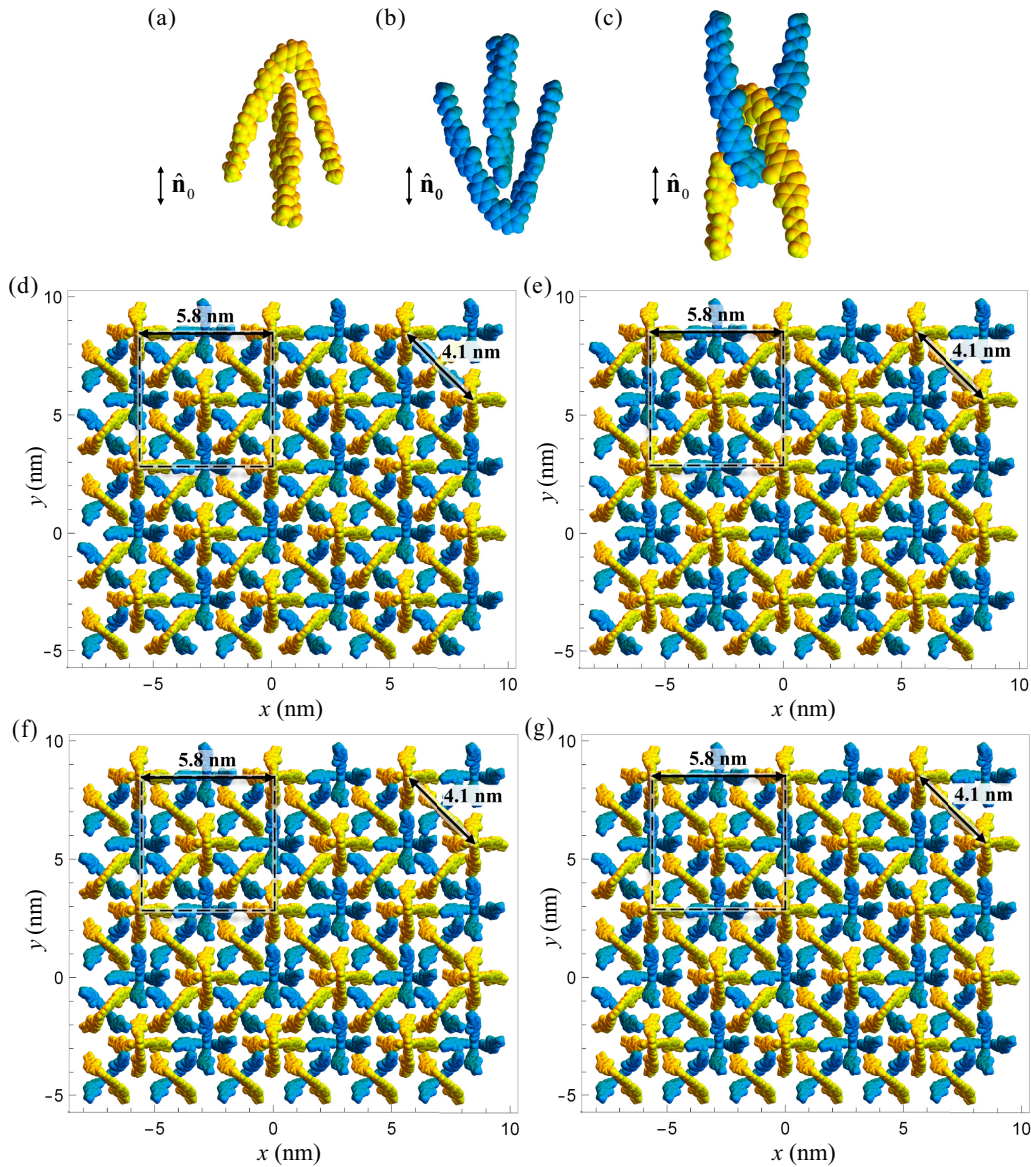


FIG. 18. Columnar packings in Col_t phase: (a) two ABC molecules point up, (b) two ABC molecules point down, and (c) two molecules point in opposite directions; (d)–(g) intercalated assembly of polar (a), (b) and apolar (c) columns into tetragonal structures of Col_t .

columnar phase observed in disklike molecules because in the Col_t phase molecular arms are almost parallel rather than perpendicular to the axes of the columns.

The chemical composition of the studied material is $\text{C}_{64}\text{H}_{56}\text{Cl}_2\text{N}_2\text{O}_{10}$, and the molecular weight is $m = 1084 \text{ amu} = 1.800 \times 10^{-24} \text{ kg}$. Assuming the mass density in the Col_t phase $\rho_a \sim 10^3 \text{ kg/m}^3$, which is typical for liquid crystals [45], one can estimate that a volume $V = 5.8 \text{ nm} \times 5.8 \text{ nm} \times 1 \text{ nm} = 3.364 \times 10^{-26} \text{ m}^3$ should contain $n = 18.69$ ABC molecules. In the proposed packing, the number of molecules in the elementary $5.8 \text{ nm} \times 5.8 \text{ nm}$ square is eight; thus the molecular separation along the z axis is $d_z = 0.43 \text{ nm}$, which is a very reasonable result. The number of molecules in an elementary square cannot be reduced below eight because for density $\rho_a \sim 10^3 \text{ kg/m}^3$, d_z would be prohibitively small.

The model in Fig. 18 places all the molecular pairs in the same plane of view. This is done for clarity only, as in

the real structure this restriction is absent: the molecules that align in the opposite direction have the centers of mass shifted along the columnar axis. The polar and apolar columns can be arranged in a variety of ways with each other. In Fig. 18, we show four possible local structures that show some of the possible geometries. A unifying theme of these arrangements is an antiferroelectric order of the polar columns with the gaps filled by apolar columns. The distinction comes from how the molecules in apolar columns contact the molecules in the polar ones. These contacts can be locally “parallel” (molecules from the neighboring columns are of the same color) or “antiparallel” (the neighboring molecules are of different colors). Note that the transition from one type of arrangement to another in Figs. 18(d)–18(g) requires only a simple 90° rotation of apolar columns. One might expect that all variations of polar-apolar column arrangements are possible when the system is cooled down from the nematic phase into the Col_t phase, since it would increase the entropy

of packing. The possibility of different geometrical arrangements between the polar and apolar columns is probably responsible for multiple periodicities revealed by TEM observations in Figs. 12 and 13.

An important feature of the proposed model of the columnar phase in Fig. 18 is that the plane of the ABC molecules is parallel to the columnar axes. This arrangement, supported by the x-ray, optical, dielectric, and electro-optical data, is very different from the conventional columnar phases formed by disklike molecules that stack on top of each other, with their planes being perpendicular to the columns.

IV. DISCUSSION AND CONCLUSION

The mesomorphism of ABC-compounds with a 1,7-naphthalene central core was reported by Lee *et al.* [46]. This family of materials exhibits a broad variety of phases [17,46]. An especially interesting phase sequence was suggested for the studied 1CI-N(1,7)-O6 [18], with the *N* phase being accompanied at lower temperatures by a tetragonal packing of cylinders with a double-twisted director. In the discussion below, we first address the properties of the *N* phase and then the properties of the Col_t phase.

Homeotropic textures of the *N* phase and the fact that its birefringence is positive suggest that the director is defined by the bisectors of each λ -shaped ABC molecule. The symmetry of a single molecule is C_{2V} , which is lower than the macroscopic nematic symmetry $D_{\infty h}$. The molecules are thus expected to rotate around the direction close to the bisector and flip-flop between up and down orientations. The measured values for twist ($K_{22} \sim 5$ pN) and bend ($K_{33} \sim 15$ pN) moduli are close to their counterparts in the rodlike nematics. The splay constant is anomalously low $K_{11} \sim 2$ pN, which we associate with the flip-flops of the λ -shaped ABC molecules that accommodate the splay easily. The inequalities $K_{11} < K_{22} < K_{33}$ in the ABC nematic phase are very different from the trends $K_{22} < K_{11} < K_{33}$ and $K_{33} < K_{22} < K_{11}$ in rodlike and OBC nematics, respectively. It would be of interest to explore whether the anomalous elastic properties of ABC materials extend also to the saddle-splay deformations and to the “biaxial splay” recently discussed by Selinger [47].

The appearance of a low-temperature Col_t phase is associated with the gradual freezing of the flip-flops and appearance of the positional order of tetragonal symmetry. The trend is evidenced already in the *N* phase, as K_{11} increases as the temperature decreases, which can be associated with the formation of molecular dimers such as shown in Fig. 18(c). This temperature behavior differs from that of the bend modulus K_{33} upon approaching the nematic to twist-bend nematic transition [7,9,14,25,26]. In the latter case, the molecules acquire a more bent shape at lower temperatures and K_{33} decreases, except in the very vicinity of the transition.

The Col_t phase is of a tetragonal symmetry. The x-ray diffraction data suggest that this phase is formed by columnar aggregates of diameter roughly equal to the distance between the legs of a single λ -shaped molecule. The polar columns are of alternating up and down polarities. The director, being parallel to the columns, is unidirectional in the ground state, but can be bent easily. The equidistance of columns makes splay and twist deformations difficult. The typical distances between columns of the same polarity are 5.8 and 4.1 nm. Apparently, the cohesive forces between the columns are weak, as the TEM study shows a broad spectrum of periods, including the values close to distances 5.8 and 4.1 nm measured by x-ray scattering. The apolar (on average) antiferroelectric character of packing explains relatively weak dielectric permittivity of the material.

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