Structural variants of RM734 in the design of splay nematic materials

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ABSTRACT
The recent discovery of the splay nematic phase, a new nematic polymorph that has been found to be both polar and ferroelectric, is the lead paragraph in an entirely new chapter in the history of liquid crystals. The potential for transformative applications utilising this state of matter – such as photonics, non-linear optics, memory applications and so on – can only be met with significant improvements in the temperature range of existing materials such as 4-(4-nitrophenoxycarbonyl)phenyl 4-methoxy-2-methoxybenzoate (RM734). Herein we present several families of materials which are structurally related to the archetypal new nematic material, RM734, including the first non-rod-like materials within the context of the splay nematic phase. We find that the incidence (or absence) of this new nematic variant in a designer material cannot be easily rationalised in terms of molecular dipole moment or polarisability. However, mixture formulation shows promise for the engineering of materials with improved working temperature ranges.

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**Introduction**

As the uniaxial nematic liquid-crystalline state is widely employed in display technology, the discovery of new nematic ground states is met with great enthusiasm owing both to the extreme rarity of such phases, but also the possibility of transformative applications in displays and beyond [1]. For example, the prediction [2] and subsequent experimental discovery [3] of the twist-bend nematic phase has led to a resurgence of interest in liquid-crystalline dimers, with possible applications now emerging. The possibility of a ferroelectric nematic phase has been acknowledged for nearly a century [4,5]; the combination of ferroelectricity with nematic-like fluidity and ease of processing would have enormous potential for applications.

Early in 2017, we reported a rod-like material (RM230, Figure 1), first prepared many years earlier [6], with a large longitudinal electric dipole moment that exhibited two nematic phases separated by an enthalpic phase transition. At high temperatures, a conventional nematic phase was observed, and at lower temperatures a nematic phase of unknown structure, which we termed N_X [7]. Unfortunately, the monotropic N-N_X transition of RM230 occurs almost 60°C below the melting point, and so detailed physical study on this material was impractical. Subsequently, in 2017 we published the first part of a larger body of work exploring how molecular features impact upon the then called N_X phase, identifying one material (RM734, Figure 1) as having transition temperatures which are better suited to detailed physical characterisation [8]. Later in the year, Nishikawa et al. reported on a rod-like material (named DIO), which exhibited two nematic phases, and possessed a giant dielectric anisotropy, shows ferroelectric properties, and exhibited similar optical textures to RM230 [9].

Mertelj et al. revisited RM734 in 2018, concluding that the lower temperature nematic phase is a splay modulated nematic phase (termed N_S), which is driven by an unusually small splay elastic constant approaching the phase transition [10]. The potential existence of a splay modulated nematic phase had been suggested many years earlier by Pleiner and Brand [11]. The N_S phase exhibits a periodic inhomogeneity in its optical texture parallel to the director, believed to be a splay modulation (Figure 1 (c, d)), with a period of ~9 microns [12]. In October 2019 Sebastian et al. demonstrated that the new N_S phase is comprised of polar domains with parallel dipole alignment, with the N-N_S transition having the characteristics of a ferroelectric phase transition, driving an orientational ferroelastic transition via flexoelectric coupling [12] and

![Figure 1](https://example.com/figure1.png)

**Figure 1.** (Colour online) (a) Molecular structure and transition temperatures of two typical splay nematic materials; RM230 (named 1 in ref [7]) and RM734 (named 2 in ref [8]). Photomicrographs of (b) the nematic phase of RM230 at 94.4°C, (c) the splay nematic phase of RM230 at 76.4°C with modulations clearly visible; both (b) and (c) are of the same area of the sample; (d) idealised nematic director map for a periodic deformation according to the splay nematic model in ref [10]; (e) Background subtracted 2D SAXS pattern of a magnetically aligned sample of RM230 in the N_S phase at 72°C; note the multiple diffuse peaks parallel to the magnetic field (B), and thus director.
is the first demonstration that the splay-nematic phase exhibited by RM734 is ferroelectric [13].

RM734 and the Ns phase were later studied by others. In March 2020 Clark et al. made a first principle demonstration of the ferroelectric nature of the Ns phase which is reported to be homogenous (and so they called it Ns, for ferroelectric nematic, although it is not indicated if the transition is intrinsic or extrinsic for proper or improper ferroelectrics). Clark et al. find RM734 to exhibit a giant spontaneous polarisation in the lower temperature nematic phase, saturating at ~6 μC cm⁻² [14]. In November 2020 Aya et al. also demonstrated the polar order and ferroelectricity of the lower temperature nematic phase of RM734 and other novel structurally related materials, noting that the lower temperature nematic is not homogenous as suggested in the Ns model [15]. Aya et al. suggest the name PN (for polar nematic), and demonstrate that the lower temperature nematic phase first observed in RM230 is the same as that exhibited by Nishikawa. Interest in this area is growing rapidly: Manabe et al. have recently reported a material that exhibits a transition directly from the isotropic to ferroelectric nematic phase (Nf) [16], and Jakli et al. have reported a material (RT11001) which exhibits multiple ferroelectric nematic phases (F1, F2, F3) and displays an even larger spontaneous polarisation than RM734, saturating at 6.9 μC cm⁻² [17].

The nomenclature describing the Ns/Ns/NF/PN/F1 phase is not the subject of this paper and is a matter for future study and debate. However, we note that mesophase nomenclature and classification of new mesophases have not to date been made based on physical properties (e.g. polar, ferroelectric), but rather on symmetry and structure (e.g. biaxial, cubic, twist-bend). Using the term nematic for thread-like defects, and splay to refer to the elastic properties (specifically the near zero K₁ measured for RM734) and the modulated structure. The classification therefore is unequivocal, and so herein we will therefore refer to the lower-temperature nematic phase exhibited by RM734 and its homologues as a splay nematic (Ns). We note that the majority of the literature already uses this term, and this description appears to us to be best supported by experimental evidence available to date. What is certain is that the discovery of the polar and ferroelectric Ns phase marks the beginning of a transformative new chapter in liquid crystal science, with distinct and technologically relevant electro-optical effects exhibited by this phase [18,19] presenting a significant motivation towards development of new materials [20]. In parallel, and complementary to ongoing experimental efforts, theoretical understanding of the splay nematic phase is advancing rapidly [21–25].

Herein, we explore further variations on the core structure of RM734, subsequent to the discovery of the Ns phase. In keeping with lessons learned thus far, we use only short aliphatic chains in conjunction with large electric dipole moments generated through the incorporation of one or more nitro groups.

Experimental

Starting materials were obtained from commercial suppliers and used without further purification unless noted otherwise, whereas solvents were purified by percolation through activated alumina prior to use. The materials were characterised by NMR (¹H and ¹³C), ESI mass spectrometry and FT-IR. For the sake of brevity, experimental details (synthetic schemes and procedures, chemical characterisation, details of instrumentation used, computational methods) are provided in the accompanying ESI. Density functional theory electronic structure calculations were performed in Gaussian G09 revision D01 [26]; semi-empirical calculations were performed in MOPAC2016 [27].

Results and discussion

We begin by considering materials analogous in structure to RM734, but with a lateral hydroxyl group in lieu of the methoxy unit. We explore variations in the position of the lateral hydroxyl group, and prepare variants without any lateral substituent. Transition temperatures and associated enthalpies of transition are presented in Table 1.

The three parent materials of the series that lack any lateral substituent (10, 11 and 12) exhibit wide temperature range nematic phases, but lack the Ns phase seen for RM230 and RM734. The inclusion of a lateral hydroxyl group has only a minimal effect on melting point, but depresses the clearing point with respect to the parent compounds significantly. Notably, compounds 1–3 all decompose upon heating beyond ~240°C and so accurate determination of TNI was not possible for these materials. It should be noted that there are few examples where the orientation of the ester functionalities is inverted. However, for the parent materials, which lack lateral substituents, the analogous ‘inverted ester’ compounds have been reported and are known by the acronym DBₙONO₂, where n is the number of carbon atoms in the terminal chain. The DBₙONO₂ compounds exhibit incommensurate and re-entrant phase behaviours. Some materials, such as DB₅ONO₂, exhibit smectic antiphases in which there is a modulated structure within the layer plane [28]. As these materials
Table 1. Transition temperatures (°C) and associated enthalpies of transition [kJ mol⁻¹]. Values for RM230, RM734, 2, and 11 were taken from Mandle et al. [8] Compound 10 was also reported independently of this study by Aya et al. [15] Monotropic transitions are shown in parenthesis ( ).

| No. | R   | X   | Y   | Z   | Cr  | N₅  | N   | Iso |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| RM34 | Me  | OMe | H   | H   |     | 139.0 (34.8) |   |     |     |
| RM230 | Et  | OMe | H   | H   |     | 139.8 (29.9) |   |     |     |
| 1    | Me  | OH  | H   | H   |     | 209.6 (29.5) | - |     |     |
| 2    | Et  | OH  | H   | H   |     | 164.7 (39.4) |   |     | 240 Dec |
| 3    | Pr  | OH  | H   | H   |     | 136.6 (35.4) | - |     | 240 Dec |
| 4    | Me  | H   | OH  | H   |     | 205.2 (31.7) | - |     |     |
| 5    | Et  | H   | OH  | H   |     | 186.2 (35.3) | - |     |     |
| 6    | Pr  | H   | OH  | H   |     | 166.4 (35.5) | - |     | 190.3 (0.6) |
| 7    | Me  | H   | H   | OH  |     | 162.5 (26.9) | - |     | 155.4 (0.7) |
| 8    | Et  | H   | H   | OH  |     | 149.7 (27.0) | - |     | 179.9 (0.4) |
| 9    | Pr  | H   | H   | OH  |     | 137.0 (22.3) | - |     | 197.4 (0.4) |
| 10   | Me  | H   | H   | H   |     | 203.6 (42.9) | - |     | 266.8 (0.7) |
| 11   | Et  | H   | H   | H   |     | 155.2 (33.1) | - |     | 276.4 (0.6) |
| 12   | Pr  | H   | H   | H   |     | 148.3 (37.3) | - |     | 274.8 (0.5) |

Figure 2. Molecular structure of compound 13, Tₘₚ = 160.3°C, ΔHᵤᵤᵤ = 27.1 kJ mol⁻¹.

Table 2. Dipole moments (μ, Debye), dipole angle (β(μ), degrees), static anisotropic polarisability (Δα, Å³) and static isotropic polarisability (αᵣₑᵣ, Å³) of RM734, compounds 1, 4, 7, 10, and 13, calculated at the B3LYP-D3/6-31 G(d) level of DFT.

| Cpd. | μ D  | β(μ)° | Δα/Å³ | αᵣₑᵣ/Å³ |
|------|------|-------|-------|----------|
| RM734 | 11.4 | 15.8  | 47.1  | 43.5     |
| 1    | 11.7 | 14.8  | 48.0  | 41.6     |
| 4    | 11.9 | 14.7  | 48.1  | 41.7     |
| 7    | 11.6 | 14.2  | 46.3  | 41.5     |
| 10   | 10.3 | 10.9  | 47.2  | 40.8     |
| 13   | 9.4  | 24.4  | 43.9  | 44.7     |

were reported in the early 1980s, and hence well before the discovery of the N₅ phase, we cannot say that this family does not exhibit splay nematic phases, but this possibility appears worthy of future investigation.

Compound 13, a structural isomer of RM230 in which the nitro group is in the meta position (Figure 2), is non-mesogenic (Tₘₚ = 160.3°C, ΔHᵤᵤᵤ = 27.1 kJ mol⁻¹). This demonstrates that position of the terminal nitro group is also critical to the observation of the splay nematic, and indeed the nematic, mesophase.

The N₅ phase has to date only been observed in materials with large longitudinal dipole moments; how the molecular electric dipole varies with substitution pattern is therefore of interest. We calculated dipole moments and polarisabilities at the B3LYP-D3/6-31 G(d) level of DFT for the methoxy-terminated materials shown in Table 2. The dipole angle was computed as the angle between the dipole vector and the inertia tensor of the molecule in question. Compared with the splay-nematic material RM734, the dipole moments of materials from Table 1 can be both smaller (e.g. 10, 13) or larger (e.g. 1, 4). Similarly, the incidence of the N₅ phase does not appear to be only dependent upon the dipole angle, or polarisability values.

Although results to date suggest that the N₅ phase is formed exclusively by molecules with extremely large electric dipole moments, dipole moments in isolation do not appear to be a particularly useful predictor for the incidence of the N₅ phase. With this in mind, we next considered the role of the lateral unit in a series of 4-nitrophenyl benzoates (Table 3). These materials are analogous to RM230, but with only a single ester unit; this gave a modest reduction in the molecular electric dipole moment.

With respect to chemical stability, it was envisaged that the biphenyl-based materials would be more robust than their diester counterparts, and indeed we do not observe the decomposition that was noted for materials such as 1–3. Although the majority of the nitrophenyl
Table 3. Transition temperatures (°C) and associated enthalpies (kJ mol⁻¹) for the 4-nitrobenzophenyl 2-alkoxy-4-ethoxybenzoates and 4-nitrobenzophenyl 2-alkenyl-4-ethoxybenzoates. Transition not observed by DSC. Values for 15 were taken from Mandle et al. [8] Monotropic transitions are shown in parenthesis ()

| No. | R     | Cr | N/N* | Iso |
|-----|-------|----|------|-----|
| 14  | H     | ●  | 174.9 [24.7] | 215.4 [0.6] |
| 15  | Me    | ●  | 151.6 [41.0] | 165.9 [0.6] |
| 16  | Et    | ●  | 150.5 [29.7] | 109.4  |
| 17  | (S)Pr | ●  | 138.1 [20.1] | 79.4 [0.6] |
| 18  | ●     | 158.1 [27.0] | 96.4  |
| 19  |       | ●  | 163.0 [34.3] | 93.7  |
| 20  |       | ●  | 166.5 [33.7] | 89.6  |
| 21  |       | ●  | 96.9 [28.6]  | 41.9 [1.1] |
| 22  |       | ●  | 160.5 [49.9] |      |

benzoate mesogens prepared exhibit nematic phases, none show splay nematic phases. The nematic phase of compound 17, which has a lateral C3 chain, can be cooled to room temperature without formation of Nₛ or crystallisation, and so can be used to exclude the possibility that the Nₛ phase is obscured by crystallisation in this family of materials. For compound 21 a branched chiral alkoxy chain was used and this gives significantly lower melting points and clearing points compared to compound 17. The inclusion of a terminal primary alcohol on the lateral C3 chain raises the onset temperature of the nematic phase significantly; however, the material rapidly crystallises at this temperature; the same is true of the related branched chiral materials 19 and 20. Compound 22 has a lateral allyl group and this material is non-mesogenic, melting and crystallising at a much higher temperature than the closely related compound 17, which possesses a lateral propoxy chain. However, the lateral allyloxy unit presents a handle for further synthetic transformations, as do the lateral hydroxyl groups of 18–20. Compound 23 (Figure 3), a structural isomer of 14 in which the nitro group is in the ortho position, is non-mesogenic.

Removal of the lateral unit from compound 14–22, to afford 24, leads to a predictable rise in melting and clearing points. We sought to compensate for this by increasing the length of the terminal chain to propoxy (25) or (S)-2-methylbutoxy (26); transition temperatures are presented in Table 4.

Although compounds 24 and 25 show wide temperature range nematic phases, the chiral compound 26 shows an additional smectic A phase. We do not observe even transient splay nematic phases in these materials. Two photomicrographs of the chiral nematic phase of compound 26 are given in Figure 4, showing the pseudo focal-conic defect texture obtained on cooling from the isotropic liquid, and a second showing the fingerprint texture obtained on heating of the smectic A phase into the chiral nematic phase. The absence of a lateral group leads to increased melting and clearing points when comparing compounds 24–26 with 14–22.

As 26 exhibits a SmA phase and is also structurally related to RM230, we considered the possibility that binary mixtures could be formulated to generate materials with an Nₛ-SmA transition. This was motivated by a wish to study the behaviour of the elastic constants at the Nₛ-SmA transition, the structure of the resulting SmA phase and the possibility of re-entrant Nₛ phases. The binary phase diagram is shown in Figure 5. Unfortunately, the SmA and Nₛ phases of the respective materials are suppressed on moving across the phase diagram before we find a SmA-Nₛ transition temperature. At low concentrations of the chiral material 26 the Nₛ phase is retained. The behaviour of the first example of a chiral splay nematic phase (we suggest Nₛ⁺ as a temporary abbreviation until the structure of this phase is elucidated) is distinct from the achiral phase and will be described at length in future papers. The monotropic nature of the ‘Nₛ⁺’ phase renders characterisation extremely challenging in this system. Nonetheless, we observe simultaneous micron scale periodic optical inhomogeneity reminiscent of the achiral Nₛ phase coupled with selective reflection of visible light (for other additives with large HTP), suggesting this to be a previously unobserved nematic-like phase with
multiple distinct modulation periods, and perhaps the third distinct nematic phase variant discovered so far in the 21st century. Placing the mixture of RM230/26 into a Cano Wedge cell with homeotropic alignment (to suppress the splay modulated structure), we observe Grandjean-Cano lines with a spacing (D) of ~300 μm which indicate a helical superstructure with pitch (P) of ~5.5 μm at 69°C. Studies into this new nematic variant are ongoing.

![Figure 4](image-url) (Colour online) Pseudo focal-conic defect texture of the N* phase of 26 (a, 215°C) and the fingerprint texture of the N* phase of 26 (b, 199°C). In both images, the scale bar is 100 μm.

Table 4. Transition temperatures (°C) and associated enthalpies [kJ mol⁻¹] of 4'-nitrobiphenyl 4-alkoxybenzoates.

| No. | R | Cr  | SmA | N/N* | Iso |
|-----|---|-----|-----|------|-----|
| 24  | Et| ●   | 162.6| ●    | 276.0●|
|     |   | [32.0]|     |      |     |
| 25  | Pr| ●   | 144.1| ●    | 218.3●|
|     |   | [21.0]|     |      |     |
| 26  |   | ●   | 163.0| ●    | 215.7●|
|     |   | [15.1]|     | [0.2]|     |

Figure 5. (Colour online) (a) Binary phase diagram for mixtures of RM230 and 26. (b) Photomicrograph of a mixture of 90 mol% of 26 in RM230 (indicated with arrow) at 69°C in a Cano Wedge cell with homeotropic alignment and an inclination angle of tanα = 0.0092; pitch was calculated as P = 2D tanα. Scale bar = 250 μm.

We next sought to explore the possibility that multiple nitro groups could induce the formation of the N₅ phase by increasing the molecular polarisability. Taking

![Figure 5](image-url)

Table 5. Transition temperatures (°C), associated enthalpies [kJ mol⁻¹] and extrapolated virtual N – I transition temperature <°C> of polynitrated nitrobiphenyl benzoates. Monotropic transitions are shown in parenthesis ()

| No | X | Y | Cr  | N  | I   |
|----|---|---|-----|----|-----|
| 24 | H | H | ●   | 162.6[32.0] | ●  | 276.0[0.5] |
| 27 | NO₂| H | ●   | 187.1[24.8] | -  | <138> |
| 28 | H | NO₂| ●   | 160.5[28.6] | (●) | 145.7[0.5] |
compound 24 as our starting point, we prepared the dinitrated analogues, 27 and 28 as shown in Table 5.

Whereas the mono-nitrated compound 24 exhibits a wide temperature range nematic phase, the introduction of a second nitro group in the first ring gives a nonmesogenic material. When a second nitro group is positioned in the middle ring of the molecule a small temperature range nematic phase is observed, albeit with a reduction of roughly 130 degrees in the clearing point. Thus, the introduction of a second nitro group in this position is detrimental to mesophase stability. However, when positioned in the opposing terminal ring the nematic phase is absent.

Consequently, the steric bulk of the second nitro group fails to confer any significant reductions in melting point over the parent material, owing to large increases in the transverse component of the dipole moment of the molecule; however, it does significantly suppress the clearing point. Binary mixtures of compounds 27 and 28 with compound 24 were prepared, and in the case of compound 27 this was used to extrapolate to give a virtual nematic to isotropic transition

Table 6. Melting point (°C), associated enthalpy [kJ mol\(^{-1}\)] for compound 29.

| No. | Cr |  |
|-----|----|---|
| 29  | ●  | 154.7 [22.7] | ● |

Table 7. Melting point (°C) and associated enthalpy of fusion [kJ mol\(^{-1}\)] of compound 30.

| No. | Cr |  |
|-----|----|---|
| 30  | ●  | 207.4 [60.6] | ● |
temperature. The phase diagrams are presented in Figure 6.

We considered the possibility that additional nitro groups may affect beneficial reductions in melting point, remaining mindful of the hazards posed by polynitrated materials. With this in mind, we devised and prepared compound 29 (Table 6), which has sufficient nitro substituents to allow us to test this idea, yet too few to pose an explosion hazard. We find 29 to be non-mesogenic; further investigation via binary mixtures with compound 24 allowed us to extrapolate a virtual clearing point of −52.1°C for 29.

We now turn briefly to the sculpting of more complex molecular arrangements, still inspired by RM734. Compound 30 is an H-shaped dimer, which can be considered as two molecules of 17 fused via a 1,6-dioxyhexamethylene linker, as shown in Table 7.

Comparison of 30 to its parent material (17) there is an increase in melting point of ~70°C. The monotropic nematic phase observed for 17 is absent in the dimer, 30. The low solubility of 30 in both commercial nematics (5CB, E7) and also novel materials available in house (e.g. RM734, 24) means we are unable to extrapolate a virtual T_{NI} for this material.

For an H-shaped dimer to exhibit nematic phases, one would anticipate an (anti)parallel alignment of the mesogenic units would be preferable; as 30 is

![Figure 7](image-url). (Colour online) (a) Global energy minimum geometry of compound 30, (b) histogram of energy as a function of the angle between the inertia axes of each mesogenic unit of 30 for a geometrically diverse conformer library.

**Table 8. Melting point (°C) and associated enthalpy of fusion [kJ mol⁻¹] of compound 31.**

| No. | Cr | l   |
|-----|----|-----|
| 31  | ●  | 55.8 [88.3] |
non mesogenic we sought to study its molecular shape computationally. First, we obtained the global minimum energy geometry at the B3LYP/6-31 G(d) level of DFT. From this geometry we then generated a geometrically diverse conformer library \((n = 5000)\) using a genetic algorithm to maximise the RMSD atom displacement [29]. Conjugate gradient geometry optimisations, using the PM7 semi-empirical method [27], were then performed for each conformer using MOPAC. We find that the global energy minimum geometry (single gauche in the central spacer) to have an angle of \(\sim 50^\circ\) between the two mesogenic units; there is a broad distribution of populated angle (Figure 7), indicating 30 to have a globular shape which is evidently not especially conducive to forming nematic mesophases.

The tetrapodal compound 31 was formed via esterification of compound 18 with a tetracarboxylic acid derived from pentaerythritol (see Table 8). While this material met the design goal of reducing melting points compared to its parent, the splay nematic phase is absent and indeed the material, like the dimer, is non-mesogenic.

As with compound 30, it is believed that the absence of mesomorphic behaviour in the supermolecule 31 is due to the alignment of the individual mesogenic units being unfavourable for the formation of a liquid crystal phase.

**Mixture formulation**

Traditional design of liquid crystal materials for use in electrooptic applications involves selection of central core units, appending terminal chains and the positioning of polar groups [30]. However, our studies show that the design of splay nematic materials is not so simple and requires delicate molecular sculpting. The usual approach to material design in such circumstances is to turn to formulation, and in the following, we describe our initial studies along this pathway.

Phase diagrams involving splay-nematic materials have to date displayed one of two behaviours: if both materials exhibit the \(N_s\) phase there is a near linear variation in \(T_{N_s-N}\) as a function of concentration; if only one material displays the \(N_s\) phase in its neat state then it is readily suppressed in binary mixtures. Having developed a large number of ‘RM734-like’ materials in this present work, we sought to explore ternary phase diagrams involving \(N_s\) materials. We prepared ternary mixtures of RM230, 2, and 15, evaluating transition temperatures by DSC and microscopy. In total, we evaluated 110 mixtures, and tabulated data is given in the ESI. Mirroring behaviour observed for binary mixtures, we find that for ternary mixtures with <80 mol% RM230, the \(N_s\) phase is absent, although below this concentration threshold it is generally retained. However, we find impressive reductions in melting point in the vicinity of the eutectic composition (minimum \(T_{MP}\) of 112°C at 0.47 mol% RM230, 0.29 mol% 2 and 0.24 mol% 15).

Gratifyingly, we find that the Schröder-van-Laar equation (see ESI, section 3) [31,32] is competent for predicting the melting points of the mixtures shown in Figure 8, while the clearing points are well described by a simple weight average of the 3 components.

This suggests that mixture formulation will be a viable route to improved temperature range splay nematics, although this will almost certainly require the synthesis of additional families of \(N_s\) materials so that a larger pool of compounds can be employed in mixture formulation.

![Figure 8](https://example.com/figure8.png)  
*Figure 8.* (Colour online) Experimental phase diagrams for ternary mixtures of RM230, 2 and 15: (a) melting point; (b) \(N_s-N\) transition; (c) \(N-I\) transition. White regions in (b) correspond to areas where no \(N_s-N\) transition occurs, as judged by optical microscopy and DSC.
Conclusions

In the few years since our report of the first rod-like to exhibit a new nematic phase of matter in early 2017, these materials have since been shown to fulfill the promise of ferroelectric nematics over a century after such a phase was envisioned. While behaviour of these materials under applied electric fields is remarkable [19], the transformative applications potential of the ferroelectric splay nematic phase will only be realised should materials be designed that exhibit this phase over a suitable temperature range for applications use, most likely including ambient temperature. To this end, we report on a number of materials, which are structurally related to RM734, the archetypal Ns material. We find the Ns phase to be extremely sensitive to structural variations; removal of a single ester unit, or the lateral methoxy group from RM734 prevents the formation of the splay nematic phase. We are unable to compensate for this with further structural modifications, such as increased aliphatic content or the use of more complex molecular architectures. Mixture formulation has the potential to offer significant reductions in melting point; however, the pool of Ns materials that are known is currently small and so there is limited scope for detailed formulation work presently. The realisation a low molecular weight splay-nematic material at ambient temperature poses a significant challenge. Much like the quest for ambient temperature uniaxial nematics for display devices in the 1960s onwards, we do not view the present challenge as an intractable problem, but rather one that will yield under the application of sufficient synthetic effort allied with physical characterisation.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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