Ideal mixing of paraelectric and ferroelectric nematic phases in liquid crystals of distinct molecular species

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ABSTRACT
The organic mesogens RM734 and DIO are members of separate molecular families featuring distinct molecular structures. These families are the first ones known to exhibit a ferroelectric nematic liquid crystal phase. Here, we present an experimental investigation of the phase diagram and electro-optics of binary mixtures of RM734 and DIO. We observe paraelectric nematic and ferroelectric nematic phases in both materials, each of which exhibits complete miscibility across the phase diagram, showing that the paraelectric and ferroelectric are the same phases in RM734 and DIO. Remarkably, these molecules form ideal mixtures with respect to both the paraelectric–ferroelectric nematic phase behaviour and the ferroelectric polarization density of the mixtures, the principal order parameter of the transition. Ideal mixing is also manifested in the orientational viscosity, and the onset of glassy dynamics at low temperature. This behaviour is attributable in part to the similarity of their overall molecular shape and net longitudinal dipole moment, and to a common tendency for head-to-tail molecular association. In contrast, the significant difference in molecular structures leads to poor solubility in the crystal phases, enhancing the stability of the ferroelectric nematic phase at low temperature in the mixtures and enabling room-temperature electro-optic effects.

Introduction
Ferroelectricity in liquids was predicted in the 1910s by P. Debye [1] and M. Born [2], who applied the Langevin-Weiss model of ferromagnetism to the orientational ordering of molecular electric dipoles. A century later, in 2017, two groups independently reported novel nematic phases of polar molecules, the antiferroelectric splay nematic in the molecule RM734 [3–5] and a ‘ferroelectric-like’ phase in the molecule DIO [6]. Ferroelectricity has subsequently been demonstrated in RM734 [7] and in DIO, as confirmed in our own experiments and by Li et al. [8]. The serendipity of this development is remarkable since, as is evident from Figure 1, RM734 and DIO are members of separate molecular families with distinctly different molecular structures. Novel polar nematics have been independently observed in close homologs and mixtures within these families.
[3,8–12]. On the other hand, DIO and RM734 have similar molecular shape and size, and both molecules have longitudinal molecular dipole moments of ~11 Debye, similarities which could favour their miscibility in an Nf phase.

These observations motivated us to pursue the study of the interactions between these distinct molecular species in the context of nematic ferroelectricity. Here, we present an experimental investigation of the phase and electro-optic behaviour of binary DIO/RM734 mixtures. Similarities in the optical textures, calorimetry, and second-harmonic generation of RM734 and DIO were recently reported by Li et al. [8], but the question of whether the ferroelectric nematics identified in RM734 and DIO are the same phase can be answered unambiguously only by investigating binary miscibility [13]. The phenomenology of mixing these materials in their ferroelectric nematic phases was unknown, but, because of their chemical differences, it appeared unlikely that these molecules would be very miscible in their crystal phases, promising an opportunity to suppress crystallisation and achieve room-temperature, ferroelectric mixtures. In relation to this study, we also investigated the M2 phase originally reported in DIO [6] but not structurally characterised. Synchrotron-based microbeam small-angle x-ray scattering (SAXS) and electro-optic polarised light microscopy show the M2 to be a lamellar, density-modulated antiferroelectric LC having a nematic director parallel to the layer planes, a phase which we term Smectic Z (SmZA) in work reported elsewhere [14].

Nematic ferroelectricity presents opportunities for novel liquid crystal science and technology thanks to its unique combination of macroscopic polar ordering and fluidity. The ferroelectric nematic (Nf) phase of RM734 shows a rapid electro-optic response at high temperature in the Nf range [15] but exhibits crystallisation and a viscosity that grows strongly on slow cooling. The room temperature Nf phase that is obtained by quenching, on the other hand, is glassy. In the applications development of liquid crystal technologies, the exploration of mixtures is a time-honoured and highly successful approach to addressing issues such as eliminating crystallisation [16], expanding phase ranges [17], and tuning liquid crystal properties [18]. Studies of mixtures are also key to advancing liquid crystal science, providing a way to test structural models of phases by continuously varying the composition [19], to find phases in mixtures that are not exhibited by any of their components [20,21], and to discover new phases [22].

**Results**

**Phase diagram**

RM734 and DIO were synthesised using, respectively, the schemes published in [7] and shown in Fig. S1. The phase diagram for different weight percent (wt %) of DIO in the mixture, c, determined upon slow cooling (at ~1K/min) from the isotropic (Iso) phase using polarised light microscopy (PLM) in transmission, differential scanning calorimetry (DSC), polarisation measurement, and SAXS experiments, is shown in **Figure 2**. A well-defined phase front passing through the cell was observed in the microscope at each of the transitions, allowing an accurate determination of the transition temperatures. The observed transition temperatures of the neat
components agree well with the published values [3,6]. Upon cooling the mixtures, we observed three different liquid crystal phases: paraelectric nematic (N); antiferroelectric smectic Z (SmZ\(_{\text{A}}\)); and ferroelectric nematic (N\(_{\text{F}}\)). We refer to the N phase as ‘paraelectric’ using the standard condensed matter terminology for the disordered phase above a ferroelectric or antiferroelectric. At the lowest temperatures, we observed crystal phases, but their properties and composition were not investigated. The Iso, N, and N\(_{\text{F}}\) phases appeared in continuous fashion across the entire phase diagram, indicating complete miscibility of the two components at all concentrations in these phases. According to the miscibility rule [13], this observation answers the question posed above, indicating that the Iso, N, and N\(_{\text{F}}\) phases in RM734 are the same phases as in DIO. The phase range of the SmZ\(_{\text{A}}\) (denoted M2 in [6]), about 15°C in neat DIO, is reduced with decreasing DIO concentration, disappearing below \(c \sim 50\) wt\%. As is evident from Figure 2, the phase boundary into the N\(_{\text{F}}\) is sloped and linear in \(c\), suggesting ideal mixing behaviour at this transition, as discussed in detail below.

Phase properties of note can be summarised as follows.

- **Isotropic Phase (Iso)** – The Iso phase shows extinction of transmitted light between crossed polariser and analyser and exhibits no detectable response to applied fields of up to 100 V/mm.

- **Paraelectric Nematic Phase (N)** – As expected, the N phase adopts planar alignment with a uniform, in-plane director field, \(n(r)\), parallel to the buffing direction. Excellent extinction is achieved when the cell is orientated with the director parallel to the polariser or analyser (Figure 4(a), S3B). Freedericksz transitions, driven by a 200 Hz square-wave field, were observed in the N phase (Fig. S3C), with in-plane fields generating a twist deformation of the director [RMS threshold voltage...
$V_{th}^T = 2\pi (D/d) \sqrt{K_T/(\epsilon_0 \Delta \epsilon)}$, and fields normal to the cell plates generating splay-bend deformation \cite{23}, where $D$ is the in-plane electrode gap, $K_T$ and $K_S$ are the twist and splay Frank elastic constants, and $\Delta \epsilon$ is the low-frequency dielectric anisotropy. The temperature dependence of the threshold voltages in RM734 and DIO is shown in Fig. S4. RM734 and DIO exhibit typical Freedericksx-like, thresholded orientational response to an applied field. Both RM734 and DIO exhibit a general increase in $\Delta \epsilon$ on cooling. In RM734, however, the Freedericksx thresholds are lower and decrease on approaching the transition to the $N_F$ phase due to the strong pretransitional growth of $\Delta \epsilon$ and decrease of $K_S$ \cite{4,5}, phenomena which do not occur in the N phase of DIO because in this material the nematic approaches an antiferroelectric phase on cooling. The observed splay threshold voltage of RM734 agrees well with $V_{th}^S$ calculated using the $K_S$ and $\Delta \epsilon$ values given in Refs. \cite{4,5}. Comparison of the measurements with the theoretical twist/splay threshold ratio enables an estimate of the elastic constant ratio $K_T/K_S$. The dashed lines in Fig. S4 give $V_{th}^S$ scaled up by 286, showing that $K_S > K_T$ in both materials, except near the N–N$_F$ transition in RM734, due to the pretransitional decrease of $K_S$ \cite{4,5}. In DIO, $K_S \sim 10K_T$ over most of the nematic range.

- **Lamellar Antiferroelectric LC with In-Plane Nematic Director (SmZ$_A$)** – We have recently determined, using non-resonant SAXS on magnetically aligned capillaries and PLM electro-optic measurements of aligned cells, that the previously reported \cite{6} but structurally uncharacterised M2 phase of DIO is a layered (density-modulated), antiferroelectric LC, which we name the smectic $Z_A$ (SmZ$_A$), comprising a periodic array of 9 nm thick, polar layers with alternating polarisation and a nematic director parallel to the layer planes \cite{14}. In cells, these layers fill three-dimensional space in well-defined, smectic-like geometries, with the layers either parallel or normal to the plates. Upon cooling from the N phase in a cell with buffed polyimide surfaces, the layers grow in normal to the plates, suppressing the in-plane twist Freedericksx response to fields applied in the plane of the cell but preserving the splay-bend Freedericksx transition for fields applied normal to the plates. These features make it easy to distinguish the SmZ$_A$ from both the N and N$_F$ phases.

- **Ferroelectric Nematic Phase ($N_F$)** – The textural evolution of the N$_F$ phase obtained on cooling a uniform domain of the SmZ$_A$ phase in neat DIO is shown in the PLM images of Figure 3 (a–d), and that on cooling a uniform domain of the N phase in the $c = 40$ wt\% DIO mixture in Figure 4, both in the absence of field. In addition to undergoing characteristic optical changes, the transition to the N$_F$ is marked by an increase in the threshold for the splay-bend Freedericksx transition, from a few tenths of a volt in the N phase to more than 100 V in the N$_F$ phase, a result of the large electrostatic energy cost of rotating the ferroelectric polarisation $P$ in an initially planar cell to give a component normal to the cell plates \cite{7}. At the same time, the threshold field for in-plane field-induced twist is reduced by about a factor of 1000 because of the development of ferroelectric coupling between $P$ and $E$ \cite{7}, giving extreme electro-optic responsivity to very weak applied in-plane electric fields (in the 0.1 to 1 V/mm range) in all of the N$_F$ director states shown. At the N to N$_F$ transition, a front characterised by local orientation fluctuations passes through the cell (Figure 4(b)), leaving behind a smooth, planar texture in the N$_F$ phase, retaining the uniform director field of the N (and SmZ$_A$) phases with $n$ parallel to the buffing axis (the $U$ state) for several degrees into the N$_F$ phase. On further cooling, however, a structural transition occurs, with distinct transition lines ($\pi$-twist disclination lines formed at one surface) passing laterally across the cell and mediating the formation of left- and right-handed ($LH$ and $RH$) $\pi$-twist domains, which are non-extinguishing and are themselves separated by another kind of distinct line defect ($2\pi$-twist lines in the cell midplane), seen in Figures 3(a) and 4(c). These twisted states appear optically identical between crossed polariser and analyser, but their equivalence is lost when the polarisers are decrossed, with the $LH$ and $RH$ domains exhibiting distinct colours that are exchanged when the polarisers are decrossed the other way (Figure 3(b–d)). This behaviour, first observed
in **ANTIPOLAR** cells of neat RM734 [15], indicates a spontaneous transformation of the uniform nematic director/polarisation state into a \( \pi \)-twisted state by passage of a \( \pi \)-twist line. This observation is critical and unambiguous confirmative evidence for nematic ferroelectricity: a spontaneous uniform to \( \pi \)-twisted transition in an antiparallel-buffed cell in the \( N_F \) phase is a uniquely ferroelectric nematic phenomenon, requiring not only macroscopic polar ordering of the bulk \( LC \) but also polar coupling to a macroscopically polar surface. The \( LH \) and \( RH \) \( \pi \)-twist states support, respectively, a half-turn of a left- or right-handed
director helix and are separated by topological $2\pi$-twist lines. The two twist states have opposite net polarisation, normal to the buffing axis, so that reversing an electric field applied in this direction can be used to switch between them, as shown in Figure 3(e-g). Such $\pi$-twist states are observed in all of the mixtures and in neat DIO, and show behaviour qualitatively similar to that observed in neat RM734 [7,15], leading us to conclude that the $N_F$ is continuous across the phase diagram. Li et al. have also noted similarities in RM734 and DIO textures observed in random-planar cells [8].

**Transition to the $N_F$ Phase**

This transition is distinctly different at the two ends of the phase diagram. In RM734-rich mixtures, upon approaching the $N - N_F$ transition, we observe a random pattern of fluctuating polar domains, as previously reported in neat RM734 [4,7] and shown in Figure 4(b). These domains are extended along the director orientation, $n$, in a manifestation of the electrostatic suppression of longitudinal fluctuations of the polarisation $P$ [7]. The details of coarsening of these domains upon cooling into the $N_F$ depends on the surface conditions, but in few-micron thick, rubbed polyimide cells the domains typically grow to several microns in size, eliminating defects in the texture and forming large, uniform monodomain and then twisted states [15]. In thicker or more weakly aligned cells, the length scale of the coarsening domains has been observed to increase continuously on cooling to millimetre dimensions [24], with irregular, macroscopic patterns of reversed polarisation extended along the director, as seen in RM734 [7,8,11,24] and in a homolog of DIO that transitions directly from N to $N_F$ [8]. In typical test cells, the uniform $N_F$ domains are separated either by pure polarisation reversal walls or by splay-bend walls [7,8]. This behaviour, along with the ferroelectric uniform and twisted states observed in DIO, suggest that the $N_F$ phase observed in the mixtures is the same as that in RM734 and DIO.

We note that we have not observed periodic birefringent (splay nematic) stripes with ~9 µm spacing of the kind previously reported in the $N_F$ phase of the RM734 family by Mandle and co-workers [5,11] in the $N_F$ phase of any preparations of RM734, DIO or their mixtures, in any standard thin cells, capillaries, or thicker (10–50 µm) cells with planar or random-planar alignment.
At the DIO end of the phase diagram, the transition sequence on cooling is first N $\rightarrow$ SmZA and then SmZA $\rightarrow$ Nf. These transitions are weakly first-order, and the phases grow in as optically distinct, uniform domains upon cooling, without the dramatic polar fluctuations seen at the N $\rightarrow$ Nf transition. We attribute this to the antiferroelectric ordering of the SmZA phase. Over most of the SmZA phase, in-plane reorientation of the director field is strongly suppressed but at lower temperatures, approaching the transition to the Nf phase, ferroelectric fluctuations appear and the susceptibility for field-induced reorientation increases, to be discussed in a later publication.

**Ferroelectric Polarisation**

A typical set of polarization current, $i(t)$, vs. time measurements in response to a 50 Hz, 104 V/mm square-wave, in-plane applied field at different temperatures, in this case for the c = 90 wt% DIO mixture, is plotted in Figure 5(a), with additional data included in Fig. S5. This weak applied field is large enough to reverse the polarisation in the Nf. In the Iso, N and SmZA phases, the current consists only of a signal that peaks shortly after sign reversal of the applied voltage and then decays exponentially. This signal corresponds to the RC-circuit linear response of the cell and series resistance, giving the initial upward curvature of the measured $P$, due to increasing $\epsilon$ in the N phase as the Nf phase transition is approached. At the transition to the Nf, a much larger current signal, resulting from the reversal of spontaneous polarisation in the sample, appears at longer times. This current peak is integrated in time to obtain the net charge flow $Q = \int i(t)dt$ and the corresponding charge density $Q/2A$, shown in Figure 5(b) and Fig. S5, where A is the cross-section of the liquid crystal sample in the plane normal to the applied field midway between the two electrodes.

Initial qualitative observations showed that the width in time of the current peak increased dramatically with decreasing $T$ (Fig. S5), motivating the choice of square-wave driving in order to minimise the temporal width of the current response. Thus, at high temperatures, polarisation reversal is completed during the available 10 msec integration time between applied field reversals. In this regime, denoted by the filled square symbols in Figure 5(b), the quantity $Q/2A$ is equivalent to the bulk Nf polarisation, with $P(c, T) = Q(c, T)/2A$. We find that in this temperature range, the dependence of $P(T)$ on temperature is quite similar in all of the mixtures: on approaching the transition to the Nf phase, the polarisation increases sigmoidally, with an initial upward curvature reflecting the pre-transitional increase in dielectric constant in the N (or SmZA) phase observed in both RM734 [4,5] and DIO [6,8].

However, as Figure 5(a,c) show, the full width at half-maximum of the current peak associated with polarisation reversal, $\tau_p$, increases rapidly on cooling. Below a temperature $T_{sat}$, even with square wave driving, polarisation reversal cannot be completed within the available 10 msec time window and the measured $Q(c, T)/2A$ values decrease rapidly with decreasing $T$ from their maximum value of $P_{sat}$ (solid circles in Figure 5(b)). Test experiments with longer integration times confirm that these data do not reflect the true polarisation, which increases by a few percent above $P_{sat}(c)$ as $T$ is lowered, as observed in RM734 and confirmed in atomistic simulations of RM734 [7]. In the following analysis of the time reversal dynamics, we approximate the polarisation at temperatures below $T_{sat}$ simply by $P_{sat}(c)$. Under this assumption, the time reversal dynamics can be used to obtain measurement of the orientational viscosity at temperatures $T < T_{sat}$.

The saturation value of the polarisation is similar in all of the mixtures, $P_{sat} \sim 6 \, \mu C/cm^2$, as seen in Figure 5(b), with $P_{sat}(c)$ decreasing slightly from the RM734-rich to the DIO-rich end, as shown in Figure 5(d).

At low temperatures, the polarisation measurements were made approximately 30 min apart to allow time for possible crystallisation. The inset in Figure 5(a) shows the current response following field reversal of the c = 90% DIO mixture at the lowest temperatures. In this mixture, crystallisation occurred between the $T = 26.5^\circ C$ and $T = 25.5^\circ C$ scans, causing a precipitous drop in the integrated current, as is evident from the plot. In general, crystallisation is observed on cooling in mixtures at both ends of the phase diagram, near $c \sim 0$ and $c \sim 100\%$, as crystallisation becomes thermodynamically favourable at higher temperatures where the fluid Nf phase still has relatively low viscosity (grey Xtal regions in Figure 2). Interestingly, crystallisation is largely suppressed in the c = 90% DIO mixture while the square-wave polarisation reversal field is applied, but the sample crystallises within about 1 hour in the absence of field at $T = 25^\circ C$. The polarisation reversal time was measured as a function of temperature for all the mixtures, with the results shown in Figure 5(c).

For $T < T_{sat}$, the measured $Q(T)$ data, although not giving the full polarisation, can be used to provide an upper bound estimate $\dot{f}(T) = (Q(T)/2A)/P_{sat}(c)$ of the fraction of the polarisation that has
Figure 5. (Colour online) Characteristics of polarisation reversal in DIO/RM734 mixtures. A 50 Hz square wave with a peak amplitude of 104 V, applied to ITO electrodes with a 1 mm gap in a d = 8 µm thick, planar-aligned, cell, results in an in-plane field of 69 V/mm in the centre of the gap. This relatively small field is large enough to achieve full reversal of the bulk polarisation in the $N_e$ phase at higher temperatures. The polarisation is determined by integrating the current through the cell over one half-cycle of the driving voltage (10 msec). (a) Polarisation current vs time for the $c = 90$ wt% DIO mixture as a function of temperature. The inset shows the current response at the lowest temperatures. The small current peak seen in the N phase (at $T = 90$ °C) is the capacitive response of the cell to the driving voltage. Upon cooling through the SmA - N$_e$ transition, a large polarisation reversal current peak develops, peaking at around $T = 70$ °C before becoming smaller and broader on further cooling due to the increasing viscosity. The polarisation reversal time, $\tau_{pr}$, is taken as the full width of the current peak at half-maximum. The inset shows the response at low temperatures. At $T = 26.5$ °C the sample still switches ($\tau_{pr} = 6$ msec) but on cooling to $T = 25.5$ °C polarisation reversal is prevented by crystallisation. (b) Integrated charge/area, Q/2A, transported during field reversal in neat RM734 and DIO and their mixtures. For $T > T_{sat}$ (solid squares), complete switching of P takes place between each field reversal and Q/2A corresponds to the ferroelectric polarisation P(c,T). The maximum polarisation, $P_{sat}(c)$, indicated with white squares here and in (d), is measured at a temperature $T_{sat}$, below which the director reorientation slows down and the polarisation reversal is incomplete (solid circles), so that Q reflects only part of the true polarisation density ($Q < 2AP$), which, based on computer simulations and additional measurements, increases weakly from $P_{sat}(c)$ as T is decreased from $T_{sat}$. (c) Plot of polarisation reversal dissipation coefficient values, $\eta(c,T) = 0.1 |P(c,T)\tau_{pr}(c,T)E|$, vs. inverse temperature: (left scale) $\tau_{sat}(T)$ scaled as $\tau_{sat}P(T)/P_{sat}$, proportional to $\eta(c,T)$; (right scale) $\eta(c,T)$. Reversal times were evaluated only at higher temperatures ($T > T_{sat}$), where reorientation was completed between field reversals. The dissipation shows an Arrhenius-like dependence on temperature. The switching times of the three-component DIO/RM734/W1027 mixture described in the text are plotted as white circles. These were measured at low temperature using a longer integration time. (d) Polarisation reversal dissipation coefficient variation with concentration (coloured circles) at fixed temperature ($T = 80^\circ$C, dashed black line in (c)). The dissipation coefficients of the two components are seen to add logarithmically in the mixtures. The saturation polarisation $P_{sat}(c)$ (white squares) varies approximately linearly across the phase diagram, indicating ideal mixing in the thermodynamics of the transition to the $N_e$ phase.
reoriented within the 10 msec integration window, under the assumption that for \( T < T_{sat} \), \( P(c, T) = P_{sat}(c) \). The precipitous reduction in the measured charge density at the lowest temperatures coincides with a sudden increase in switching time, which results from a rapid rise in the effective orientational viscosity on approaching the glassy state. In the middle range of concentrations, there is no evidence of crystallisation, which is impeded at low \( T \) by the high viscosity and by freezing-point depression, with cooling resulting instead in a glassy state. Crystallisation could be suppressed at all DIO concentrations by rapid cooling, enabling any mixture to be quenched into a room-temperature glass.

**Polarisation reorientation dynamics: orientational viscosity measurement**

The characteristic time for electric field driven polarisation rotation (ROT) in the \( N_F \) phase is \( \tau = \gamma_1/PE \), the intrinsic response time for an induced 90° rotation starting from the high-torque situation where \( P \) is normal to \( E \) [15]. This \( E \)-field-induced director reorientation process is analogous to that occurring when a magnetic field rotating with frequency \( \omega \) is applied to a nematic, in which case the net local torque applied to the fluid is the same everywhere, resulting in no fluid motion, and the orientational drag is simply \( \gamma_1 \omega \), where \( \gamma_1 \) is the principal 'nematic rotational viscosity' [23]. \( \tau(E) \) was measured optically in the \( N_F \) phase of RM734 and found in 90° ROT dynamics to scale as \( 1/E \), as expected from this picture. The optical response probes \( \varphi_E(t) \), the orientation of a uniform polarisation field, and \( \gamma_1/PE \) is measured using the equation of motion \( \dot{\varphi}_E(t) = 2\tan^{-1}[\tan(\varphi_0/2)\exp(-tPE/\gamma_1)] \), where \( \varphi_0 \) is the starting angle between \( P \) and \( E \). This enables a direct measurement of the orientational viscosity \( \gamma_1 \) [15].

The polarisation reversal process is in general much more complex, involving flow, domain growth and the motion of domain walls. However, in RM734 we noticed previously that, in spite of this complexity, the response time \( \tau_R \) in the polarisation measurement cell with a 1 mm electrode gap also scaled as \( 1/E \), with \( \tau_R = 10\tau = 10\gamma_1/PE \) [15]. Polarisation reversal takes this long because \( P \) is generally oriented antiparallel to \( E \) immediately after the field is reversed, at a very low-torque orientation through most of the cell volume. We used the same 1 mm-gap cell geometry and voltage waveform to obtain the polarisation REV data for DIO shown in Figure 5. Assuming that the same scaling relation \( \tau_R \sim 10\tau \) applies in DIO, we can extract the effective ferroelectric nematic polarisation reversal dissipation coefficient, \( \eta(c, T) \), from the \( \tau_R(c, T) \) data as \( \eta(c, T) = 0.1 \{P(c, T)\tau_R(c, T)\}/E \). \( \eta(c, T) \) also has units of viscosity: torque per unit volume (N/m²)/reorientation rate (sec⁻¹).

The measured polarisation reversal dissipation coefficient of all of the mixtures is \( \eta \sim 0.05 \) Pa s at the highest temperatures in the \( N_F \) phase, increasing on cooling to \( \eta \sim 3 \) Pa s at the longest measurable times (when \( \tau_R \) reaches 10 msec). The dissipation coefficient of each mixture shows a nearly Arrhenius-type dependence on temperature (Figure 5(c)), suggestive of a barrier-limited dissipation process. The experimental data do generally exhibit upward curvature, trending above the Arrhenius line at the lowest temperatures, which we attribute to the approach to a transition to a glassy state. An onset temperature, \( T_g(c) \), taken to be where the measured polarisation has dropped to 80% of \( P_{sat} \) \((f(T) = 0.8) \), which is coincidentally also where \( \tau_R \sim 5 \) msec, is shown as open triangles in Figure 2. This transition temperature varies nearly linearly with concentration, paralleling that of the \( T_{N F} \) transition.

**Room temperature ternary mixture**

The low-temperature dynamics of the \( c = 90 \) wt% DIO mixture, whose \( N_F \) phase persists to room temperature, were explored further by mixing in a third component, W1027 (shown in Fig. S2), to make a \((70 \) wt% DIO)/(15 wt% RM734)/(15 wt% W1027) mixture. Samples of this mixture formed a room temperature, fluid \( N_F \) phase that was stable against crystallisation for many hours. The temperature dependence of the viscosity of this mixture is plotted as white circles in Figure 5(c).

**Phase behavior**

In the case of DIO/RM734, we observe binary mixtures that exhibit a first-order transition between two phases that span the phase diagram across all DIO concentrations \( c \). Such mixtures are considered 'ideal' if, in the calculation of the phase boundary temperature \( T(c) \), the entropy of mixing is the only specifically mixing-related thermodynamic contribution that needs to be considered, besides a linear weighting of the transition enthalpy \( \Delta H \) and entropy \( \Delta S \) change of the individual components, based on their mole fraction. This is to say that 'excess' contributions to the difference of Gibbs potential between the two phases, \( \Delta G \), are negligible. Such contributions would appear in an A/B mixture, for example, if there were attraction, repulsion, disordering, or ordering in A-B molecular pairing that differed from the simple averaging of these effects in A-A and B-B pairing. Under conditions of ideal phase
behaviour, $T_{NF}(c)$, the centre temperature of the phase coexistence range at the transition to the $N_F$ phase, is described by the Schroeder – van Laar (SvL) equations \cite{25,26}:

$$T_{NF}(x) = \frac{\Delta H_{av}(x)}{\Delta S_{av}(x)} = \frac{xT_{DIO} + (1-x)T_{RM734}}{x\Delta S_{DIO} + (1-x)\Delta S_{RM734}}$$

where $x$ = mole fraction, $T_{DIO} = 343$ K and $T_{RM734} = 405$ K are the neat DIO and RM734 transition temperatures to the $N_P$ and $\Delta S_{DIO} = 0.07R$ \cite{6}, $\Delta S_{RM734} = 0.06R$ \cite{9}, $\Delta H_{DIO} = 0.2$ kJ/mol \cite{6}, and $\Delta H_{RM734} = 0.2$ kJ/mol \cite{9} are the per-mole quantities of the pure components. This theoretical SvL phase boundary is generally curved in the $x,T$ plane, but is confined in temperature to the range $T_{DIO} < T(x) < T_{RM734}$. Under ideal mixing conditions, $\Delta S(x)$ should linearly interpolate between these limits. Inspection shows that if $\Delta S_{DIO} = \Delta S_{RM734}$, then the condition observed in the RM734/DIO mixtures is obtained: $\Delta S(x)$ is constant and is eliminated from the equation, with $T(x)$ becoming a linear function of $x$, and the phase boundary forming a straight line between $T_{DIO}$ and $T_{RM734}$ across the phase diagram in $x$, and an almost straight line in $c$ because of the small difference in molecular weights (MW$_{RM734} = 423$, MW$_{DIO} = 510$). DSC measurement of $\Delta S(x)$ at the intermediate concentrations gives $\langle \Delta S(x) \rangle = 0.056 \pm 0.02$ R, comparable to the values of $\Delta S_{DIO}$ and $\Delta S_{RM734}$ given above.

At the RM734 end of the phase diagram, the $N_N - N_F$ transition is direct and first-order, whereas at the DIO end, the phase sequence involves two first-order transitions: $N - SmZ_A - N_F$. However, the linear variation of $T(x)$ vs. $x$ is maintained irrespective of whether the transition into the $N_F$ is from the $N$ or the SmZ$_A$ phase. Since $T(x)$ is governed by the intersection of the Gibbs free energy surfaces governing the $N - N_F$ transition, which linearly interpolate between those of the pure components, the linearity of $T(x)$ suggests that the thermodynamic effect of the $N - SmZ_A$ transition is minor. This is likely a consequence of the extremely small $N - SmZ_A$ transition enthalpy ($\Delta H_{NZ} = 0.003$ kJ/mol \cite{8}), and is also consistent with the $\langle P = 0 \rangle$ nature of both the paranematic N and antiferroelectric SmZ$_A$ phases: all of the net polarisation of the $N_F$ phase is developed through the final transition to the $N_F$, at the phase boundary marked with magenta dots in Figure 2. The small $\Delta H_{NZ}$, the linearity of the dependence of $T_{NF}(c)$ vs. $c$, and the similarity across the phase diagram of the transition entropy of the final transition to the $N_F$ are consistent with the $P(T,c)$ curves having comparable saturation values.

The current proposed models for the phase change from the quadrupolar but non-polar N phase to the quadrupolar and polar $N_F$ phase are that it is either a first-order Landau-de Gennes mean-field transition \cite{4,5}, or an Ising-like orientational transition of molecular dipoles having a binary choice of orientations (along $+n$ or $-n$), made first-order by long-range dipole-dipole interactions \cite{7}. In both cases, the polarisation $P(T)$ is the principal order parameter of the transition. Figure 5(b) shows that the growth of $P(T)$ is similar for the different concentrations, and Figure 5(d) that $P_{sat}(c)$ has a weak linear dependence on $c$. In the context of ideal mixing, this observation constrains the dependence on $c$ of the parameters in such theories of the transition. In the Ising-like system, for example, since $T_{DIO}$ is somewhat smaller than $T_{RM734}$, the Ising interaction energy $J_p(x)$, which gives the local ferroelectric interaction between pairs of dipoles ($iji = DIO,DIO$; $i = DIO, j = RM734; ij = RM734, RM734$), and which is proportional to $T(x)$, must linearly interpolate like $T_{NF}(x)$. This happens only if $J_{DD} = (J_{DD} + J_{RR})/2$, for which condition $\Delta G$ will have no ‘excess’ internal energy. For the nearest-neighbour Ising model (giving a second-order phase transition in 3D), the entropy is a universal function of $T/J$, in which case there will also be no ‘excess’ entropy contribution to $\Delta G$.

However, the transition to the $N_F$ has been found to be first-order and mean-field-like \cite{4,5}, and to exhibit highly anisotropic orientational correlations in the $N$ phase \cite{7}, features which can be understood with a model that includes the effects of the long-range dipole-dipole interactions on the fluctuations in the $N$ phase. The critical behaviour of Ising systems with long-range interactions has been studied extensively in the context of certain magnetic materials that have short-range ferromagnetic exchange forces, but where the long-range dipolar interactions are also important \cite{27–29}. Renormalisation group analysis shows that the long-range interactions make the magnetic correlations dipolar-anisotropic near the transition in the high-temperature phase \cite{30,31}, as observed in RM734 \cite{4,7}, extending them along $n$, the $z$ axis, by strongly suppressing longitudinal charge-density fluctuations, $\partial P_z/\partial z$ \cite{27,28}. Specifically, starting with the free energy expression Eq. (1) from \cite{5} and adding a dipole–dipole interaction term \cite{7}, the structure factor for Ornstein-Zernicke polarisation fluctuations of $P_z$ about $q = 0$ becomes $\langle P_z(q)P_z(q)^* \rangle = k_BT\chi(q)$, with $\chi(q) = 1/[\pi(T)(1
Polarisation reversal dissipation coefficients of the mixtures

The measured dissipation coefficient values, $\eta(c,T) = 0.1[P(c,T)\tau_s(c,T)]E$, were fit to the Arrhenius form $\eta(T) = A \exp[E_n/k_BT]$, as shown in Figure 5(c), in order to determine the effective barrier height, $E_n$. As can be seen from the uniformity of the slopes, $E_n$ is essentially independent of $c$, with an average value of $E_n = 7800$K across the phase diagram. The coefficient $A$, in contrast, varies substantially with $c$, behaviour that can be quantified by measuring the viscosity vs. concentration at a single temperature, for example 80°C. The plot in Figure 5(d) shows logarithmic additivity of $\eta(T)$ for the DIO/RM734 mixture: $\ln[\eta(80°C)] = (x)\ln[\eta_{DIO}(80°C)] + (1-x)\ln[\eta_{RM734}(80°C)]$. A basic understanding of this behaviour can be gained by using the combined Cohen-Turnbull free volume [33]/Eyring rate theory [34] model proposed by Macedo and Litovitz [35]. This model is based on Maxwell's intuitive picture [36], or its contemporary embodiments [37,38], in which viscosity $\eta = G/\nu$, the ratio of $G$, a typical elastic modulus for local shear deformation, to $\nu$, the average rate per molecule of randomly occurring, local structural deconfinement/relaxation events. The rate $v$ is given by $v = v_e p = v_T p_k p_v$, where $v_T$ is a trial frequency, and $p$ the probability of success, a product of the probability $p_k = \exp(-E_k/E)$ that sufficient energy, $E$, will be available [34], and $p_v = \exp(-V_\nu/V)$ [33], the probability that sufficient free volume, $V$, will be available, where $V_\nu$ is the average free volume per particle. These probabilities relate viscosity to temperature and density, respectively, giving the generalised relationship, $\eta(T) = G/(v_T p_k p_v) = (G/\nu_T) \exp(c V_\nu/V + E_n/k_BT)$, where $V_o$ is the close-packed volume per particle, and the available energy is on average $k_BT$. Applying this to the DIO/RM734 mixtures, we can consider $G$ and $\nu_T$ to be the same for the two components and, since the Kelvin range is rather narrow, also to be independent of temperature, with the difference in viscosity of the components being the result of a difference in $V_\nu$. Generally, in a binary mixture we will have

$$v = v_T p = v_T (p_{DIO}^x (p_{RM734}^{1-x})$$

This expression can be simplified by noting from the similar slopes of the $\ln[\eta(T)]$ vs $1/T$ fits in Figure 5(c) that we can take $E_n$ to be the same for the two components, $(E_n)_{DIO} = (E_n)_{RM734}$ from which simplification we get $(p_{DIO}) = (p_{RM734})$, $p_v = \exp(-E_n/k_BT)$. The viscosity of the mixture is then given by $\eta(x,T) = (G/\nu_T) p_{DIO}^x (p_{RM734}^{1-x}) V_\nu$, which predicts logarithmic additivity of the viscosities, behaviour that is evident from the experimental data plotted in Figure 5(d). In the context of the model above, given that $(E_n)_{DIO} = (E_n)_{RM734}$, this logarithmic additivity implies that the effective free volume in the mixtures is obtained from a linear combination of $V_\nu$ for the two components.

Enantiotropic $N_F$ and SmZ_A phases

All single-component $N_F$ materials reported to date, including RM734 and DIO, are monotropic, with the $N_F$ phase observed only on cooling, implying that the $N_F$ state is thermodynamically metastable relative to the crystalline state. When held at a fixed temperature in the $N_F$ state, such single-component materials eventually crystallise, on timescales ranging from seconds to days [8]. For practical applications of $N_F$ materials, enantiotropic behaviour (i.e., the existence of a thermodynamically stable $N_F$ phase) is highly desirable. Mixing of multiple components is a well-established route to achieving enantiotropic behaviour in liquid crystals, and, in fact, enantiotropic $N_F$ behaviour has been described previously by Mandle and co-workers, in mixtures of homologs of RM734 [9]. In order to study the enantiotropic behaviour in mixtures of RM734 and DIO, samples were filled into 8 µm-thick cells in the isotropic phase and cooled to room temperature, where they were left undisturbed for two months. Of all the mixtures exhibiting a glassy state, only the 90% DIO sample showed some recrystallisation in parts of the cell after this time. The cells were then heated slowly, with no applied field, and the phase behaviour observed
the polarised light microscope. The spontaneous polarisation was measured as a function of temperature using in-plane fields in a subsequent heating cycle. Based on these observations, we determined that the N_F phase is enantiotropic in RM734/DIO mixtures over a range of compositions from 10% to 80% DIO (Fig. S8, Table S1). In 10% DIO for example, the concentration that exhibits the broadest enantiotropic N_F temperature range, a thermodynamically stable N_F phase is observed from T = 97.5°C to 124.7°C. The SmZA phase, which is observed in the heating experiments over a wide range of compositions, is also enantiotropic, in contrast to neat DIO, in which the SmZA is monotropic.

Discussion

For the isotropic–nematic liquid crystal transition, commonalities observed in the phase behaviour for different molecular species having widely different molecular structure have stimulated and supported the notion that the essential elements of nematic liquid crystal structure and ordering could be modelled based on a few relevant molecular features. Thus, nematics were found to be dielectric and non-polar in the absence of a field, separated from the isotropic by a first-order phase transition with transition enthalpies ~1 kJ/mol, and optically uniaxial, with a birefringence that increased slowly with decreasing temperature or increasing concentration. Maier-Saupe [39] and Onsager [40] showed that anisotropic steric shape and/or van der Waals forces, employed to describe intermolecular interactions in simple mean-field or second-virial statistical mechanical models, were the molecular features required to get a basic description of nematic ordering.

The results presented in this paper suggest that a similar distillation might be possible with respect to the ferroelectric nematic phase, showing that the effects of family origin on the interactions of molecularly distinct species leading to the ferroelectric nematic phase can be accounted for by the simplest averaging procedures to get ΔH(T,x) and ΔS(T,x). This means, for example, that at low concentration of either of the components, its isolated molecules interact with the sea of the other molecular family in a fashion similar to how they interact with their own kind.

What are the required generic molecular features for nematic ferroelectricity? There are currently ~60 molecules among the two families known to induce nematic ferroelectricity, including more than 40 molecules synthesised from the two families reported in recent papers by Li et al. [8] and twenty-five variants in the RM734 family reported by Mandle et al. [11]. Figure 1 and Table S1 of [8] summarise the observed phase behaviour of the Li compounds as pure materials, dividing them into three categories: green (9 molecules) – exhibiting a long-lived monotropic N_F phase; blue (12 molecules) – exhibiting a short-lived monotropic N_F phase that was difficult to study because of rapid crystallisation; and red (21 molecules) – exhibiting no N_F phase. This impressive exploration of the effects of a variety of substitutions shows that within these families there is a general tendency to form the N_F phase.

The similar molecular-rod shape and size (~three rings long), and the similarly large molecular dipole moments (~11 Debye) in the two families, suggest that these attributes are essential to exhibiting an N_F phase. While this combination may be necessary, it is certainly not sufficient, based on: (i) the extensive pre-N_F literature of longitudinally polar LCs [41] which exhibit only re-entrant nematic/smectic paraelectric or antiferroelectric phases; and (ii) the observation that substituting -CN for -NO_2 eliminates the N_F phase in otherwise identical molecules, in spite of their comparable dipole moments [8,9]. This latter result may suggest the importance of details of the electrostatic head-to-tail self-assembly and side-by-side interaction of the resulting aggregates found in atomistic simulations [7,42]. The structure of the on-axis diffuse peaks in the WAXS patterns of RM734 and DIO exhibit common features, summarised in Figs. S6, S7. These features are unusual among nematics, and may indicate a common enhanced tendency for head-to-tail self-assembly.

Mertelj, Mandle, and co-workers have posited [4,5,10,11] that in the RM734 family, a bulky side group like MeO in the ortho-position is required to stabilise the new N_X phase, an antiferroelectric, periodic array of splay stripes, by making the molecules more pear-shaped. More recent papers [7,8,15,24], and the observations reported here, show that the textures of the N_F phase are often not macroscopically modulated or locally splayed on any observable length scale. Furthermore, some of the more recent additions to the molecular pallet that exhibit the N_F phase have side groups in the middle or on the other end of the molecule (e.g., the RM734 family compounds 2a-2c and 3 in [8]), or lack side groups altogether (e.g., many members of the DIO family, and the RM734 family compound 12 in [8], which is the same as compound 10 in [11]).

The nearly ideal mixing behaviour of the chemically dissimilar compounds DIO and RM734 is at first blush surprising but suggests that the thermodynamics of mixing in binary mixtures of these materials is dominated by electrostatic interactions
and electrostatic intermolecular association. Despite their distinct functional groups and patterns of chemical substitution, DIO and RM734 have similar dipole moments (~11 D) and charge distributions characterised by an alternation in the sign of charge along the length of the molecule, features that are strongly correlated with typical pair-association motifs (e.g., head-to-tail ‘chaining’ and side-by-side ‘docking’) observed in atomistic simulations of RM734 and related compounds [7,43]. The role of longitudinal charge density modulation in stabilising the _NT phase has also recently been addressed in theoretical work by Madhusudana [44]. We hypothesise that the near-ideal miscibility of RM734 and DIO derives from their similar molecular shape, charge distribution, and electrostatic interactions, a hypothesis that may be tested by investigating the mixing behaviour of analogs of RM734 and DIO having modified intramolecular charge distributions.

NT materials are highly unusual polar solvents that quite generally induce polar orientational order in dipolar solute molecules, a phenomenon we term ‘solvent poling’. The degree of induced polar order can be quite large, as evidenced by the ferroelectric polarisation measurements in binary mixtures of RM734 and DIO reported here, which show that an RM734 NT host imparts nearly perfect order to DIO solute molecules in the limit of low DIO concentration (and similarly for a low concentration of RM734 solute molecules in a DIO NT host). This solvent poling phenomenon may simply result from orientation of solute electric dipoles in the large (~10⁹ V/m) local electric fields present in the NT host, but, more generally, will depend on details of intramolecular charge distribution and molecular shape. Solvent poling is a facile route to the creation of novel functional materials with optimised materials properties. For example, materials with large second-order non-linear optical susceptibility may be engineered by solvent poling of high-beta chromophore molecules in NT hosts.

Disclosure statement
In accordance with Taylor & Francis policy and our ethical obligations as researchers, M. A. Glaser, J. E. Maclennan, D. M. Walba, and N. A. Clark are reporting that they have a financial and business interest in a company that may be affected by the research reported in the enclosed paper. We have disclosed those interests fully to Taylor & Francis, and we have in place an approved plan for managing any potential conflicts arising from that involvement.

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