SUPPLEMENTARY INFORMATION

The Smectic Zₐ Phase: Antiferroelectric Smectic Order as a Prelude to the Ferroelectric Nematic

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Abstract

We have structurally characterized the liquid crystal phase that can appear as an intermediate state when a dielectric nematic, having polar disorder of its molecular dipoles, transitions to the almost perfectly polar-ordered ferroelectric nematic. This intermediate phase, which fills a 100-year-old void in the taxonomy of smectic liquid crystals and which we term the “smectic Zₐ”, is antiferroelectric, with the nematic director and polarization oriented parallel to smectic layer planes, and the polarization alternating in sign from layer to layer with a 180Å period. A Landau free energy, originally derived from the Ising model of ferromagnetic ordering of spins in the presence of dipole-dipole interactions, and applied to model incommensurate antiferroelectricity in crystals, describes the key features of the nematic–SmZₐ–ferroelectric nematic phase sequence.
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**SECTION S1 – Materials and Methods**

**Synthesis of DIO** – First reported by Nishikawa et al. [1], DIO (2,3',4',5'-tetrafluoro-[1,1'-biphenyl]-4-yl 2,6-difluoro-4-(5-propyl-1,3-dioxane-2-yl)benzoate, **Fig. S1**, compound 3) is a rod-shaped molecule about 20 Å long and 5 Å in diameter, with a longitudinal electric dipole moment of about 11 Debye. Their synthesized compound was found to melt at $T = 173.6^\circ C$ and have an isotropic (Iso) phase and two additional liquid crystal phases, the unidentified M2 and ferroelectric-like MP. The transition temperatures on cooling were Iso – 173.6°C – N – 84.5°C – M2 – 68.8°C – MP – 34°C – X, very similar to those of the Iso – N – SmZA – NF sequence reported in Fig. 1.

Our synthetic scheme, shown in **Fig. S1**, is based on a general synthetic reaction. The key intermediate 1 was purchased from Manchester Organics Ltd., UK and intermediate 2 from Sigma-Aldrich Inc., USA. Reactions were performed in oven-dried glassware under an atmosphere of dry argon. Purification by flash chromatography was performed with silica gel (40–63 microns) purchased from Zeochem AG. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F$_{254}$ TLC plates from Millipore Sigma (Darmstadt, Germany).

Compounds were visualized using short-wavelength ultra-violet (UV). Nuclear magnetic resonance (NMR) spectra were obtained using a Bruker Avance-III 300 spectrometer. NMR chemical shifts were referenced to deuterochloroform (7.24 ppm for $^1$H, 77.16 ppm for $^{13}$C).

To a suspension of compound 1 (3.44 g, 12 mmol) and the intermediate 2 (2.91 g, 12 mmol) in CH$_2$Cl$_2$ (125 mL) was added dicyclohexylcarbodiimide (DCC, 4.95 g, 24 mmol) and a trace of 4-(dimethylamino)pyridine (DMAP). The reaction mixture was stirred at room temperature for 4 days, then filtered, washed with water, and with brine, dried over MgSO$_4$, filtered, and concentrated at reduced pressure. The resulting product was purified by flash chromatography (silica gel, petroleum ether/10% ethyl acetate). The crude product was crystallized by dissolving in boiling 75 mL petroleum ether/20% ethyl acetate solvent mixture, followed by cooling down to -20°C for 1 hour, yielding 2.98 g (49%) white needles of compound 3.

$^1$H NMR (300 MHz, Chloroform-d) δ 7.64 – 7.35 (m, 1H), 7.24 – 6.87 (m, 6H), 5.40 (s, 1H), 4.42 – 4.14 (m, 2H), 3.54 (ddd, J = 11.6, 10.3, 1.5 Hz, 2H), 2.14 (tddd, J = 11.4, 9.2, 6.9, 4.6 Hz, 1H), 1.48 – 1.23 (m, 2H), 1.23 – 1.01 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H).

$^{13}$C NMR (75 MHz, Chloroform-d) δ 162.50, 162.43, 160.85, 159.08, 159.00, 157.52, 150.87, 150.72, 145.60, 145.47, 130.51, 130.46, 117.99, 117.94, 113.22, 113.17, 113.02, 112.93, 112.88, 110.65, 110.30, 110.26, 110.00, 109.95, 98.65, 98.62, 98.59, 72.41, 33.72, 30.05, 19.35, 14.01.
Isomeric composition – The DIO molecule is diastereomeric, with local internal energy minima having its dioxane ring in either a cis or trans conformation. One of these minima is lower in energy than the other, and there is a local energy maximum of unknown height between them. If this barrier energy is large then a molecule can be effectively trapped in either state, but if it is small, the equilibrium population of the two states will be achieved for finite $T$. These energies will depend on the molecular environment, and may be collectively determined at high concentration, as one has in the liquid crystal melts or crystal phases of interest here. With the exception of Ref. [2], work to date, for example [1,13], has employed DIO as synthesized, without specific consideration of the value its isomeric composition, raising a question as to the role of the latter in LC behavior. However, this issue is explicitly addressed in Ref. [2], in which synthesized DIO is “completely” separated chromatographically into independent cis and trans fractions. It was found that these fractions are stable to a degree that enables the measurement of a binary trans/cis phase diagram over the weight percent range 100/0 to 50/50, and temperature range (-20°C < $T$ < 180°C), as well as study of a wide range of other relevant physical properties (x-ray, dielectric, thermal) over similar temperature and concentration ranges. The cis isomer is non-mesogenic, while the trans isomer exhibits an Iso – N – SmZA (M2) – Nf (MP) – X phase sequence, with transition temperatures that depend significantly on cis concentration [Iso – 174 °C – N – 83°C – SmZA – 68 °C – Nf at 100% trans/0% cis]. A principal result of Ref. [2], relevant to this paper and previously reported studies of DIO, is that the 100% trans phase sequence and the phase transition temperatures on cooling observed in Ref. [2] match well those reported here and those previously reported in DIO: [Iso – 174 °C – N – 85°C – SmZA – 70 °C – Nf [1,13]]. We conclude from this that the DIO sample studied in this paper and in Refs. [1,13] are close to 100% trans as synthesized, which must be due to the kinetics of the synthesis.

Non-resonant SAXS & WAXS measurements were carried out in-house and on the microfocus SMI beamline 12-ID at NSLS II at Brookhaven. DIO was filled into 1 mm-diameter, thin-wall quartz capillaries and the director magnetically aligned normal to the beam using a field of ~2 kGauss from rare-earth magnets. Resonant SAXS measurements were carried out at the Carbon Kα-edge on beamline 11.0.1.2 at the Advanced Light Source, Lawrence Berkeley National Laboratory, on powder samples in ~5 µm-thick cells with 100 nm-thick silicon nitride windows.

Electro-optics and optical microscopy – For making optical and electro-optical measurements, DIO was filled into planar-aligned, in-plane switching test cells with unidirectionally buffed alignment layers arranged antiparallel on the two plates, which were uniformly separated by $d$ in the range 3.5 µm < $d$ < 8 µm. In-plane ITO electrodes were spaced by a 1 mm wide gap and the buffing was almost parallel to the gap. Such surfaces give a quadrupolar alignment of the N and SmZA directors along the buffing axis and polar alignment of the Nf at each plate. The antiparallel buffing makes ANTIPOLAR cells in the Nf, generating a director/polarization field parallel
to the plates, and with a π-twist between the plates [3]. ITO Sandwich cells with \( d = 4.6 \mu m \) for studying the splay-bend Freedericksz transition in the N phase were also used. Cells were temperature controlled in Instec hot stages. Phase behavior and x-ray structure data were taken upon cooling at rates between 0.1 °C/min to 1 °C/min.

**Polarization measurement** – The ferroelectric polarization density \( P \) was measured by applying an in-plane square-wave electric field to generate polarization reversal while measuring the induced current between the electrodes, the REV mode in Ref. [3]. A 50 Hz, 104 V peak-to-peak square-wave voltage was applied across a 1 mm-wide electrode gap in the sample cell. The polarization current, \( I(t) \), was obtained by monitoring the voltage across a 55 kΩ resistor connected in series with the cell. Polarization current vs. time data for different temperatures are shown in Fig. 5. The polarization reversal is symmetric, with the +/- and –/+ reversals giving essentially identical data sets. In the isotropic, nematic and smectic \( Z_A \) phases, the current consists only of a small initial peak, appearing following the square-wave voltage sign-reversal and then decaying exponentially. This current corresponds to the RC circuit response of the cell and resistor. Upon entering the \( N_F \) phase, an additional, much larger, current signal appears at longer times which comes from the field-induced polarization reversal. The switched polarization charge, \( Q \), is obtained as the time integral of the polarization current, and the \( N_F \) polarization density is given by \( P = Q/2A \), where \( A \) is the cross-sectional area of the liquid crystal sample in the plane normal to the field and passing through the mid-line of the electrode gap.
**SECTION S2 – X-ray Diffraction from RM734 and DIO**

**Figure S2:** Comparison of WAXS from RM734 and DIO. The samples have the nematic director magnetically aligned along \( z \) by a \(~1 \text{ Tesla}\) magnetic field. The color gamuts are linear in intensity, with the (black) minima corresponding to zero intensity. Scattered intensity line scans \( I(q_z) \) from such WAXS images are shown in **Figure S7**. The WAXS scattering patterns that appear in RM734 and DIO upon cooling into the N phase are strikingly similar, and do not change very much on cooling into the lower temperature phases, apart from the appearance of the SmZ\(_1\) layering peaks (also visible in SAXS images [4]). (A-D) The WAXS patterns exhibit familiar nematic diffuse scattering features at \( q_z \sim 0.25 \text{ Å}^{-1} \) and \( q_y \sim 1.4 \text{ Å}^{-1} \), arising respectively from the end-to-end and side-by-side pair-correlations, that are typically generated by the steric rod-shape of the molecules and are located respectively at \((2\pi/\text{molecular length} \sim 0.25 \text{ Å}^{-1})\) and \((2\pi/\text{molecular width} \sim 1.4 \text{ Å}^{-1})\) [1,4]. In contrast to typical nematics, RM734 also exhibits a series of scattering bands for \( q_y < 0.4 \text{ Å}^{-1} \) and \( q_z > 0.25 \text{ Å}^{-1} \), initially reported in RM734 and its homologs [4,5,6,7]. Interestingly, DIO presents a qualitatively very similar scattering pattern (A,B,D), but with an even more well-defined peak structure, likely a result of the higher variation of excess elec-
tron density along the molecule associated with the fluorines. Also notable is that the \( q_z \sim 0.25 \text{ Å}^{-1} \) feature in RM734 is weak compared to that found in typical nematics such as 5CB and all-aromatic LCs [8,9]. We attribute this weak scattering to the head-to-tail electrostatic adhesion in RM734, which makes the molecular correlations along \( z \) more polar and chain-like, reducing the tail-to-head gaps between molecules. The resulting end-to-end correlations are then like those in main-chain LC polymers, where there are no gaps, and, as a result, the scattering along \( q_z \) is weaker than in monomer nematics [10,11,12]. In DIO, on the other hand, the trifluoro group at the end of the molecule generates large electron density peaks that periodically mark chain-like correlations along \( z \), even if there are no gaps, resulting in strong scattering at \( q_z \sim 0.25 \text{ Å}^{-1} \). The signal around \( q = 0 \) (for \( q < 0.1 \text{ Å}^{-1} \)) in \( B,C \) is from stray light. From [13].
**Figure S3:** Line scans, \( I(q_z) \), of WAXS images of scattering from DIO and RM734 similar to those in **Figure S2** along \( q_z \) at \( q_y = 0.004 \) Å\(^{-1}\). (A) Comparison of RM734 at \( T = 160^\circ C \) and DIO at \( T = 85^\circ C \), the temperatures where the peak structures of \( I(q_z) \) are the strongest, reveals common features. These include the previously reported intense diffuse scattering features at \( q_z \sim 0.25 \) Å\(^{-1}\) and \( q_y \sim 1.4 \) Å\(^{-1}\) [1,4], and the multiplicity of diffuse peaks along \( q_z \) previously observed in the RM734 family [4,5,6,7]. The pairs of similarly colored dots show analogous peaks for the two compounds. The diffuse peaks located at \( q_y \approx 0.25 \) Å\(^{-1}\) (white dots) correspond to short-ranged order with a quasi-periodic spacing of \( 2\pi/q_y = p \approx 24 \) Å in both materials, comparable to the molecular lengths of DIO and RM734, and, in RM734, to the periodicity of the molecular spacing along the director in head-to-tail assemblies seen in simulations [14].

Viewing such head-to-tail assemblies as one-dimensional chains with displacement fluctuations along the chains, the root mean square relative displacement of neighboring molecules along the chain, \( \sqrt{\langle \delta u^2 \rangle} \), can be estimated from the ratio of the half-width at half maximum of the scattering peak at \( q_y \) (0.04 Å\(^{-1}\)) to \( q_y \) [see Ref. 15, Supplementary Figure S13]. This ratio is 0.2, which gives \( \sqrt{\langle \delta u^2 \rangle}/p \sim 0.25 \) and \( \sqrt{\langle \delta u^2 \rangle} \sim 5 \) Å. This is somewhat larger than the rms displacement found in atomistic computer simulations of ~400 RM734 molecules [14], implying that longer length-scale fluctuations may also be contributing to the peak width. (B,C) Temperature dependence of WAXS in DIO and RM734. In the N phase of RM734, the peaks in \( I(q_z) \) become better defined with
increasing temperature, unusual behavior in agreement with the results of [7]. In DIO, in contrast, $I(q_z)$ looks the same through most of the N range and below, with the well-defined peaks appearing at $T = 85^\circ C$ (B), and broadening with increasing temperature only near the N–Iso transition, before disappearing in the Iso phase. In the N phase, the sequence of peak positions in DIO at $q_z = [0.25, 0.50, 0.78, 1.25, 1.58 \, \text{Å}^{-1}]$ are in the ratios $q_z/q_{zp} = [1, 2.0, 3.1, 5.0, 7.8]$ which can be indexed approximately as a one-dimensional periodicity giving a harmonic series of multiples of $q_{zp} \approx 0.25 \, \text{Å}^{-1}$. In the case of RM734, at $T = 100^\circ C$ similar indexing of the peak sequence $q_z = [0.28, 0.60, 0.85, 1.46, 1.96 \, \text{Å}^{-1}]$ is possible, with $q_z/q_{zp} = [1, 2.2, 3.1, 5.3, 7.0]$, but there are significant deviations from harmonic behavior at $T = 160^\circ C$, as observed in other members of the RM734 family [16]. In the Iso phase this structure is lost altogether. The nature of the correlations that produce this multiband structure, and their relation to the ferroelectric ordering are currently not understood. From [13].
Figure S4: BOX scans of the SAXS images of DIO showing the temperature dependence of the lamellar reflection from the SmZ\textsubscript{A} layering. \( I(q_y) \) is obtained by measuring \( I(q_y,q_z) \) over a rectangular area \([-0.3 \text{ Å}^{-1} < q_y < +0.3 \text{ Å}^{-1}), (-0.009 \text{ Å}^{-1} < q_z < 0.009 \text{ Å}^{-1}) \] centered on the peaks and then averaging over the \( q_z \) range. The scans are displaced vertically for clarity, by equal intensity increments. The lowest temperature scan (\( T = 64.7 \degree \text{C} \)) is not displaced, showing that the amplitude of the layering peak is comparable to the background at this temperature. The shoulders appearing at \( T \approx 76\degree \text{C} \) are due to spontaneous rearrangement of the layers upon cooling. Peak amplitude and position are plotted in Figs. 2F,G. The inset above shows typical BOX and LINE (yellow) scan areas of a SAXS image.

Figure S5 (below): LINE scans of the SAXS images of DIO showing the temperature dependence of the lamellar reflection from the SmZ\textsubscript{A} layering. \( I(q_y) \) is obtained by measuring \( I(q_y,q_z) \) along a line passing through the peak centers. The profiles obtained from BOX scans are shown at the highest and lowest temperatures. The transmitted beam is blocked around \( I(q_y) = 0 \) by the beamstop. The shoulders appearing for \( T \approx 76\degree \text{C} \) are due to spontaneous rearrangement of layers upon cooling. The principal peak amplitude and position are plotted vs. \( T \) in Figs. 2F,G, and the peak half-width at half maximum (HWHM) in Fig. 2H.
Figure S5 (continued)

DIO SAXS LINE scans

$T = 86.6 \, ^\circ C$

LINE scan

BOX scan

83.5

Intensity $I(q_y)$ (AU)

82.8

$q_y (\AA^{-1})$
Figure S5 (continued)

(B)

![Graphical representation of the data with intensity I(q_y) (AU) plotted against q_y (Å⁻¹). The graph shows multiple peaks at different q_y values.](image-url)
Figure S5 (continued)

(C)

Intensity $I(q_y)$ (AU)

$q_y$ ($\text{Å}^{-1}$)

79.0

76.8

76.3

-0.30 -0.20 -0.10 0 0.10 0.20 0.30
Figure S5 (continued)

(D)

Intensity \(I(q_y)\) (AU)

\(q_y\) (Å\(^{-1}\))

75.8

75.4

74.9
Figure S5 (continued)

(E)
Figure S5 (continued)

(F)

Intensity $I(q_y)$ (AU)

$q_y$ (Å$^{-1}$)

Sm$Z_A$

Transition region

BOX scans

N$_F$

72.4

72.0

69.9

65.2
Figure S5: (G) Resonant carbon K_\alpha-edge x-ray scattering from DIO (incident x-ray wavelength = 44 Å). The DIO sample was filled by capillarity into a d ~ 5 µm thick gap between untreated 100 nm thick SiN windows. Depolarized transmission optical microscopy (DTOM) showed random planar alignment of DIO between the plates in the N, SmZ_A, and N_F phases. The x-ray scattering patterns were two-dimensional powder rings, which were circularly averaged to give the scattered intensity vs. radial wavevector $q_r$ curves plotted here. Scans are shifted vertically for clarity. In the SmZ_A temperature range, the scattered intensity $I(q,T)$ shows a single scattered peak in the wavevector range (0 < $q_r$ < 0.08 Å^{-1}). This peak is located at $q_R \approx 0.035$ Å^{-1}, comparable to that expected for Bragg scattering associated with a cell doubling of the periodicity of the lamellar electron density modulation at $q_M \approx 0.070$ Å^{-1}. Plots of 2$q_R$ and $q_M$ show very similar dependence on temperature over the SmZ_A range, as seen in Fig. 2H. This indicates that the SmZ_A lamellar structure is bilayer, comprising layers which have identical electron-density modulation but different resonant scattering cross-sections. We attribute this difference to the periodic alternation of polarization direction in adjacent layers. Upon cooling, a pretransitional diffuse resonant peak appears at $T = 85^\circ$C in the N phase, with an integrated intensity that: increases abruptly over a ~2 °C interval entering the SmZ_A phase; is nearly constant for 81°C > $T > 70^\circ$C through the SmZ_A range; and then decreases over a 5 °C interval due to SmZ_A – N_F phase coexistence.
The chevron is inherently vectorial along $y$, creating a class of defect lines (the zig-zag walls [17,18,19,20] which mediate flips in the chevron direction, e.g., $\langle \langle \langle \cdot \rangle \rangle \rangle$) to $\langle \langle \langle \cdot \rangle \rangle \rangle$. The chevron tips point out from the diamond wall $\langle \langle \langle \cdot \rangle \rangle \rangle$, as shown in the sketch of the chevron structure on passing through a diamond wall in the upper right of Fig. 4D. The number of layers per unit length on the cell surfaces is the same everywhere, so that the “empty” space in the center between the out-pointing chevrons must somehow be filled with effectively thicker layers. It is filled by the diamonds, which are layer elements tilted away from $y$ by an angle $\delta_d$, larger than the chevron tilt, $\delta$, effectively making them appear thicker (Figs. 4D,S7). Measurement of the sample orientation that gives extinction of the diamond wall line shows that $\delta_d = 23^\circ$ (Fig. S8). The broad walls, which run nearly parallel to the layers (Figs. 4C,S8B), correspond to places where the chevron tips point toward each other $\langle \rangle \langle \langle \langle \cdot \rangle \rangle \rangle$. In these walls, the layers are tilted by less than $\delta$, making their effective thickness smaller in order to accommodate the chevrons pointing toward the wall.

Comparing the zig-zag walls in the SmZA (Figs. 4A,B) and SmC phases (Fig. S6,S7), one sees that the optical contrast between domains of opposite chevron direction is much more dramatic in the SmC. This is because the SmC director is on a cone about the layer normal, and the director orientation in the cell adjusts to accommodate the chevron sign, the boundary conditions on $n$ at the cell and chevron interfaces, and any applied field, greatly affecting the local optical appearance. In the SmZA, in contrast, $n$ is parallel to the surface and does not reorient with chevron tilt, nor in the formation of the broad walls, which, therefore have lower visibility than in the SmC, as comparison of Figs. 4A,S8B with Figs. S6,S7 shows. Since the layers in the diamond walls are birefringent and they are twisted relative to the average layer orientation, they are visible when the rest of the cell is at extinction, as in Figs. 4A,S8.

In a sandwich cell (Fig. S9), ITO electrodes cover the entire active area, enabling application of an electric field, $E_x$, normal to the cell plates. In the N phase, this produces a splay-bend Freedericksz transition by rotating $n$ out of the plane of the cell. In a bookshelf or chevron cell in the SmZA phase, reorientation of the director takes place about the layer normal and is therefore resisted only by splay-bend Frank elasticity, as in the N phase. The splay-bend Freedericksz transition is readily observed in the SmZA phase as a field-induced reduction in the effective in-plane birefringence $\Delta n_{BB} = n_n - n_q$, as the molecules stand up normal to the plates. Once this reorientation is saturated, the induced polarization in the tilted layers is still not fully parallel to the applied field, so that the field produces torque on the layers that tends to orient them to be normal to the plates. The resulting dilative strain on the layering system generates, irreversibly, massive arrays of broad-wall zig-zag defects that fill nearly the entire cell, as shown in Fig. S9B,C. These walls develop internal, periodic birefringent structures (Fig. S10D-F) suggesting that the broad wall can
break up into small zig-zag loops, or that the dilation causes a local strain-induced periodic rotation of $n$ out of the plane of the layers, as would occur for the smectic dilative layer undulation instability [21]. These defect arrays are comparable to those obtained in ferroelectric SmC* cells at high applied field, shown in Fig. S10.

**Figure S6:** Zig-zag defect lines in SmC cells mediating changes in the direction of the chevron bend of the layers. Zig-zags are a typical smectic layering defect in thin smectic C LC samples between glass plates treated to impose a preferred uniform molecular orientation (yellow arrow). Regions with uniform chevron orientation, located within an area where the layer chevrons point the other way are bounded by closed loops [22], the detailed structure of which is shown in Fig. S7. Chevron bends point toward the broad walls that run parallel to the layers, and away from the diamond walls running obliquely to the layers. Image width: A- 300 µm; B,C - 2 mm.
Figure S7: Geometrical features of the chevron layer structure and zig-zag defect loops in smectic C cells. (A,B) Photomicrographs of the narrow and broad walls of zig-zag defects in cells 3 to 4 µm thick. (C) The three-dimensional structure of a closed zig-zag defect loop, the spontaneously formed defect separating one direction of chevron layering from the other in a SmC, here in a sample between solid plates that was cooled from the smectic A phase. The loop consists of narrow (diamond) walls running nearly parallel to z and a broad wall running parallel to y. These walls are delimited by the lines which focus sharply in (A) and (B), also indicated by the heavy solid and dashed lines in (C). In this example, the chevron layer-bend plane is displaced from the cell mid-plane. The defect structure is an assembly of planar layer elements continuously connected to one another by sharp layer-bend discontinuities. The mean layer pitch $p = d$, established by layer anchoring at the surfaces, is the same everywhere. (D) Section showing layer structure change upon passing through the diamond (⟨⟨⟨⟩⟩⟩) and broad ⟨⟩⟩⟨⟨⟨⟩⟩ walls for the symmetric case where the chevron interface is at the cell center. (E) Schematic of a single layer in the diamond wall. The scale bar in (B) is 15 µm long. From [23].
Figure S8: Diamond walls in the SmZ\textsubscript{A} phase of DIO in the cell of Figs. 3,4 viewed using DTLM. (A) Extinction obtained when $n$ is along the polarizer direction. The diamond zig-zag walls are bright because the diamond layer elements at the core of the walls have a different azimuthal orientation than the layers (and hence the bulk director, yellow) in the rest of the sample. (B) The cell reoriented to the extinction orientation for one set of diamond walls. (C) Geometry of the diamond wall, showing the top view of a single layer passing through the wall. The tip of the chevron bend discontinuity (cyan), the diamond plane, normal to the surface (red), and the intersection of the part of the layer above the chevron with the top surface (black) are highlighted. In this cell orientation, the diamond plane is aligned with the optical polarizer and gives extinction. The white arrows indicate the chevron polarity, as in Fig. 4D.
Figure S9 below: Sandwich cell (electric field normal to the plates) (A-E) DTLM images of cell texture changes induced when a 200 Hz square wave electric field of peak field $E_p = V_p/d$ is applied normal to the cell plates to a tilted-layer/chevron layer/bookshelf cell filled with DIO. This cell has $d = 4.6 \mu m$ and an antiparallel buffed, planar-aligned, sandwich electrode geometry giving peak field $[E_p(V/\mu m)] = 0.22[V_p(V)]$. As cooled from the isotropic, the N and SmZ phases grew in as well-aligned planar monodomains. In the N phase they exhibited the splay-bend Freedericksz transitions, with threshold $V_p$ values given in (F). Upon cooling into the SmZA phase the layers grow in as a BK geometry, with some evidence for zig-zag walls indicating the presence of some chevron BK layer structure with layer normal $q_M$, normal to the buffing direction, $n$. The field, normal to the cell plates, induces the splay-bend Freedericksz transition also the SmZA, with a threshold field is somewhat higher than in the N phase (F). (A-C) The field-induced start of the splay-bend Freedericksz director reorientation generates the formation of additional zig zag defects, which develop into massive arrays filling the cell. Mechanisms for generating zig-zags are (a) field-induced standing up of the layers as the polarization $P$ is rotated about the layer normal such that $P$ in adjacent layers is rotated away from their antiferroelectric opposition. The non-zero $E_x$ couples to the resulting induced $\delta p$ to apply a torque $\tau_z = \delta p \times E_x$ to the LC that tends to stand the layers up normal to the plates, a process that dilates the layer system and creates zig-zag walls; (b) expulsion of layers if the field-induced ferroelectric state is layerless. The intensive creation of broad walls, evident in (B,C) may be evidence for the antiferroelectric-to-ferroelectric transition, the layering may simply disappear in the induced ferroelectric state, especially at lower temperatures in the SmZA. The diamond walls are darker in the images and the broad walls, running parallel to the layers, are brighter. (D) As the field is increased to $V_p = 10V$, well above the Freedericksz threshold, the zig-zag defects anneal and coarsen to leave a bookshelf monodomain in the cell, with layers and the director nearly normal to the plates. (E) When the field is returned to zero, the director reorients to be everywhere parallel to the plates, and the layering must return, a compressive transition on the layering system so the zig-zags disappear. Image width: 2.2 mm. (F) Freedericksz threshold values of $V_p$ vs. $T$. 

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Figure S9 (continued):

(A) DIO SmZ$_A$ $T = 75^\circ$C

$V_p = 0$ V
Figure S9 (continued):

(B) $q_M$ $V_p = 0.5 \text{ V}$

$DIO$ $SmZ_A$ $T = 75^\circ\text{C}$
Figure S9 (continued):

(DIO SmZ\textsubscript{A} \( T = 75^\circ\text{C} \))

\( q_M \)
Figure S9 (continued):

(D) \( V_p = 10 \text{ V} \)

\[ q_V = 10 \text{ V} \]

\[ \text{DIO SmZ}_A \ T = 75^\circ C \]

\[ n \]

\[ q_M \]
Figure S9 (continued):

(E) BK

DIO SmZA T = 75ºC

Vp = 0 V

-27-
Figure S9 (end):

![Graph showing the relationship between threshold voltage (V) and temperature (°C). The graph indicates a transition from smectic $Z_A$ to nematic phases.]
Figure S10: Photomicrographs showing structural similarities of arrays of zig-zag defects induced by electric field in chevron/tilted layer cells, SmC on the left, and SmZA on the right. The black lines are the diamond walls and the brighter lines running across the images are the broad walls, parallel to the layers. The cell thickness is comparable to the broad wall width. Image width: A–C, E, F - 200 µm; D - 600 µm. In (D–F) some of the broad walls have broken up into strings of small defects. These may be zig-zag loops, or evidence of a periodic dilative undulation instability of the layers [24].
**SECTION S4 – Coexisting parallel (PA) and bookshelf (BK) SmZ\(_A\) domains**

**Figure S11:** Coexisting domains of BK and PA layer orientation in the cell of Fig. 3, enabling measurement of features of the optical biaxiality of the SmZ\(_A\) phase. (A) An in-plane field induces the twist Freedericksz transition in the N phase, and flips part of the SmZ\(_A\) region from bookshelf (BK) to parallel (PA), also inducing twist in the PA region. (B) When the field is removed, the twist relaxes rapidly in the SmZ\(_A\) PA region, but slowly in the N domain. (C) Here both the N and PA regions have relaxed back to uniform states with \(n\) along the buffing. (D) The biaxial principal axes of the optical dielectric tensor of the SmZ\(_A\) are \((l,q_M,n)\) such that in the BK geometry the effective in-plane birefringence measured is 
\[
\Delta n_{\text{BK}} = n_n - n_q = \left(\frac{1}{2\langle n\rangle}\right)\Delta \varepsilon_{\text{BK}}
\]
where \(\Delta \varepsilon_{\text{BK}} = \varepsilon_{nn} - \varepsilon_{qq}\) and \(\varepsilon_{ij}\) is the optical dielectric tensor, and \(\langle n\rangle\) is the average refractive index. In the PA geometry, we have 
\[
\Delta n_{\text{PA}} = n_n - n_l.
\]
The difference between these measurements, \(\Delta n_b = \Delta n_{\text{BK}} - \Delta n_{\text{PA}}\) yields the biaxial birefringence, \(\Delta n_b \equiv n_l - n_q\) that distinguishes the modulated SmZ\(_A\) from the uniaxial nematic. (D) shows that \(\Delta n_{\text{BK}} < \Delta n_{\text{PA}}\) and therefore that \(n_q > n_l\) with \(\Delta n_{\text{BK}}\) giving a purple color and \(\Delta n_{\text{PA}}\) blue.
**Figure S12:** (A) Grayscale DTLM images of a sample area of the RM734 texture and selected optical Fourier transforms near the N–N phase transition. In the N phase (T < 133°C), the images represent an optical-resolution integration of the birefringent phase accumulated by the light upon traversing the sample thickness, t. The resulting averaging captures the extension of the domain shape along n, which gives a wing-shaped optical Fourier transform. (B) The pink inset shows a contour of \( \chi_P(q) \), the susceptibility for scattering by polarization fluctuations given by the Aharony model [25,26,27,28]:

\[
\chi_P(q) \propto \langle P_z(q)P_z(q) \rangle \propto \frac{1}{\{1 + \xi(T)^2[(q^2 - hq_z^2 + (2\pi/\varepsilon)(q_z/q)^2)]\}},
\]

where \( \xi(T) \propto T_{ce}/(T-T_{ce}) \). \( \chi_P(q) \) describes the anisotropy in the polarization fluctuations in the N phase generated by short range ferroelectric interactions, giving the Ornstein-Zernicke term.
about \( q = 0 \), and the last term from long-range polarization space charge interactions. The favorable qualitative comparison with the optical Fourier transform at \( T = 133^\circ C \) indicates that charge stabilization is as important a factor governing fluctuations of the N phase of RM734 as it is in the SmZA phase of DIO. The Aharony model is directed toward understanding certain crystalline magnetic materials that have short-range ferromagnetic exchange forces but where long-range dipolar interactions, which can favor mutual parallel or antiparallel alignment of dipoles depending on their relative position, are also important. In these systems, short-range interactions are included in a model Hamiltonian as nearest-neighbor Ising or Heisenberg-like, and the long-range interactions are calculated explicitly. Renormalization group analysis shows that the long-range interactions make the magnetic correlations dipolar-anisotropic near the transition in the high temperature phase [27,28,29], extending them along the dipole-dipole (third) term produces extended correlations that grow as \( \xi(\tau) \) along \( x \) and \( y \) but as \( \xi(\tau)^2 \) along \( z \) [28], suppressing \( \chi(q) \) for finite \( q_z \), as is observed qualitatively from the visual appearance of the textures upon passing through the phase transition, and from their optical Fourier transforms. Because of this anisotropy, the correlation volume in this model grows in 3D as \( V \sim \xi(\tau)^4 \) rather than the isotropic \( V \sim \xi(\tau)^3 \), reducing the upper marginal dimensionality of the transition to 3D, and making the transition mean-field-like with logarithmic corrections rather than fluctuation-dominated with 3D Ising universality [30]. LC cell thickness \( d = 11 \ \mu m \). Scale bar = 200 \( \mu m \) (image corrected from the misassembled version shown in Ref. [14]).
**Figure S13**: Temperature-field \((T,E)\) phase diagrams for electric field applied along the polarization direction \((z\) in the case of DIO). (A) \((T,E)\) phase diagram computed using \textit{Eq. 1} with \(B < 0\) and \(C > 0\), fitting the \(P \rightarrow A \rightarrow F\) phase behavior of \(\text{NaNO}_2\) \([31,32]\). \((T_c,E_c)\) is a tricritical point, and \((T_c,E_c)\) the critical end point. (B) Temperature-field \((T,E)\) phase diagram computed using \textit{Eq. 1} with \(B > 0\) and \(C = 0\), fitting the \(P \rightarrow A \rightarrow F\) phase behavior of \(\text{SC(NH}_2)_2\) \([33,34,35]\). (C) Temperature-field \((T,E_z)\) phase diagram showing the \(P \rightarrow A \rightarrow F\) phase behavior of DIO. Data are from \(V_{FA}(\square)\), \(P_{FA}(\bigcirc)\) in \textit{Fig. 5B}, \(T_{FZ}\) at zero field \((\square)\), and \(T_{ZN}\) at zero field \((\bigdiamond)\). The corresponding field \(E_{FA}(T) = V_{FA}(T)/(100 \ \mu\text{m})\). The open squares give the first-order \(\text{SmZA} \rightarrow \text{NF}\) phase boundary in the \((T,E_z)\) plane, and the open circles the polarization change \(P_{FA}\) at this transition, which decreases with increasing field. According to the Clausius/Clapeyron equation, the transition entropy \(\Delta S\) also decreases along this line to zero at the point of maximum \(\text{SmZA}\) stability, \((T_m,E_m)\), and then changes sign with increasing \(T\). The solid red curve is a fit to \(T_{FZ}\), the \(\text{SmZA} \rightarrow \text{NF}\) transition line, and the dashed line an estimate of the \(T_{NZ}\) line based on the data at its two ends, both curves computed using the model described by \textit{Eq. 1}. In the \(F_{IS}\) model, the \(P \rightarrow A\) transition can be weakly first order or second order and have a tricritical point \((T_{tr},E_{tr})\). The \(N_F \rightarrow \text{SmZA}\) transition is observed to be weakly first order at zero field but has not yet been studied as a function of applied field.
**SECTION S7 – Pretransitional correlations in the \( \langle P_z \rangle = 0 \) minimum**

**Figure S14:** Comparison of the temperature dependence of the pretransitional increase in low frequency dielectric anisotropy \( \Delta \varepsilon = \varepsilon_{zz} - \varepsilon_{yy} \approx \varepsilon_{zz} \) as the transition to the NF phase is approached in the SmZA phase of DIO (data from Ref. [1]), with that as the N\(_F\) phase is approached in the N phase of RM734 (data from Ref. [36]). The common \( 1/(T - T_{oF}) \) behavior indicates that these divergences are both trajectories in a \( \langle P_z \rangle = 0 \) free energy minimum, a feature the F\(_{IS}\) model, in which a ferroelectric state can be approached in either a paraelectric or a modulated antiferroelectric phase. This increase is due to that of \( \varepsilon_{zz} \), which varies as \( \varepsilon_{zz} = 1/a(T - T_{oF}) \), where \( a(T - T_{oF}) \) is the curvature of F\(_{IS}\) near the \( \langle P_z \rangle = 0 \) minimum. Far away from the transition \( \varepsilon_{zz} \) may also be written as \( \varepsilon_{zz} = \varepsilon_o \), where \( p \) is the molecular dipole moment, \( v \) the molecular volume, and \( P \) the saturation polarization density. As the transition is approached, dipole reorientation becomes correlated and this equation still applies, but now with \( p(T) \) being the dipole moments of the correlated reorienting units, and \( v(T) = \frac{p(T)}{P} \propto 1/a(T - T_{oF}) \) their effective volume.
**SECTION S8 – Antiferroelectric, dielectric-like, response of the SmZA to in-plane field**

As in the N phase, the SmZA parallel domains respond to in-plane applied fields by exhibiting a field-induced azimuthal reorientation of \( n(x) \) about \( x \), the normal to the cell plates. EO observations with in-plane fields normal to \( n \), are summarized in Fig. S15 showing this orientational response to be a strictly dielectric-driven, twist Freedericksz transition as in the N phase. This confirms that the bulk polarization density along \( n \) is zero, i.e., that, at fields well below those required to induce the AF to F transition, the field-free SmZA phase has zero net ferroelectric polarization and its linear response at small field is purely dielectric.

*Figure S15:* Twist Freedericksz response to applied in-plane field in the N and parallel-aligned (PA) SmZA phases. The buffing orientation is 93° from the applied field direction. **(A)** Extinction of the starting planar-aligned nematic state. **(B,C)** In the N phase, the dielectric torque-induced orientational Freedericksz response gives a clockwise (CW) rotation of the director everywhere except near bubble inclusions (black circles), where the anchoring conditions induce CCW orientation in the wing-shaped domains at the first and third quadrants of the circle. The starred bubble has a diameter of 105 µm. **(C)** This dielectric behavior is duplicated exactly in the SmZA phase, showing that the response of the parallel-aligned SmZA to in-layer fields parallel to the layers is strictly dielectric, and that the phase is therefore antiferroelectric. **(D)** At higher field the bulk orientation becomes more uniform and therefore optically more extinguishing. This decouples the \( \pi \)-surface domain walls (magenta dots), enabling them to move apart (red dots), leaving a \( \pi \)-twist domain in between. The \( \pi \)-surface domain walls are together on the line marked by the green dot. Scale bar = 100 µm.
**SECTION S9 – SmZA Biaxiality**

**Figure S16**: Coexisting SmZA domains in the cell of Fig. 3 with bookshelf (BK) and parallel (PA) layer orientation as in Fig. S11, enabling measurement of the optical biaxiality of the SmZA phase.  

(A) Orientation of \((l, q, m, n)\), the principal axes of the optical dielectric tensor \(\varepsilon\) of the SmZA in a BK domain.  

(B) Field-induced growth of a PA domain of SmZA.  

(C) Comparative geometry of the BK and PA domains.  The difference in the birefringence of the BK and PA two regions yields the biaxiality, \(\Delta n_{biax} \equiv n_l - n_q\) that distinguishes the modulated SmZA from the uniaxial nematic.  

(D) When the field is removed, both BK and PA domains adopt uniform director alignment.  

(A-D) With \(d = 3.5 \mu m\) and since \(\Delta n \sim 0.18\) in both domains, the path difference is \(\Delta nd \sim 630 \text{ nm}\), corresponding to birefringence colors in a magenta-to-purple-to-blue-to-green band for increasing \(\Delta nd\) on the Michel-Levy chart [37].  With the director oriented at \(45^\circ\) to the polarizers, the BK regions are purple while the planar-aligned regions are blue, indicating that \(\Delta n_{BK} < \Delta n_{PA}\) and therefore that \(n_q > n_l\) which implies that the director modulation of the layering is splay, rather than twist (Fig. 4D).  

(E) Use of a Berek compensator enables measurement of \(\Delta n_{BK}\) and \(\Delta n_{PA}\) from which \(\Delta n_{max}(T)\) can be calculated.  

This biaxiality indicates molecular orientational anisotropy, some combination of:  

(a) a quadrupolar azimuthal distribution of the lath-shaped molecules about their long axes and \(n_l\); and  

(b) a splay orientational modulation of the long axes, rotating them about \(l\), as in Figs.2E, 4D.
**Bookshelf to-parallel layering transformation** – If a low frequency (20 mHz) in-plane triangle electric field is applied to the bookshelf SmZ_A cell and its amplitude increased above about 80 V/mm, ferroelectrohydrodynamic flow is generated [14] which disrupts the SmZ_A layering. The field-induced polarization tends to orient along the field direction, and in doing so restructures the layers in some areas, switching them from the bookshelf (BK) orientation to be parallel to the plates (PA), a process shown in Figs. S11,S16. When the field is reduced, the PA areas anneal into highly ordered monodomains filling the thickness of the cell with the SmZ_A layers parallel to the plates as sketched for the PA geometry in Fig. 1D. The director $n$ remains along the buffing direction, so that the layers have effectively been rotated by 90° about $n$ from the original bookshelf geometry. Near the N–SmZ_A transition, a typical cell treated in this way can simultaneously exhibit N, SmZ_A bookshelf, and SmZ_A parallel domains, as seen in Figs. S11, S16B-D.

In the cell of Fig. S11, the applied field, normal to $n$, generates a Freedericksz transition in both the parallel and N regions, but the transition is suppressed in the bookshelf region, as shown earlier in Fig. 3F. Below the Freedericksz thresholds, the bookshelf, parallel and N regions all relax to highly extinguishing, uniform monodomains, as shown in Figs. 6S16D. The Freedericksz thresholds in the parallel and N regions are similar but it is notable that once the field is removed, the relaxation of the field-induced twisted state in the SmZ_A parallel regions back to the uniform state is $\sim 10\times$ faster than in the N phase.

**Biaxiality and the modulation structure of the SmZ_A phase** – The simultaneous presence of bookshelf and parallel domains enables a measurement of features of the optical biaxiality of the SmZ_A phase. The principal axes of the optical dielectric tensor of the SmZ_A, shown in Fig. 4, are $(l,q_M,n)$. In the bookshelf (BK) geometry, the effective in-plane birefringence is $\Delta n_{BK} = n_l - n_q = [(1/(2\langle n \rangle))\Delta \epsilon_{BK}]$ where the optical dielectric anisotropy is $\Delta \epsilon_{BK} = \epsilon_{nn} - \epsilon_{qq}$ and $\langle n \rangle$ is the average refractive index. In the parallel (PA) domains, we have $\Delta n_{PA} = n_n - n_l$. The difference between these measurements yields the weak biaxial birefringence in the plane normal to $n$, $\Delta n_{biax} \equiv n_l - n_l = \Delta n_{PA} - \Delta n_{BK}$, that distinguishes the modulated SmZ_A from the uniaxial nematic, which effectively has $n_l = n_q$. With a cell thickness $d = 3.5 \mu m$ and $\Delta n_{BK} \approx \Delta n_{PA} \approx \Delta n_{Nem} \approx 0.18$, the path difference for each of these is $\Delta nd \approx 630 \text{ nm}$, near the magenta-to-purple-to-blue-to-green band for increasing $\Delta nd$ on the Michel-Levy chart [37]. The DTOM image in Fig. 6D shows $\Delta n_{BK}$ giving a purple color and $\Delta n_{PA}$ blue, implying that $\Delta n_{BK} < \Delta n_{PA}$ and therefore that $\Delta n_{biax} > 0$. Use of a Berek compensator enables the simultaneous measurements of $\Delta n_{BK}$ and $\Delta n_{PA}$ shown in Fig 6I, indicating that the SmZ_A has weakly biaxial, with $\Delta n_{biax} > 0$. This biaxiality indicates anisotropy of molecular orientational distribution, some combination of: (a) a quadrupolar azimuthal distribution of the lath-shaped molecules about their long axis; and/or (b) a splay orientational modulation of the long axes, rotating them about $l$, as in Figs.2E, 4D, having a peak rotation amplitude of $\delta \theta_p < +/-6^\circ$, as discussed in detail in SI Sec. S8.
Birefringence measurements do not distinguish ferroelectric [38] from antiferroelectric [39,40,41] modulation. However, as noted above, the EO observations in the bookshelf and parallel SmZ$_A$ domains indicate that the response to low fields is dielectric rather than ferroelectric, and therefore that the zero-field state has zero net polarization, i.e., is antiferroelectric. Correspondingly, the SmZ$_A$ is the least electrically polarizable among the N, SmZ$_A$, and N$_F$ phases, as shown directly by the electric field, $E$, temperature, $T$ phase diagram of DIO in Fig. S13.

The DIO molecules are somewhat lath shaped, with dimensions $a > b > c$, and $\chi_{bb}$ the intermediate eigenvalue of the molecular polarizability tensor. The effective biaxial molecular binding site provided by the biaxial SmZ$_A$ structure will necessarily generate a quadrupolar distribution of azimuthal molecular orientation about the director, which will in turn make $n_q$ different from $n_l$ and contribute to optical biaxiality. Assuming maximum optical polarizability $\chi_{aa}$ along the DIO molecular long axis, $a$, and intermediate susceptibility $\chi_{bb}$ for polarization parallel to the plane of the rings, the observed $\Delta n_{biax} = n_q - n_l > 0$ would imply that the DIO molecular rings lie preferably parallel to the $n - q_M$ plane. Smectic C phases are optically biaxial for similar reasons due to the monoclinic symmetry of their molecular environments, with the biaxial $\Delta n_{biax}$ increasing with SmC tilt angle $\delta$. SmC biaxiality is in the range $0.001 < \Delta n_{biax} < 0.01$ for tilt angles in the range $10^\circ < \delta < 45^\circ$ [42,43,44], comparable at low $\delta$ to that of the SmZ$_A$.

Alternatively, the effects of molecular reorientation on $\Delta n_{biax}$ could be interpreted in the context of spatial modulation of the nematic. If this modulation is primarily through molecular long-axis reorientation, $\Delta n_{biax}(y)$, then, given that $q_M$ is normal to $n$, the choices for such reorientation are only twist $\delta n_t(y)$, or splay $\delta n_s(y)$, as illustrated for periodic waves with wavevector parallel to $q_M$ in Fig. 4D. These sketches show immediately that splay increases $n_q$, making $\Delta n_{biax} > 0$ in accord with experiment, whereas the twist wave makes $\Delta n_{biax} < 0$. These changes can be related to $\langle \delta \theta(y)^2 \rangle$, where $\delta \theta(y)$ is the rotation of the local director about $l$ in the $\delta n_t(y)$ splay deformation, which changes $\Delta n_{biax}(\delta \theta) = [(1/(2(n)))][\Delta \epsilon_{biax}(\delta \theta)]$ according to $\Delta \epsilon_{biax}(\delta \theta) = \Delta \epsilon_{PA} - \Delta \epsilon_{BK} = \epsilon_{qq}(\delta \theta) - \epsilon_{ll}$. Taking $\delta \theta$ to be a function of $y$, averaging over this dependence, and applying a 2D rotational similarity transformation in the $(q_M,l)$ plane to get $\epsilon_{qq}(\delta \theta)$, gives $\langle \epsilon_{qq}(\delta \theta) \rangle = \langle \epsilon_{nn} \sin^2 \delta \theta + \epsilon_{ll} \cos^2 \delta \theta \rangle$ and therefore, since $\Delta n_{biax} \ll \Delta n_{Nem}$, $\Delta \epsilon_{biax}(\delta \theta) = (\epsilon_{nn} - \epsilon_{ll}) \langle \sin^2 \delta \theta(y) \rangle$, and therefore $\Delta n_{biax} \approx \Delta n_{Nem} \langle \sin^2 \delta \theta(y) \rangle$. Upon inversion we find $\delta \theta_{RMS} \approx \sqrt{\langle \delta \theta^2(y) \rangle} = \sqrt{(\Delta n_{biax}/\Delta n_{Nem})} \approx \sqrt{(\Delta n_{biax}/0.185)}$, with the result shown in Fig. S16E. At a particular temperature, the range of values of $\delta \theta(y)$ as a periodic function will depend on the waveform of $\delta \theta(y)$. For example, if $\delta \theta(y)$ is a square wave, then its peak amplitudes $\delta \theta_p = \delta \theta_{RMS}$ and $\delta \theta_p \sim 4^\circ$. If $\delta \theta(y)$ is sinusoidal, then $\delta \theta_p = (\sqrt{2})\delta \theta_{RMS}$ and the peak amplitudes will be $\delta \theta_p \sim +\sim -6^\circ$ if the biaxiality is due solely to splay. However, the theoretical estimate outlined in the main text shows that splay modulation is strongly suppressed by electrostatic interactions in the SmZ$_A$ and N$_F$ phases (Fig. 2E1,2). This biaxiality indicates anisotropy of molecular orientational distribution, some combination of: (a) a quadrupolar azimuthal distribution of the lath-shaped molecules about their long axis; and/or (b) a splay orientational modulation of the long axes, rotating them
about \( \ell \), as in Figs. 2E, 4D, having a peak rotation amplitude of \( \delta \theta_p < +/-6^\circ \), as discussed in detail in SI Sec. S8. However, a theoretical estimate in Sec. S7 below shows that splay modulation is strongly suppressed by electrostatic interactions in the SmZA and \( N_f \) phases (see Fig. 2E and discussion in text).

Referring to Fig. 2E Other biaxial smectic structures, such as the SmC, sketched in E3) have spontaneous antiferroelectric polarization in the tilt plane [45,46] as well as splay modulation [47,48], but in different geometries.
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