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From understanding structures in antiferro- ferri and ferroelelectric liquid crystals to an unusual electro-optic effect in a bent-core nematic; a celebration of innovative materials.

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Abstract.

The field of liquid crystals is truly multidisciplinary with numerous examples of virtuous circles of interaction between chemistry, physics, theory and engineering resulting in breakthroughs in both fundamental understanding and novel applications. This paper, written to mark John Goodby's 65th birthday, offers a personal perspective of the synergy between chemistry and physics from a collaboration that has spanned three decades. The first part of the paper reviews some of the physics insights that resulted from chiral liquid crystals fundamental to understanding structures in ferroelectric, ferrielectric and antiferroelectric systems. The second part of the paper describes some of the remarkable consequences of the anomalous elasticity and flexoelectricity found in the nematic phases of bent-core materials. In particular, we present unusual bowing of disclination lines in the nematic phase of a bent-core material in the presence of a field. Finally, the paper summarises some future prospects relating for bent-core materials. The paper by no means captures the amazing breadth of contribution that John's chemistry has made to the subject, but aims to exemplify how his generous collaborative approach coupled with innovative chemistry and physical insight has led to paradigm changes in our subject.

Introduction.

All liquid crystal scientists and engineers recognise the importance of clever material design coupled with excellent chemistry. This article aims to celebrate some of the contributions of John W Goodby FRS to the remarkable evolution of liquid crystal systems over the past decades[1], describing the way in which two families of materials that he designed, chiral and bent-core systems, allowed insight into the physics of a wide range of novel liquid crystal phases. These systems are chosen as they allow a personal reflection of our group's work with John, but undoubtedly this special volume will serve to demonstrate the enormous impact that he has had on the subject. The first part of the paper concentrates on chiral materials that exhibit liquid crystal phases in the ferroelectric family, detailing how clever molecular design allowed a deep insight into phase structures and stability. The inclusion of Selenium and Sulfur in the liquid crystal cores allowed a sophisticated suite of resonant x-ray scattering experiments to be undertaken, giving an unequivocal description of the structures of the antiferroelectric and intermediate phases. Importantly, the Selenium-based materials allowed resonant x-ray scattering experiments in the presence of a field, again offering an unambiguous understanding of the field-dependence of ferro- ferri- and antiferro-electric phases. The second section of the paper moves onto bent core materials, a hot topic for the last 15 years or so, instigated by the anticipation of biaxial nematic phases. Although thermotropic biaxial nematic phases remain elusive, other exciting discoveries were made. This paper describes some of the extreme physical constants and the associated new observations in phases formed by achiral, bent core molecules.

1. The ferroelectric and antiferroelectric family.

Shortly after the discovery of the antiferroelectric (SmC^*_A) phase[2,3], with its two-layer sub-structure, it was realised that many other phases with different layer periodicities could exist. This family of phases was found in chiral, tilted smectic systems and had ferroelectric, antiferroelectric or ferrielectric properties, properties depending on the layer periodicity. Determining which intermediate phases exist was a real challenge as a multitude was predicted theoretically[4] and most experimental techniques couldn't provide unambiguous information about the layer structures. There is now unequivocal evidence for the existence of a ferrielectric 3-layer (SmC^*_{Fi1}) phase, an antiferroelectric 4-layer (SmC*$_{Fi2}$) phase, a 6-layer (SmC*$_{d6}$) phase and a highly chiral SmC*$_{\alpha}$ phase, all of which can exist between the SmC*$_A$ phase and the untilted SmA phase. The SmC*$_{\alpha}$ phase typically exists between the SmC* and SmA phases. Other phases with higher interlayer periodicities are still implicated, as will be discussed.

The puzzle surrounding the layer structure in the family of intermediate phases occupied researchers from the early 1990s until around 2010. Early research showed that optical purity was a critical factor in the observation of the phases, providing a challenge for both chemists and physicists as materials that were superficially identical could exhibit very different phase sequences. Further, x-ray diffraction, normally a powerful probe of the layer structure in smectic liquid crystals, was insensitive to the subtle differences in layer structure in the intermediate phases. Three distinct models had been proposed for the intermediate phases: an Ising model; a Clock model;[5,6,7] and a 'distorted clock' model[8]. It was realised in the late 1990s that resonant x-ray scattering experiments could provide unambiguous information about the layer structures of the phases and that the distorted clock model was the most appropriate.

In resonant x-ray scattering[9, 10], the x-ray energy is tuned to the absorption edge of an atom, usually sulfur or selenium, in the rigid core of the molecule. The local environment modifies the scattering from the resonant atom so that polarization-dependent 'forbidden' reflections are observed. Levelut and Pansu[11] derived the equations predicting the positions and polarizations of the resonant peaks in smectic liquid crystals, equation 1,

$$\frac{q_z}{q_0} = l + m\left(\frac{1}{\nu} \pm \varepsilon\right);\ \varepsilon = \frac{p}{d}. \qquad (1)$$

In equation 1, q_z *and* q_0 are the scattering vectors of the resonant and Bragg peaks respectively, *l* is an integer, *m* can take values of 0, ±1 or ±2, *p* is the helicoidal pitch of the phase, *d* the layer spacing and ν is the number of layers in the superlattice (e.g. $\nu = 2$ for the antiferroelectric SmC$_A$* phase). The models could be distinguished because the polarization, the relative height of the peaks and, in some cases the peak separation, all depend on details of the structure.

John's work on antiferroelectric materials with novel structures and high degrees of chiral purity led to a family of materials that proved invaluable in understanding the intermediate phases. One of the most studied materials studied at the time was MHPOBC (4-(1-methylheptyloxylcarbonyl)phenyl 4'octylbiphenyl-4-carboxylate) which did not include a resonant atom suitable for experiments at the time (more recently, exiting resonant scattering experiments based on carbon have been carried out[12]). In a project aimed at understanding the role of the bend angle in the core of molecules that exhibited antiferroelectric phases, a family of heterocyclic esters was synthesised, Figure 1, which were ideal for resonant scattering experiments[13]. It is important to add a personal note at this point as John's name does not appear in Ref 13. On his return from Bell Labs, John helped Mike Hird and me to establish a collaboration around antiferroelectric liquid crystals and this family of materials came from a project that John helped us to get funded. It is typical of his generous nature that he wanted to support early career researchers (myself and Mike at the time) by taking a back seat to this work. However, his input to the project design was invaluable and it was he who realised that the thiophene and selenophene materials could be used for resonant scattering experiments. Indeed, John ensured that I met Ron Pindak who he had worked with at Bell labs at one of the British Liquid Crystal Conferences, who then included me in experiments that followed his team's pioneering work[14, 15].

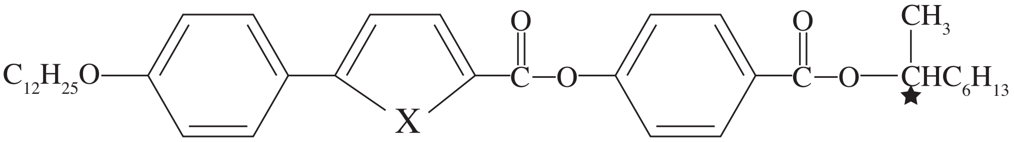

Figure 1. The heterocyclic esters synthesised originally to determine the influence of bend angle on the antiferroelectric behaviour, but later invaluable in resonant x-ray scattering experiments. X= S, Se and O, though the oxygen substituted material had no liquid crystalline behaviour.

A particular novelty of the work that we collaborated on in the following years was based around selenophene materials. X-rays with energy at the sulphur edge (2.47 keV) are easily absorbed by glass; indeed the experiments on free-standing films were undertaken in helium-filled ovens and it was impossible to carry out field-dependent studies on such materials. However, 12.66 keV x-rays (selenium edge) are reasonably well transmitted by glass and we found that field-dependent experiments in device geometries could be carried out.[16] Further, the suite of materials and hence intermediate phases that could be studied, was significantly extended. Features of what was a decade-long collaboration, detailing both the structures and field-induced phase transitions are summarised as follows:

- The SmC$^*_\alpha$ structure was shown to be a temperature-dependent super-lattice of periodicity incommensurate with the layer spacing and is strongly material dependent[17] with periodicities typically between 5 and 10 layers. Although the SmA-SmC$^*_\alpha$ -SmC* phase transitions are complex, experiments showed that the SmA-SmC$_\alpha$* transition is continuous with XY-like critical exponents while the SmC$_\alpha$*-SmC* transition is either 1st order or 2nd, depending on the material[17,18.]
- The periodicities and structures of the 4-layer and 3-layer phases were determined. The biaxial model proposed by Lorman[8] fits the resonant scattering data[19,20,21] and the degree of biaxiality (also known as the distortion angle) can be determined from the intensity ratio of the split peaks obtained from resonant scattering.
- Resonant x-ray scattering proved to be a powerful probe of the field-temperature switching mechanisms and phase diagrams of intermediate phase systems.[16, 22] Resonant x-ray scattering studies of devices allowed the field-temperature phase diagram to be deduced[23,24,25], with one such form shown in Figure 2. At least one additional ferrielectric phase is induced between the SmC$^*_{Fi1}$ and SmC* phase. Although full details of its structure are still unclear, resonant x-ray scattering showed it to have a 3-layer periodicity.

This work served to detail the structures of the intermediate phases and their field-induced transformations. Other groups have used resonant scattering experiments to continue this work and the existence of other phases has been confirmed. The 6-layer phase (predicted theoretically) was found in 2010 in binary mixtures of two chiral smectic mesogens *via* resonant x-ray scattering[26]. Further study[27] revealed a large coexistence region comprising local SmC$^*_{d6}$ and SmC$^*_{Fi2}$ structures on a sub-micron scale. Recently, further field-dependent resonant x-ray experiments have been carried out on a selenium-containing material in a device geometry[28]. This work has revealed additional sub-phases; five-, six-, and seven-layer periodicities appeared in as a function of applied field. This exciting work implies that the book is not yet closed on the family of phases that can appear in antiferroelectric and ferroelectric liquid crystals with both experimental and theoretical challenges to be solved.

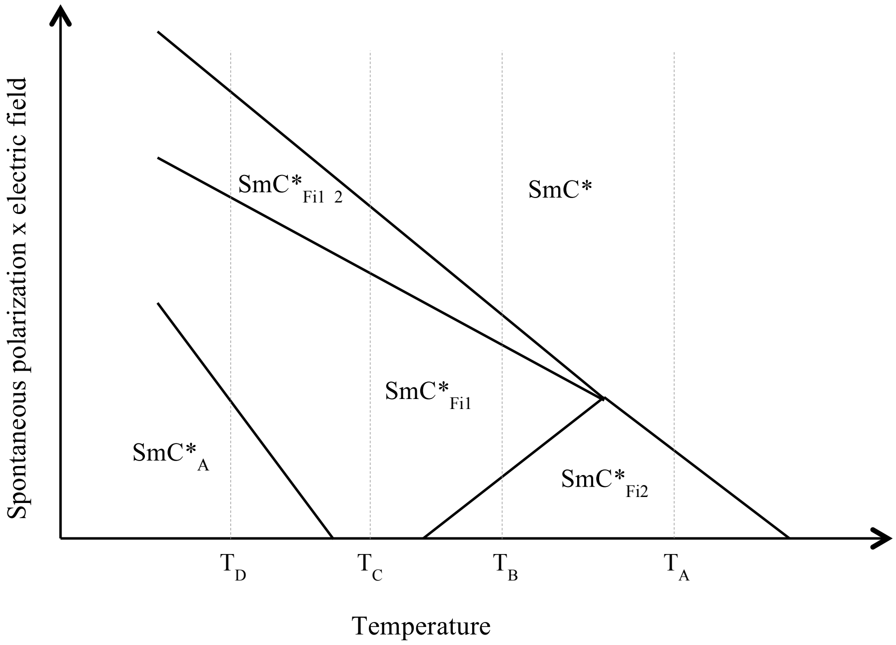

Figure 2. A cartoon of the field-temperature phase diagram reported in some antiferroelectric liquid crystals. The dashed lines indicate some of the possible field-induced transitions. The possible field-dependent phase sequences observed in [26] are as follows. At T_A, SmC^*_{Fi2}-SmC*; at T_B, SmC^*_{Fi2}- SmC^*_{Fi1}- $SmC^*_{Fi1\_2}$-SmC*; At T_C, SmC^*_{Fi1}- $SmC^*_{Fi1\_2}$-SmC*; and at T_D, SmC^*_A- SmC^*_{Fi1}- $SmC^*_{Fi1\_2}$-SmC*. Theories predict other periodicities that can be stable both in the ground state and as a function of fields with some recent reports of observations of such sub-phases.

2. Unexpected behaviour in bent core liquid crystals.

Liquid crystals formed from bent molecules have been of interest for over a century, but it is really only in the last couple of decades that some of their remarkable properties have been fully appreciated[29, 30, 31]. Two recent reviews describe some of the unusual aspects of bent-core systems in detail[32, 33]. Bent-core mesogens have a strong tendency to form smectic phases, which exhibit both a tilt of the major molecular director with respect to the layer normal and a spontaneous polar order along the short molecular axis. Nematic phases are less common in bent-core systems, but a family of oxadiazole liquid crystals became hugely important in 2004 following the first experimental observations that suggested a thermotropic biaxial nematic phase.[34] Although there is still no absolute confirmation of such biaxiality, these fascinating and complex materials have stimulated considerable research, and there is no question that they have properties that are quite distinct from their calamitic analogues. These include anomalous elastic behaviour, relatively large flexoelectricity, spontaneous deracemization and unusual electro-convection, which are now well-known, but there are other unusual phenomena that can be observed that we report here.

Our work on the oxadiazole materials came from a collaboration that produced a wide range of nematic systems[35]. In addition to understanding the influence of the bend-angle on the elastic constants[36], we were able to determine the flexoelectric coefficients[37] in the bent-core materials. It is to be expected that the anomalous values of these physical parameters found in bent-core nematics could lead us to make new observations. This section of the paper describes one such novel observation made in a twisted nematic geometry.

2.1. Unusual behaviour in a twisted nematic device.

Most of the experiments on the nematic phases of bent-core materials have been carried out in planar or homeotropic devices and the electro-optic response of such materials in a twisted nematic (TN) geometry has effectively been neglected. However, we found that in the TN geometry, otherwise linear disclination lines separating domains of opposite twist curve when an electric field is applied perpendicular to the substrates. Such behaviour is not seen in calamitic nematic liquid crystals studied under similar experimental conditions. After considering all possible mechanisms that could explain our observations, we suggested that the most likely explanation is the decrease in the free energy density of the system under applied electric field due to the flexoelectric term in the nematic free energy.

In a TN device, the rubbing direction on the two surfaces has a relative angle $\alpha = \pi/2$. On filling with a nematic liquid crystal, the degeneracy of the $\pm\pi/2$ twist can cause reverse twist domains to form[38] where the director alignment between the domains half way through the device, at $z = d/2$, has opposite orientations. For a liquid crystal with positive dielectric anisotropy, the opposite twist domains in a TN device can reorient in two directions when a field is applied, causing regions known as 'reverse tilt' domains[39] separated by linear disclination lines which can run between the spacer beads in the device or other small particles in the material. Most of these lines, however, are closed into loops and the energy per unit length of the line (or the line tension) is proportional to the average elastic constant, K of the material[40]. If the nematic material includes a chiral additive, opposite handed domains are still observed but the disclination lines are now bowed[41]; domains with the same handedness as the chiral additive grow at the cost of opposite handed domains. The radius of curvature of the disclination lines decreases as the concentration of the chiral additive increases and the twist energy per unit volume is

$$F = \frac{K_{22}}{2}\left(\frac{\alpha}{d} - \frac{2\pi}{P}\right)^2,$$

where K_{22} is the twist elastic constant, α is the twist angle and P is the pitch. The difference in energy between the two twist domains is $\Delta F = \frac{\pi^2 K_{22}}{dP}$. The pitch of long pitch N* materials can be evaluated since the radius of curvature, R, of the bowed disclination line is proportional to the pitch ($P = 2R$). However, the bowing of the disclination lines in an achiral nematic material is unexpected and additionally exhibits a specific pattern that has not been seen before.

We used both planar ($\alpha = \pi$) and TN devices to fully investigate the phenomenon. Both the devices (nominally 5μm thick, with antiparallel-rubbed polyimide alignment stable at high temperatures) and the electro-optic observations (0.1K temperature stability provided by a Linkam hot stage, polarizing microscopy for observations of the textures) were standard and as described in many of our previous papers. The liquid crystal material was OC12-Ph-ODBP-Ph-C5, an oxadiazole-based, material with negative dielectric anisotropy throughout the nematic range. This material has been studied extensively and has been the topic of several reports:

- Unusual EC behaviour was observed in the nematic phase with different characteristics in the higher and lower temperature nematic regimes[36(a)];

- The splay (K_{11}), twist (K_{22}) and bend (K_{33}) elastic constants have been measured across the entire nematic regime. K_{33}, is much lower than in calamitic materials and is also considerably smaller than the splay constant, K_{11} ($K_{33} < K_{11}$)[36(b)];
- The flexoelectric coefficients have been determined across the nematic phase range, with values approximately twice those of calamitic materials[38].

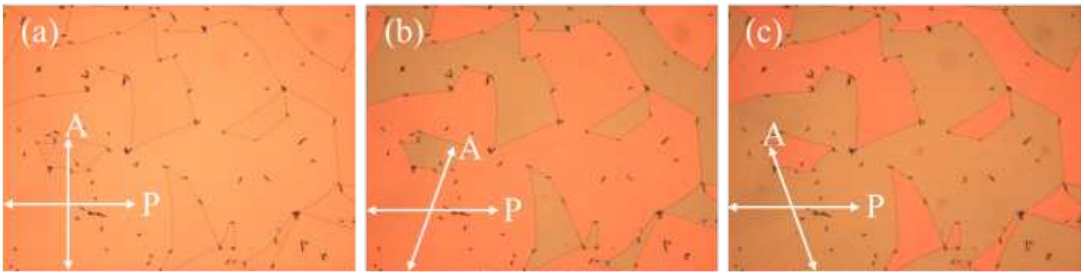

Figure. 3: Polarizing optical microscopy textures in a 5 μm twisted cell in the nematic phase at 175 °C. (a) is under crossed polarizers and (b) and (c) are under uncrossed polarizers. Opposite twist domains separated by linear disclination lines are seen. The black spots are spacer particles.

The textures of OC12-Ph-ODBP-Ph-C5 in a TN geometry at $T-T_{NI} = 55$ K are shown in Figures 3(a-c). The material clearly shows domains of opposite twist separated by disclination lines running between spacer particles; the disclination lines are linear, as expected. When a low amplitude AC electric field is applied perpendicular to the substrates, interesting behaviour of the disclination lines is observed. Most of the linear disclination lines start to bow under the applied field. This is unexpected; the material has negative dielectric anisotropy, the field direction is perpendicular to the substrates and the amplitude is below the threshold for electroconvection. The bowed disclination lines can be seen in Figure 4(a-f) as the applied voltage is increased (contrast has been enhanced for clarity). The radius of curvature of the lines decreases with increasing field up to ~0.6-0.7 V/μm. For fields between ~0.7-0.8 V/μm, there is no change in the texture and higher amplitude fields lead to electro-convection. Similar behaviour is detected throughout the nematic phase range and at frequencies from 100 Hz to 5 kHz. There is no significant temperature dependence of the field at which bowing is initially observed (~0.3 to 0.4 V/μm). When the same experiment is carried out on cells including MBBA, a calamitic nematic with negative dielectric anisotropy, no such bowing is observed for fields up to ~2-3 V/µm. Again, application of higher fields leads to electro-convection. The bowing is clearly related to the nematic phase of the bent-core material, though the origins of such peculiar behaviour are not obvious.

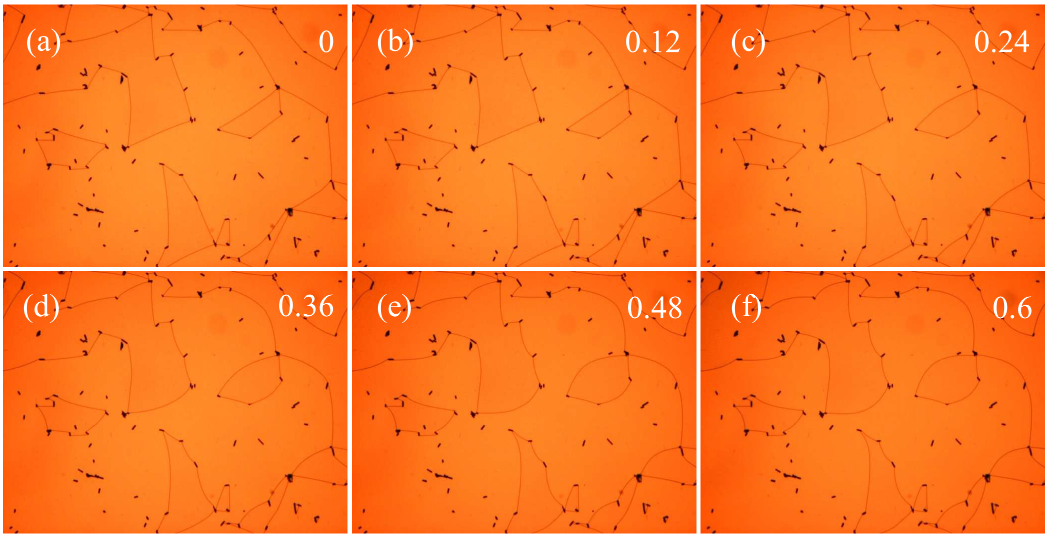

Figure. 4: Polarising microscopy textures in a 5µm TN cell as a function of increasing voltage (fields from 0 to 0.6 V/µm) applied in a direction normal to the substrates. The sample is held at T-T$_{NI}$ = 55 K. The majority of the disclination lines bow as the voltage is increased. (magnification 4x).

In order to understand the physics behind the bowing phenomena it is helpful to consider the behaviour of the opposite twist domains in more detail. Figures 5(b) and 5(c) are taken at T-T$_{NI}$ = 40 K under uncrossed polarizers for fields of magnitude 0 and 0.55 V/µm respectively. Care was taken to align one of the rubbing directions of the cell parallel to the plane of polarization of the incoming light. At this temperature, the two opposite twist domains appear Green (G) and Orange (O) in colour. We assume that at $z = d/2$, for an angle of 70° between the polarizer and the analyser, the O and G domains correspond to director orientations of $+\pi/4$ and $-\pi/4$ respectively (fig. 4a). As the line bows, the director near the disclination must reorient such that one domain grows over the other. We carefully analysed fig. 4c to examine whether there is any growth of only one type of domain over the other when the field is applied. In fact there are two perpendicular directions, (shown as D and D $'$ in fig. 4d) so we can define four coordinates, which are symmetric with respect to the centre. The preference for the growth of O or G domains depends on the orientation of the disclination line with respect to D and D′ (or, equivalently, to which quadrant of the coordinate system they belong). For instance, if β is the angle between direction D and the orientation of the disclination line, for $0 < \beta < \pi/2$ and $\pi < \beta < -\pi/2$ (1st and 3rd quadrants respectively), the orange domains grow over the green ones and in the 2nd and 4th quadrants the green domains are preferred over the orange ones. It is interesting to note that no bowing is observed for the disclination lines parallel to D and D′ .

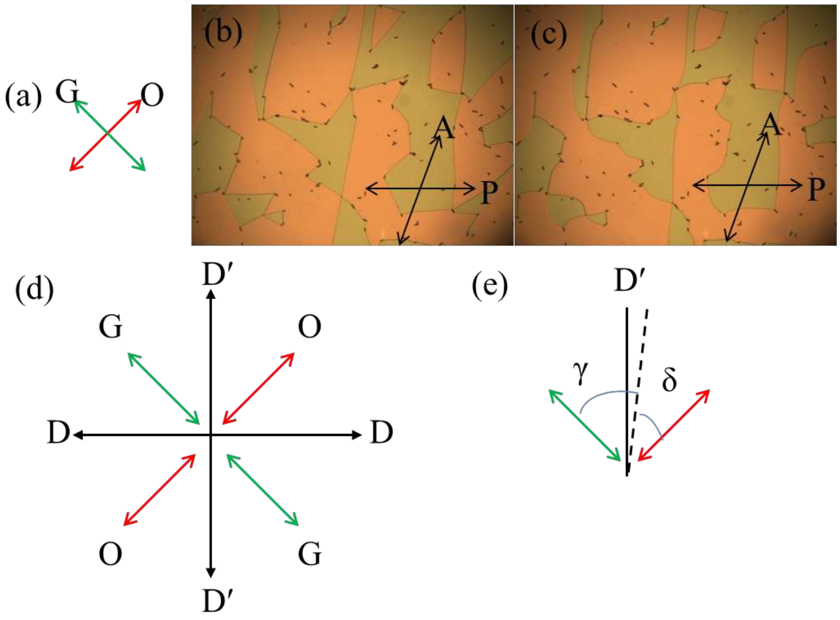

Figure. 5: (a) Cartoons of director orientation at the middle of the device in opposite twisted domains, (b) and (c) POM textures of a twisted cell under uncrossed polarizers at $T-T_{NI}$ = 40 K at 0 and 0.55 V/µm respectively. (d) Representation of the coordinate system formed by D and D’ and the preferred domain in each coordinate, (e) Director orientation in opposite twist domains around a disclination line in the first coordinate, γ and δ are the angles between the directors and the disclination line.

We first considered whether the presence of chirality could reasonably explain the bowing of the disclination lines as oxadiazoles are known to form chiral domains. The bowed lines could be explained if the electric field breaks the surface-induced symmetry and favours the formation of domains of opposite handedness. This could, cause bowing *via* a similar mechanism to that described on the addition of a chiral additive. However, we do not see any physical mechanism that could lead to such symmetry breaking in the presence of electric field.

In a field-free TN device, regions of opposite twist have equal free energy density. Thus, if bowing in the presence of an electric field is due to a physical phenomenon which contributes to the free energy, this must occur in such a way that the when the electric field is applied across the device, the two twist domains no longer have equal energy. The electric energy density of the system depends on the angle between the applied field and the mean direction of the director. Further, the existence of the disclination line is an energetically unfavourable situation. Consequently, when an field is applied, regions of lower energy grow at the expense of those with higher energy, giving an overall decrease in the free energy of the system. This could appear as bowing of disclination lines. The question is what physical phenomenon could be responsible for the origin of the energy difference between opposite twist domains when the field is applied.

To analyse this, let us consider the free energy density of the system, which is given by

$$F = \frac{1}{2}\left(K_{11}(\nabla\cdot\boldsymbol{n})^2 + K_{22}(\boldsymbol{n}\cdot\nabla\times\boldsymbol{n})^2 + K_{33}(\boldsymbol{n}\times\nabla\times\boldsymbol{n})^2\right). \quad (1)$$

Also the surface anchoring energy, W_s, which can be expressed in terms of ***n*** and ***v*** (where ***v*** is the outward unit normal at the liquid crystal-substrate interface) as

$$W_s = \frac{1}{2}\tau_0\left(1+\omega(\boldsymbol{n}\cdot\boldsymbol{v})^2\right)$$

where $\tau_0 > 0$ and $\omega > -1$. As discussed above, we observe that, the preference for the growth of one domain over the other depends on the orientation of the disclination line. Even though this hints that there is an effective anchoring energy associated which is proportional to the angle between the disclination line and the director orientation close to the line, such an effective anchoring energy should be the same for both handed domains, so this term cannot produce the preferred motion of the disclination lines in one direction over the other. Similarly, when an electric field is applied, an additional term equivalent to $-\frac{\varepsilon_0\Delta\varepsilon}{2}(\boldsymbol{E}\cdot\boldsymbol{n})$, must be included in equation (1), where, ε_0 is the dielectric permittivity of free space and

$\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$ is the dielectric anisotropy of the material. However, there is no physical mechanism where the $\Delta\varepsilon$ term could produce a difference in energy between opposite twist domains thus causing the motion of the disclination lines in the specific manner observed.

The director distribution very close to the disclination lines must involve a splay-bend deformation which, in the presence of electric field, can give rise to a flexoelectric contribution to the nematic free energy through the term (***EP***). The associated energy of the electric field - nematic director interaction is:

$$F_{electr} = \frac{1}{2}\int_V \left\{-\frac{\boldsymbol{ED}}{4\pi} - 2\boldsymbol{EP}_{\mathrm{f}}\right\} dV,$$

where the flexoelectric polarization ($\boldsymbol{P}_{\mathrm{f}}$) of the nematic liquid crystal induced by the director $\boldsymbol{n}$ is given by

$$\boldsymbol{P}_{\mathrm{f}} = e_{11}\boldsymbol{n}\ div\ \boldsymbol{n} + e_{33}[curl\ \boldsymbol{n}\times\boldsymbol{n}] \quad (2)$$

and e_{11} and e_{33} are the flexoelectric coefficients[37]. Interestingly, the 2nd term in eq. (2) has opposite signs for right and left handed domains. Therefore, in the presence of electric field, the flexoelectric terms corresponding to the opposite twist domains have a different contribution to the free energy, creating an energy difference in the vicinity of disclination lines thus inducing the motion of the disclination lines when an electric field is applied across the device. This energy difference is independent of the sign of applied electric field as it is the curl of $\boldsymbol{n}$ term in eq. (2) that creates an opposite sign for the right and left domains. Further, as the orientation of a disclination line at an angle to the rubbing direction has more splay-bend on one side of the line than on the other side, the lines choose to bow in one direction over the other. This could explain the observations of the preference for the growth of O and G domains discussed in figure 5.

It is noteworthy that the bowing phenomenon was not seen in a TN device filled with MBBA, studied as a control. There are three obvious differences between the bent-core and the MBBA materials that would result in a different response; the elastic constants, the flexoelectric coefficients and the dielectric anisotropy; we suggest that all play a role allowing this unusual response at such a small electric field. In the bent-core material, K_{22} varies from 0.6 pN to 0.9 pN over the nematic phase range and K_{33} ~ 3 pN, i.e. both are much smaller than in MBBA where K_{22} ~ 4 pN and K_{33} ~

7.3 pN. K_{11} is almost of the same magnitude in both materials. Thus the elastic contribution to the free energy is relatively low in the bent-core system. Further, the flexoelectric coefficient in OC12-Ph-ODBP-Ph-C5 is approximately twice that of calamitics[34]. Finally, the normal force acting on a disclination is known to be proportional to the anisotropy of the medium, the magnitude of the electromagnetic field, the thickness of the medium and the angle between the field and the mean orientation of the director ($\Delta\varepsilon\, E_0^2\, d\, \varphi$). $\Delta\varepsilon$ is approximately –0.5 for MBBA and varies from –1.4 to –3.2 in OC12-Ph-ODBP-Ph-C5 and the higher value $\Delta\varepsilon$ allows bowing of the disclination lines at a lower electric field in the bent-core liquid crystal as the line tension acting on the disclination line is proportional to the $\Delta\varepsilon$. It is interesting to consider the possibility of deducing material parameters from detailed measurements of the bowed disclination lines as was done by Raynes et al. However, in this case, the radius of curvature depends on the orientation of the disclination lines, so a simple measurement of the curvature cannot lead to any meaningful parameter (though a complex analysis may). Further, because several physical parameters are implicated in the only physical explanation we can offer of the phenomenon, deducing meaningful quantitative values would not be straightforward.

In summary, another unexpected behaviour is observed in a bent-core nematic material, namely bowing of reverse twist disclination lines in a TN device under an applied electric field. We attribute the phenomenon to flexoelectricity as that is the only asymmetric contribution to the free energy. It seems that the relatively small elastic contribution, the larger flexoelectric coefficients and the larger dielectric constant all play a part in allowing this bowing to be observed. As the orientation of a disclination line at an angle to the rubbing direction has more splay-bend on one side of the line than on the other side, the lines choose to bow in one direction over the other.

Summary and conclusions.

This paper has described two very different topics, differentiated by their chemistry. The first can be considered ‘mature’. The area of calamitic ferroelectric, ferrielectric and antiferroelectric liquid crystals is now reasonably well-understood as a consequence of strong collaborations between chemists and physicists, combining novel chemistry with novel experimentation. The second system, bent-core liquid crystals, is still giving surprises. In this paper, we have described a new observation in which the very different physical constants seen in bent core materials allows us to access new phenomena. In the case described, a new flexoelectric response in a twisted nematic geometry emerged. However, there are many more exciting consequences of the anomalous physical properties in bent core liquid crystals that are just emerging. For example, the very low elastic constants are implicated in the formation of the dark-conglomerate (DC) phase[42]. As the DC phase is optically isotropic, it was somewhat neglected as a possible electro-optic system until it's field-dependent refractive index was discovered[43], the consequence of complex antiferroelectric and ferroelectric ordering[44]. Such an electro-optic effect has enormous potential for novel devices, such as switchable lenses[45]. Indeed, new kinds of ordering continue to be discovered, including some rather unexpected filaments reminiscent of self-assembling polymers[46] which will ensure that the story continues for some time.

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