Multiple ferroelectric nematic phases of a highly polar liquid crystal compound

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ABSTRACT

Ferroelectric nematic liquid crystals represent not only fascinating, fundamental science, but they also hold promise for new technologies including high-density power storage or sub-millisecond switching information displays. In this work, we describe the synthesis and measurements of the physical properties of a new compound, 4-nitrophenyl 4-[(2,4-dimethoxybenzoyl)oxy]-2-fluoro-benzoate (RT11001). This material exhibits multiple, highly polar, ferroelectric nematic phases that have not been previously reported. We employ a wide range of physical characterisation methods including differential scanning calorimetry (DSC), mass density measurement, optical birefringence, polarising optical microscopy (POM), dielectric spectroscopy, electric current analysis, electro-optical switching, small-angle and wide-angle x-ray scattering measurements to show that RT11001 has multiple, distinct ferroelectric phases. We argue that the highest temperature phase is a polar nematic fluid with non-polar smectic clusters. Directly below appears to be a transition to another polar nematic phase containing polar positionally ordered clusters. Lastly, there are indications of an additional, polar biaxial liquid crystal phase at lower temperatures.

1. Introduction

Uniaxial nematic liquid crystal materials are anisotropic fluids with a single optical axis; this axis may be reversibly reoriented under the influence of an AC electric field when the dielectric tensor is also anisotropic. Moreover, the long-range order in nematic states is only orientational; long-range positional correlations are absent. The ability to change optical properties with a small electric field has made nematic liquid crystals the dominant technology for electronic information display, such as today’s flat panel displays. Over the last 130 years, several other nematic liquid crystal states,
such as chiral [1,2] biaxial [3] and twist-bend nematic phases [4] have been both predicted and observed. Although in bent-core nematic [5] materials there are indications of the presence of microscopic ferroelectric smectic clusters [6], until recently no nematic liquid crystals have been found to be macroscopically polar. This is surprising given that the first mean-field theory of the nematic-isotropic transition (proposed by Born in 1916) envisioned strong dipole–dipole interactions leading to polar ordering in nematic liquid crystals [7].

It was later predicted that moderate electric dipole interactions between disk-shaped molecules may be sufficient to induce a ferroelectric nematic phase [8]. However, there were no unequivocal experimental indications of a fluid ferroelectric nematic phase until Nishikawa et al. [9] reported a polar nematic phase formed by a rod-shaped molecule (abbreviated as DIO) having a large dipole moment; this phase showed a polarisation up to 5 µC/cm² and dielectric constant of ε~10⁴ at 1 kHz. In addition, Mandle et al. reported a nematic-nematic transition in a thermotropic compound (referred to as RM734) having molecular dipole moment of about 10 Debye [10,11]. The lower temperature nematic phase was subsequently identified as the splay nematic phase [12], with the splay deformation being the result of polar molecular ordering and with a dielectric constant approaching ε ~ 10⁴ at 100 Hz [13]. More recently, Chen et al. proposed that this compound’s polar nature does not induce a spontaneous splay deformation, but rather that the lower temperature phase is a uniform ferroelectric nematic phase with a spontaneous polarisation as high as 6 µC/cm² [14].

Ferroelectric nematic liquid crystals are not only extremely interesting from the point of view of basic science, but they are also promising for high energy and high power density capacitors [15] and for novel information displays capable of sub-millisecond electro-optic responses [16]. All of these seminal developments make the synthesis and characterisation of a wide-range of new ferroelectric nematic liquid crystal materials very significant.

A widely studied class of compounds exhibiting multiple nematic phases (including the ferroelectric nematic phase) are 4-nitrophenyl 4-[(2,4-dialkoxybenzoyl)oxy]-2-fluorobenzoate (RT11001). This acid chloride was reacted with commercial 2-fluoro-4-hydroxybenzaldehyde to provide the two-ring phenyl benzoate ester bearing the aldehyde group. In the subsequent step, we chose to oxidise the aldehyde to the carboxylic acid with Ozone [17]. All of these initial steps were efficient and did not require any significant intervention with crystallisation or chromatography. In the final step the two-ring phenyl benzoate ester now bearing a carboxylic acid group was esterified with 4-nitrophenol. Amongst the many options available [18,19] to perform the esterification we chose general Steglich conditions (DCC/DMAP) to create the final three-ring diester. At this stage chromatography and recrystallisation were required to obtain the final product in a high state of purity. The spectroscopic data obtained for the intermediates and the final product (see Supplemental Online Material) all concurred with expectations and comparisons with similar reported structures.

The DSC scans were run in an aluminium pan under a nitrogen atmosphere. The main pane in Figure 1 show the DSC curves recorded in the third heating and cooling of RT11001 cycle at 5°C/min rate. At

2. Material and methods

2.1. Material synthesis

The thermotropic compound RT11001 was synthesised in four steps as outlined in the scheme shown in the inset of Figure 1 and generally follows the route prescribed by Mandle [10] with modifications noted.

Commercial 2,4-dimethoxybenzoic acid was converted to the acid chloride with excess oxalyl chloride. This acid chloride was reacted with commercial 2-fluoro-4-hydroxybenzaldehyde to provide the two-ring phenyl benzoate ester bearing the aldehyde group. In the subsequent step, we chose to oxidise the aldehyde to the carboxylic acid with Ozone [17]. All of these initial steps were efficient and did not require any significant intervention with crystallisation or chromatography. In the final step the two-ring phenyl benzoate ester now bearing a carboxylic acid group was esterified with 4-nitrophenol. Amongst the many options available [18,19] to perform the esterification we chose general Steglich conditions (DCC/DMAP) to create the final three-ring diester. At this stage chromatography and recrystallisation were required to obtain the final product in a high state of purity. The spectroscopic data obtained for the intermediates and the final product (see Supplemental Online Material) all concurred with expectations and comparisons with similar reported structures.

The DSC scans were run in an aluminium pan under a nitrogen atmosphere. The main pane in Figure 1 show the DSC curves recorded in the third heating and cooling of RT11001 cycle at 5°C/min rate. At
room temperature, RT11001 is crystalline; during heating, two distinct peaks were observed: an exothermic peak at 92°C (ΔH = 15.28 J/g), and an endothermic peak at 161.9°C (ΔH = 100.9 J/g). During cooling, four distinct peaks were observed. The first transition observed at 163°C (ΔH = 1.13 J/g) corresponds to the transition from the isotropic to a nematic phase. The second sharp peak is observed at 140.5°C (ΔH = 3.2 J/g). It is followed by a broad peak at 93.3°C (ΔH = 10.23 J/g) indicating phase coexistence, and another one at 67.5°C (ΔH = 36.16 J/g) marking transition to a crystal phase. We note that very recently, Brown et al. has also published the synthesis of the same material among several others [20]. The NMR characterisation data for the RT11001 and the corresponding NMR characterisation data of Compound 2 and the carboxylic acid precursor in Ref. [20] are very similar. After that, the synthesis followed by Brown et al. [20] is different from the approach we used, but RT11001 and compound 2 of Ref. [20] appear identical based on spectroscopic evidence. Despite this, the phase sequences reported are different in that they report only one polar phase without giving its range. We cannot comment on the difference, because unlike us, they have not provided any DSC scan, electric polarisation, electro-optical switching, and X-ray measurements that we describe below.

2.2. Experimental methods

Electric current measurements were done using triangular and rectangular waveform electric signals that were generated using a HP 33120A function generator and amplified by an FLC F20AD amplifier. The current was monitored using a 20kΩ resistor in series. The usual sandwich cell geometry does not provide the full polarisation because when the field between the substrates rotates the polarisation towards the field by an angle θ, the polarisation vector has a component $P_\perp = P_0 \cdot \sin \theta$ that terminates at the insulating substrates. Consequently, an internal electric field $E_{in} = \frac{P_0 \sin \theta}{\varepsilon (\varepsilon_\parallel \cos^2 \theta + \varepsilon_\perp \sin^2 \theta)}$ builds up, where $\varepsilon_\parallel$ and $\varepsilon_\perp$ are the dielectric constants parallel and perpendicular to the director. This field acts against the externally applied field $V/d$ that has to overcome the maximum of the internal field $E_{in}^{max} = \frac{P_0}{2\varepsilon_\parallel} \cdot \frac{1}{\sqrt{\varepsilon_\parallel - \varepsilon_\perp}}$ so that $V - E_{in}^{max} \cdot d \geq V_s$, where $V_s$ is the voltage needed to switch the polarization. Assuming $\varepsilon = \varepsilon_\parallel - \varepsilon_\perp > 10^3 \gg \varepsilon_\perp$ and polarisation $P_0 = 6 \cdot 10^{-2} \frac{C}{m^2}$ (as found for RM737 and DIO with similar dipole moments), we estimate $E_{in}^{max} = 20 \frac{V}{\mu m}$. For $d = 10\mu m$ thick-sandwich cells, this gives $V_{in}^{max} = 200 V$, which is larger than we could apply without causing formation of air bubbles and burn damage to the samples. For this reason, the electric current induced by an in-plane electric field was measured as described in Ref. [14]. We
used cells having planar alignment with the in-plane field applied between 2-mm-wide parallel, conductive stripes (2 mm wide) separated by 1 mm gap, deposited on only one plate. As the film thickness \( d = 10 \mu m \) is much smaller than of the 1\( mm \) gap between the electrodes, we can assume that the net polarisation charge \( Q \) appearing on the in-plane electrodes is independent of the size of the electrodes and is determined only by the area \( A = 1cm \times 10\mu m = 10^{-7} m^2 \) (length of the electrodes multiplied by the film thickness) normal to the polarisation vector, as \( Q = P \cdot A \). We also used the in-plane cell geometry to measure the temperature dependence of the switching voltage, \( V_s \), the saturated polarisation, \( P_s \), and the switching time, \( \tau \).

Measurement of the dielectric permittivity \( \varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) \) have been performed in the frequency range of 20\( Hz \) – 10\( MHz \) at 30 mV applied voltage with a HP2194 LCR meter using gold coated glass sandwich cells (cell gap: 20.5 \( \mu m \), measuring area: 0.64 \( cm^2 \)). The gold makes homeotropic alignment, thus allowing to measure the dielectric permittivity parallel to the long axis \( (\varepsilon_||) \) [13].

For polarised Optical Microscopy (POM) measurements, the sample cell was placed in an Instec HS2000 heat stage and viewed through crossed polarisers with an Olympus Bx60 microscope.

The birefringence measurements were done using standard photo-elastic modulator techniques at wavelength \( \lambda = 632.8 nm \). This technique directly measures the phase difference between the ordinary and extra ordinary rays, \( \varphi = \frac{4\pi n d}{\lambda} \), where \( \Delta n \) is the birefringence and \( d \) is the cell thickness. The data was taken during cooling at 0.2K/min.

Relative density measurements were done by placing the material in a rectangular borosilicate glass capillary with 50 \( \mu m \) inner thickness and monitoring the meniscus position as the entire capillary was cooled at 1°C/min. The temperature dependence of the LC-air interface was measured at three points as shown by blue arrows in the inset to Figure S3, and the average values were used to determine the temperature dependence of the density normalised to the density measured in the isotropic phase at 165°C.

Simultaneous Small-angle X-ray scattering (SAXS) and Wide-angle X-ray scattering (WAXS) measurements were carried out at the CMS beamline 11-BM at NSLS II in Brookhaven National Laboratory with 17 keV X-ray energy and the adjustable beam size of 0.2\( mm \) \( H \times 0.2\( mm \). Samples were loaded in 2 mm diameter quartz capillaries and placed in a customised Instec hot stage equipped with SmCo magnets, which produced 1.5 Tesla magnetic field across the sample to align the nematic director. 2D SAXS and WAXS patterns were recorded on a Pilatus 2 M and Pilatus 1 M detector (Dectris, Inc.) at 2 m and 259 mm distance from the sample, respectively, as seen in Figure 2(a). The bottom left corner of the WAXS detector has an empty hole allowing the scattered beam to reach the SAXS detector (see Figure 2(b)). The sample was heated to the isotropic phase and cooled slowly into the liquid crystal phases, where SAXS and WAXS data were taken.

3 Results

3.1 Electric properties

The electric current responses under various triangular waveforms applied in-plane are shown in the inset to Figure 3. The temperature dependence of the saturation voltage, \( V_s = E \cdot d \), at which point the polarisation current peak reverts to the background signal, is plotted in the main pane of Figure 3. Below 140.5°C \( V_s \) slowly increases on cooling from 43 V to 53 V, then sharply increases at 113°C to reach a plateau of about 0.09 V/\( \mu m \). At 99°C that corresponds to onset of the broad DSC peak with about \( V_s \) transition enthalpy (see Figure 1), the saturation voltage sharply increases and reaches the maximum voltage that we could apply with our power supply. The changes observed in the temperature

![Figure 2](https://example.com/figure2.png) (Colour online) Instrument setup of X-ray experiment: (a) the SAXS and WAXS measurement setup. The distances from the sample to WAXS and SAXS directors were 259 mm and 2 m respectively. (b) A schematic illustration of the WAXS detector with a hole. The x-rays scattered at small angles pass through this hole and are capture by the SAXS detector.
dependence of \( V_s \), indicates a second-order phase transition at 113°C between a higher and lower temperature range ferroelectric nematic state, which we shall call \( N_{F1} \) and \( N_{F2} \), respectively. The sharply increasing voltage needed for polarisation switching below 100°C in correlation with the broad DSC peak may indicate the formation of some order that hinders the director rotation.

The applied voltage dependence of the effective polarisation (the integral area above the background line as shown in the inset to Figure 3) at a few selected temperatures are shown in the inset to Figure 4. At low voltages the slopes are very small, then they increase at moderate voltages and reach saturation at \( V_s \) where the polarisation, that is, the switching is completed. This behaviour indicates a soft antiferroelectric-type arrangement at low voltages, due to presence of domains with oppositely aligned polarisation.

The temperature dependence of the saturated ferroelectric polarisation corresponding to the area under the peak in the electric current (see shaded area in the inset of Figure 3) is shown in Figure 4. The polarisation continuously increases from zero at 140°C to about 5.8μC/cm² at 113°C then increases further and reaches a value of 6.9 μC/cm² at 90°C. The temperature where the additional increase is observed coincides with the temperature where \( V_s \) increased sharply just reinforcing the conclusion about the second order phase transition between two ferroelectric nematic phases. Note that the highest value of the polarisation is slightly larger than that previously reported on materials purported to be \( V_s \) [9,14]. Notably, in contrast to the rapid increase of \( V_s \) measured below 100°C the saturated polarisation values do not reveal any transition.

The time dependence of the electric current induced by polarisation switching was measured at various temperatures by 200 Hz square-wave voltage of \( V_{p-p} = 130 \text{ V} \) applied between in-plane electrodes separated by 1 mm spacing. Results are shown in the inset to Figure 5. As was found by Chen et al. [14], the rise time \( \tau \) (the time until the polarisation current reached 90% of its maximum) is proportional to the polarisation reversal time \( \Delta T \) taken as the FWHM of the polarisation current peak (see inset to Figure 5). For RT11001 at 130 \( V_{p-p} \) we find \( \tau = 0.2 \times \Delta T \). The temperature dependence of \( \tau \) is plotted against the left axis of Figure 5. On cooling from 140°C to 90°C the rise time increases from 20 μs to 200 μs. The curve does show changes in the slopes at the same temperatures where DSC peaks occur at around 113°C and 100°C (see Figure 1).

The rotational viscosity \( \gamma_1 \) estimated from the rise time as \( \tau \sim \gamma_1 / P_s E \) [21] was found to increase monotonically in the \( N_{F1} \) phase between 140°C and 113°C from ~10 mPa·s to ~100 mPa·s, which is typical for low molecular weight nematic fluids. The
increase becomes more pronounced below 113°C when it increases to about 0.4 Pa·s. Below 100°C the slope $\frac{dy_1}{dT}$ increases to about 0.2 Pa·s/K, indicating the onset of a short-range translational order.

The frequency dependences of the parallel component of the relative dielectric constant $\varepsilon_\parallel$ was measured in 20 µm gold-coated sandwich cells that provide homeotropic alignment \[13\] at various temperatures under 30 mV voltages. The frequency dependences of
the imaginary part of the dielectric constant $\varepsilon$ at various temperatures are shown in Figure 6(a). One can see that the amplitudes of the peaks corresponding to the half of the susceptibility of the molecular flip-flop relaxation mode are almost constant ($\sim 6 \cdot 10^4$) in the entire $N_{F1}$ and $N_{F2}$ phase range indicating that the susceptibility of the dipole flipping is $\sim 1.2 \cdot 10^4$. The susceptibility then decreases below 100°C that well corresponds to the range where the saturation voltage and rotational viscosity was found to increase sharply, indicating some additional order. It is worthwhile to note that in this $N_{F3}$ temperature range there is an additional relaxation mode at the kHz frequency range (see the green arrow indicating it at 82°C). We also point out that at high temperatures $\varepsilon''$ strongly increases towards lower frequencies, which is likely related to electric conductivity. The relaxation frequencies $f_1$ and $f_2$ (the fitted peak positions of $\varepsilon''$ as shown in the inset) are plotted at the function of temperature in Figure 6(b). In the nematic phase the relaxation frequency $f_1$ decreases rapidly from 600 kHz to 10 kHz before it transitions to the $N_{F1}$ phase indicating that the flipping of the molecular dipoles becomes increasingly collective process. In the $N_{F1}$ phase $f_1$ decreases to about 3 kHz from 140°C to 130°C then stays constant until 113°C that marks the transition to the $N_{F2}$ phase. Such relaxation frequencies are in the same order as of the Goldstone mode of the ferroelectric SmC* materials corresponding to the collective rotation of the ferroelectric polarisation [22]. In the $N_{F2}$ phase $f_1$ slowly decreases to 1 kHz, then the rate of decrease amplifies upon transitioning to the $N_{F3}$, falling to about 40 Hz at 73°C. The temperature dependence of the second relaxation frequency $f_2$ that appears in the $N_{F3}$ phase is shown by red dots in Figure 6(b).

Figure S1 of the SOM shows the frequency dependences of $\varepsilon''$ at various temperatures showing that at low frequencies it reaches about $2 \cdot 10^4$ in the $N_{F1}$ and $N_{F2}$ phases. Such values are comparable to those measured on RM734 [13] and DIO [9] and are about twice of Compound 2 of Brown et al. [20].

3.2. Optical measurements

Representative polarised optical microscopy (POM) textures of RT11001 in a 10-μm-thick cell with planar alignment are presented in Figure S2 of Supplemental Online Material (SOM). Upper images show the textures in heating. The left image represents a crystal phase at 58°C. In agreement with the exothermic peak in DSC, at 92°C there is a phase change to a low birefringence state shown in the middle image at 98°C. This texture does not change until 161°C when it transitions to a uniformly aligned uniaxial nematic phase, as shown at 161°C in the top-right corner of Figure S2 of SOM. Lower images show three representative textures below 140.5°C at 128°C (right), 104°C (middle) and 94°C (left). All three are similar, showing stripes roughly parallel to the rubbing direction. The thickness of the walls separating the uniform birefringence stripes increases on cooling, being approximately 5 μm, 10 μm and 20 μm at 128°C, 104°C and 94°C, respectively. Other than the width of the defect walls, the textures do not change upon temperature decrease until 67.5°C at which point a low birefringent crystalline texture shown in the inset of Figure S5 appear.

Figure S3 shows the temperature dependence of the birefringence and the relative mass density. As the temperature is decreased, Δ$n$ increases from zero to 0.12 from 164°C to 140°C in the nematic range, then
increases sharply up to 0.14 within a 1°C range below 140.5°C where the DSC shows a phase transition, then increases smoothly up to 0.2 at 90°C Figure S3 also shows relative density measurements that reveal an abrupt increase upon cooling to the $I-N$ transition and then a fairly linear increase between 160°C and 140.5°C. At 140.5°C there is an abrupt change in the slope $dp/dT$. The slope then remains roughly constant until about 113°C where there is an additional small increase (see Figure 1).

Figure 7 presents POM textures of 10 µm RT11001 films in the vicinity of the $N-N_{F1}$ transition. Figure 7 (a and d) represent textures at 140.3°C showing the first-order $N-N_{F1}$ transition with the uniform nematic texture at the top-right and the $N_{F1}$ phase with grainy texture at the bottom-left. Note that in the planar cell the nematic phase has a uniform birefringent texture, while in a homeotropic cell the nematic texture is dark between crossed polarisers. The $N_{F1}$ phase, however, has a grainy birefringent texture in both alignments, indicating that the homeotropic alignment is not achieved. The textures in Figure 7 (b and e) at 139.6°C show annealing of the grains to a more uniform texture with fine stripes parallel to the rubbing direction for the unidirectionally antiparallel rubbed planar cell (Figure 7), while in the non-rubbed homeotropic cell the stripes have random directions (Figure 7). The planar texture in Figure 7 at 138°C shows a fully annealed texture with about 100 µm wide uniform domains separated by defect walls that are about 10µm thick. At 2°C below the $N-N_{F1}$ phase transition, the optical path difference (estimated from the Michel-Levy chart) is $\Delta n \cdot d \sim 1600\, nm$, which corresponds to a birefringence of $\Delta n \sim 0.16$. This value is lower than that reported for RM734 [14] (~0.22) but is in agreement with our direct birefringence measurements in Figure S3. The texture in the homeotropic cell in Figure 7 at 138°C shows a birefringence colour comparable to that seen in Figure 7 for the planar cell, indicating degenerate planar alignment on the homeotropic substrates.

The stripes separated by defect walls shown in Figure 7 are similar to those observed by Chen et al. [14] where the stripes were described as domains with alternating directions of ferroelectric polarisation. To verify this in RT11001, we applied a small ($\pm 10^{-4}$ V/µm) in-plane, DC electric field and compared the stripe textures. As seen in Figure 7, under zero field, adjacent stripes appear the same (similar to Figure 7). When the

**Figure 7.** (Colour online) POM textures of 10 µm cells of RT11001 at and a few degrees below the transition from the N phase after cooling from the isotropic state. (a-c) Planar alignment (SE2170 without ITO) cooling rate: 0.5°C/min. Axis with double arrowheads indicate rubbing direction (R); (d-f) Homeotropic alignment (SE5661 without ITO), cooling rate: 1°C/min. (g-i) POM textures of the film at 130°C under in-plane electric fields. Left: $E=0$. Uniform birefringence colours separated by about 10–15 µm thick defect walls, middle and right: $E=\pm 1$V/cm electric field applied in the direction of yellow arrows.
field is applied, we see slight differences of the colour between adjacent stripes; these changes alternate when the field is reversed. We note that this field is too small to induce a switching of the polarisation direction and we attribute these observations to the enhancement/suppression of the polar order (and hence the birefringence) when the electric field is aligned/opposite with the polarisation direction. In addition, under prolonged application of the DC field we also observe a slight reduction in the width of stripes having lower birefringence, indicating a slow realignment of the polarisation; this realignment presumably takes place within the defect walls. This antiparallel arrangement of the polarisation in adjacent stripes can explain the low (antiferroelectric-type) slope of the voltage dependence of the effective polarisation shown in the inset to Figure 4.

3.3. X-ray measurements

Small-angle and wide-angle X-ray scattering (SAXS/WAXS) measurements were carried out on the CMS beamline (11-BM) at NSLS2 to investigate any structural differences amongst the different ferroelectric nematic phases. Typical 2D WAXS and SAXS scattering patterns are shown in the bottom left and top right areas of Figure 8, respectively. The nematic director was magnetically aligned along the figure’s vertical direction. For this reason, the diffuse WAXS peaks arising from short-range lateral correlations between the molecules (and normal to the average long axis/director) are distributed along the horizontal, and the diffuse SAXS peaks due to positional correlations along the director are centred about the vertical.

Temperature dependences of the wave numbers \(q_s\) and \(q_{W1}\) corresponding to the maxima of the SAXS and WAXS peaks are plotted against the left and right axes, respectively, in Figure 8. In the isotropic phase the SAXS signal has a broad ring at 0.3 Å\(^{-1}\) corresponding to a density modulation of Å, equivalent to the length of the molecules. On cooling to the \(N\) phase the value of \(q_s\) only slightly increases, and the maximum intensity is concentrated along the magnetically aligned director, as can be seen in Figure S4. A sharper increase in \(q_s\) from 0.300Å\(^{-1}\) to 0.306Å\(^{-1}\) (corresponding to a decrease in average intermolecular spacing of 0.47Å) occurs upon the \(N\) – \(N_{F1}\) transition. At the same time, the SAXS intensity spreads over a −30° to +30° range from the vertical axis, and the 2D SAXS diffraction pattern changes from an arc (with maximum intensity along the director) to a horizontally extended, ‘peanut’-like shape. This and the decreased layer spacing indicate short-range positional correlations (i.e. cybotactic groups) and a transition from smectic-A to smectic-C correlations, with tilt angles varying up to ~30°. As the temperature is lowered further, \(q_s\) remains approximately constant until ~113°C whereupon it increases by an additional 0.003Å\(^{-1}\), signalling the \(N_{F1}\) – \(N_{F2}\) transition. Such increase indicates further decrease of the smectic layer spacing in the clusters, which can be interpreted as

![Figure 8](https://example.com/figure8.png)

**Figure 8.** (Colour online) Summary of the x-ray measurements. Temperature dependence of the q-values at the maximum scattering intensities plotted against the left and right axes for the SAXS and WAXS signals (red triangle and blue dots), respectively. Insets in the bottom left and top right areas show typical 2D WAXS and SAXS scattering patterns, respectively, at different temperatures.
an increased tilt angle at the $N_{F1} - N_{F2}$ transition. Concurrently, the scattering intensity decreases along the vertical axis and increases at the $\pm 30^\circ$ angular positions from this axis. The value of $q_s$ slightly increases (by $\sim 0.002$ Å$^{-1}$) on cooling in the $N_{F2}$ range, then $q_s$ becomes essentially constant below around 100°C that coincides with the onset of the broad DSC peak.

The WAXS peak of RT11001, in agreement with measurements reported for RM734 [23], cannot be fitted by a single Gaussian, but appears to be a combination of two diffuse peaks (see inset on the top-left corner of Figure S5); these are indicated with arrows on the pattern insets in Figure 8. The wave vector $q_{w2}$ of the weaker peak has lower values that increase from $q_{w2} \sim 1$ Å$^{-1}$ (corresponding to a lateral $d$-spacing of about 6 Å) in the isotropic phase to $q_{w2} \sim 1.2$ Å$^{-1}$ (corresponding to $\sim 5.2$ Å) in the $N_F$ phases. These spacings are larger than the diameter of the benzene ring, indicating separation between molecules consistent with free rotation around their long axis, that is, a uniaxial nematic. The temperature dependence of $q_{w1}$ of the higher intensity peak is plotted in Figure 8. In contrast to RM734, in our case the height of the peak with higher $q$ values is larger in all fluid phases, and both the magnitude and the position of the larger peak increases on cooling. It shows distinct increases at both the $N - N_{F1}$ and $N_{F1} - N_{F2}$ transitions and another at 93°C that coincides with the peak position of the broad DSC peak seen in Figure 1. This strongly indicates that the form factor changes (perhaps from circular cross-section to elliptical), that could be assigned to the increasing biaxial packing. Importantly, the WAXS peaks are still broad even between 100°C and 68°C proving that it is still a nematic phase. Additionally, we could measure the ferroelectric polarisation down to 90°C (see Figure 4), therefore, in agreement with our assignment based on dielectric studies, we can denote this phase as $N_{F3}$.

In the isotropic and nematic phases $q_{w1} \cong 1.51$ Å$^{-1}$ corresponding to a $d$-spacing of 4.15 Å. This value is smaller than that Mertelj et al. [12] measured for RM734 ($\sim 5.5$ Å) and decreases considerably upon cooling, unlike RM734 where it was found to be basically temperature independent. At the $N - N_{F1}$ transition, the value of $q_{w1}$ increases to $1.57$ Å$^{-1}$ (giving a $d$-spacing of 4.0 Å) and at the $N_{F1} - N_{F2}$ transition it increases further to $1.61$ Å$^{-1}$ ($d = 3.90$ Å). On further cooling $q_{w1}$ increases up to $1.66$ Å$^{-1}$ ($d = 3.78$ Å) at 68°C when it transitions to the crystal phase that shows a weakly birefringent, grainy texture (see inset on the bottom-left corner of Figure S5). The intermolecular distances corresponding to the $q_{w1}$ peaks are clearly less than values that would allow free rotation of the molecules around their long axes, indicating increasingly biaxial ordering on cooling through the $N_{F1}$, $N_{F2}$ and $N_{F3}$. From the full width at half maxima (FWHM) of the WAXS peaks we estimate that the correlation length normal to the director increases to about 2 nm in the $N_{F3}$, meaning short (about 5-6 molecules) range positional ordering normal to the director.

Figure S5 also shows the WAXS peaks in the Cr-phase below 68°C where the molecular alignment is lost and the 2D WAXS pattern features rings with peaks at 0.94 Å$^{-1}$, 1.12 Å$^{-1}$, 1.71 Å$^{-1}$ and 1.93 Å$^{-1}$ corresponding to a rectangular lattice with edge lengths of 6.62 Å and 3.67 Å.

4. Discussion

Our experimental results indicate that RT11001 exhibits multiple, distinct, fluid-like ferroelectric phases below the ordinary, non-polar, nematic phase. Since RT 11001 differ from RM734 (that has only one $N_F$ phase) only by one fluorine atom that replaces one hydrogen atom, it maybe unexpected. However, considering that in RM734 a methoxy group replacing one hydrogen atom of benzoic acid, 2,4-dimethoxy-, 4-[(4-nitrophenoxy)carbonyl]phenyl ester (ARES2-N02) [24], in which no $N_F$ phase has been reported, it may not be surprising. The observation of polarisation switching, and the absence of long-range translational order indicates that all these phases are nematic. Based on the DSC, the $N_{F1} - N_{F2}$ transition is of second order, while the $N_{F2} - N_{F3}$ transition is first order with significant overlap between them. The temperature dependence of the field required to switch the polarisation, and the rotational viscosity and SAXS/WAXS results each show distinct behaviour in the individual ferroelectric phases.

The precise structural differences between these states are not yet established. One possible distinguishing feature among these phases could be the different degrees of the spontaneous splay deformation conjectured by Mertelj et al. [12] and Sebastian et al. [13] from elastic constant and optical measurements in RM734, and theoretically predicted by Rosseto and Selinger [25] and by Kats [26]. Accordingly, we could envision a proper non-modulated ferroelectric nematic ($N_F$) structure associated with the $N_F$ phase, as proposed by Chen et al [14]; a one-dimensionally splayed ferroelectric nematic ($N_{F1}$) structure for the $N_{SF}$ phase; and a two-dimensionally splayed nematic (NSF) structure for the $N_{SF}$ phase. Such a phase sequence is consistent with the increasing switching threshold and rotational viscosity we observe in RT11001. However, the theories [12,25,26] predict $N_{2SF} - N_{SF} - N_F$ sequence on
cooling, and in the splay modulation scenario one would also expect to see a decrease in the birefringence upon both a $N_F - N_{F1}$ and a $N_{F1} - N_{F2}$ transition, which is not the case for either transition observed in RT11001.

We conjecture that the multiple polar nematic phases are not distinguished by changes in the nematic director, because probes sensitive to optical anisotropy do not find measurable signatures at the phase transition temperatures. This is understandable if these phases are distinct due to variations in molecular correlation in direction(s) normal to the director. Furthermore, the temperature dependence of the density, spontaneous electric polarisation measurements clearly show the $N_{F1}$ to $N_{F2}$ transition, but not the $N_{F2}$ to $N_{F3}$ transition. This behaviour indicates an increase in dipole density in the plane perpendicular to the polarisation vector upon entering the second polar phase, which is manifested as an increase of both the polarisation and of the mass density. The rotational viscosity and the switching field show stepwise increases at the $N_{F1} - N_{F2}$ transition, which also suggests that the molecules pack more densely in the directions normal to the director at this transition.

Moreover, our WAXS measurements reveal the presence of two characteristic spatial correlations in the direction normal to the molecular long axes (and hence the polarisation vector). The first is large enough to allow free rotation of the molecules about their long axis. The second is considerably smaller (small enough to restrict rotation) and shows abrupt decreases at the $N - N_{F1}$, $N_{F3} - N_{F2}$, and $N_{F1} - N_{F2}$ phase transition temperatures. This behaviour can be understood by the presence of smectic-like, cybotactict groups. We envision that at higher temperatures these groups transition from apolar to polar order, which provides closer packing between the polar nitro groups and as the temperature decreases, a transition from normal smectic to tilted smectic cybotactic clusters, where the tilt biases the free rotation along the molecular axis so that it favours the $\pi - \pi$ stacking; the latter clusters are of course biaxial.

Based on the above points, we conjecture the following structural distinctions among the nematic phases of RT11001. The ordinary $N$ phase exhibits cybotactic groups; these groups possess only short range, non-polar, smectic-A type positional order (see Figure 9(a)). The $N_{F1}$ phase has long range polar nematic order, but the ordering of the clusters is non-polar, as in the N phase. The onset of the $N_{F2}$ phase corresponds to the clusters transitioning to polar order. This may explain the ~10% increase of the ferroelectric polarisation measured upon the $N_{F1} - N_{F2}$ phase transition (Figure 4) and indicates the volume of the clusters is about 10% of the entire material. Such a change does not affect measurably the birefringence and density in agreement with measurements in Figure S2. The ratio of the tilted and non-tilted clusters does not change during the $N_{F2} - N_{F3}$ transition, but their volume fraction seems to increase strongly on cooling below the transition, which does not change the amount of the total polar volume, therefore, does not measurably affect the macroscopic polarisation, but only the switching threshold and switching time will increase in agreement with our results. During the $N_{F2} - N_{F3}$ transition, the structure of the smectic cybotactic clusters do not change, but only their number.

**Figure 9.** (Colour online) Schematic illustration of the building blocks present in the different phase. (a) The N phase contains continuous non-polar nematic medium and non-polar smectic clusters with non-tilted clusters being in the majority; (b) The $N_{F1}$ phase is characterised by polar nematic fluid medium and non-polar non-tilted and tilted smectic clusters; (c) The $N_{F2}$ phase has polar nematic medium and the mixture of polar non-tilted and tilted smectic clusters with the tilted clusters being in the majority.
5. Conclusions

In this work, we describe the synthesis and measurements of the physical properties of a new highly polar ferroelectric nematic compound, 4-nitrophenyl 4-[(2,4-dimethoxybenzoyl)oxy]-2-fluorobenzoate (RT11001). The combination of DSC, mass density measurement, optical birefringence, POM, dielectric spectroscopy, electric current analysis, electro-optical switching, small-angle, and wide-angle x-ray scattering measurements show that RT11001 has three distinct ferroelectric states, \( N_{F1}, N_{F2}, N_{F3} \). The \( N_{F1}(N_{F2}) \) phase is a polar nematic phase containing non-polar (polar) smectic clusters. \( N_{F3} \) seems to be a biaxial polar nematic phase due to the result of the increasing number of tilted (biaxial) smectic clusters.

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Disclosure statement

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