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Kaur, S, Panov, VP, Greco, C et al. (4 more authors) (2014) Flexoelectricity in an oxadiazole bent-core nematic liquid crystal. Applied Physics Letters, 105 (22). 223505. ISSN 0003-6951

https://doi.org/10.1063/1.4903242

Flexoelectricity in an oxadiazole bent-core nematic liquid crystal

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We have determined experimentally the magnitude of the difference in the splay and bend flexoelectric coefficients, $|e_1 - e_3|$, of an oxadiazole bent-core liquid crystal by measuring the critical voltage for the formation of flexodomains together with their wave number. The coefficient $|e_1 - e_3|$ is found to be a factor of 2-3 higher than in most conventional calamitic nematic liquid crystals, varying from 8 pCm^{-1} to 20 pCm^{-1} across the $\sim$60K $-$ wide nematic regime. We have also calculated the individual flexoelectric coefficients e_1 and e_3, with the dipolar and quadrupolar contributions of the bent-core liquid crystal by combining density functional theory (DFT) calculations with a molecular field approach and atomistic modelling. Interestingly, the magnitude of the bend flexoelectric coefficient is found to be rather small, in contrast to common expectations for bent-core molecules. The calculations are in excellent agreement with the experimental values, offering an insight into how molecular parameters contribute to the flexoelectric coefficients and illustrating a huge potential for the prediction of flexoelectric behaviour in bent-core liquid crystals.

The phenomenon of flexoelectricity has recently received much attention in advanced materials research; the flexoelectric mechanism induces a spontaneous electrical polarisation in response to a strain gradient and is of interest in fast electro-optic switching, energy harvesting and bioflexoelectric applications.[1–3] Research is also being carried out to exploit flexoelectricity for small power generation, in order to replace the toxic lead-based ceramics presently used. Liquid crystals (LCs) are of significant interest in these contexts; flexoelectricity was first discovered in such soft matter systems some time ago[4] but the associated electro-optic response is currently of relevance to developing fast display modes. The flexoelectric response in nematic LCs occurs as a result of splay or bend deformations in the director field that induce polarity. The macroscopic expression for the flexoelectric polarization is given by $\mathbf{P} = e_1\mathbf{n}(\nabla\cdot\mathbf{n}) + e_3(\nabla\times\mathbf{n})\times\mathbf{n}$, where $\mathbf{n}$ is the nematic director field and e_1 and e_3 are the splay and bend flexoelectric coefficients respectively. There are rather few measurements of the separate coefficients in nematic LCs, and more commonly the sum $(e_1 + e_3)$ or difference $(e_1 - e_3)$ is deduced.[5] Typical magnitudes of $(e_1 - e_3)$ in calamitic (rod-like) nematic LCs lie between 1 pCm^{-1} and 17 pCm^{-1}, most falling at the lower end of the range. Understanding the flexoelectric behaviour of nematic LCs is increasingly important with its immediate relevance to fast electro-optic switching and emerging interest in using LCs for energy harvesting.

The few measurements of flexoelectric coefficients in nematic phases formed by bent-core molecules suggest that the bent structure enhances the flexoelectric response, recently stimulating much discussion in the literature.[6–11] Despite the numerous methods that can, in principle, be utilized to measure flexoelectric coefficients, described in Ref.[5] and references therein, the measurement of these coefficients is not a straightforward task due to the approximations and complex analysis required in most experiments. Indeed, there are only a few reports of flexoelectric coefficients in bent-core materials, mostly at a single temperature or over a narrow temperature range,[9–14] and none across the complete temperature range of their nematic phase. In this paper, we report a study of the temperature dependence of the flexoelectric coefficients determined for an oxadiazole-based bent-core LC across its complete $\sim$60K wide nematic regime. The values of $|e_1 - e_3|$ are obtained experimentally using both the critical voltage measured for formation of flexodomains and their wavenumber. The coefficients e_1 and e_3 are also calculated using a molecular field approach with atomistic modelling and compared with the experimental values.[15,16]

For our experimental measurements, we follow the approach of Bobylev and Pikin[17] who demonstrated an instability based on the flexoelectric effect in a nematic material, which occurred on the application of electric field above a certain threshold. The direction of the instability patterns, later termed longitudinal rolls (LRs), was found to be parallel to the director. In the case of a DC driving voltage, the critical voltage U_{th} and critical wave number q_c of the Flexodomains (FDs) are described by:

$$U_{th} = \frac{2\pi K_{avg}}{|e_1 - e_3|(1+\mu)}, q_c = \frac{\pi}{d_{cell}}\sqrt{\frac{1-\mu}{1+\mu}}, \qquad (1)$$

where d_{cell} is the cell gap, $\mu = \frac{\epsilon_0 \Delta\epsilon K_{avg}}{(e_1-e_3)^2}$, ϵ_0 is the permittivity of free space, $\Delta\epsilon$ is the dielectric anisotropy and $K_{11} = K_{22} = K_{33} = K_{avg}$ are the splay, twist, bend and average elastic constants of the nematic LC respectively (this is the one elastic constant approximation). According to eqn (1), the FDs only exist if $|\mu| < 1$, i.e.,

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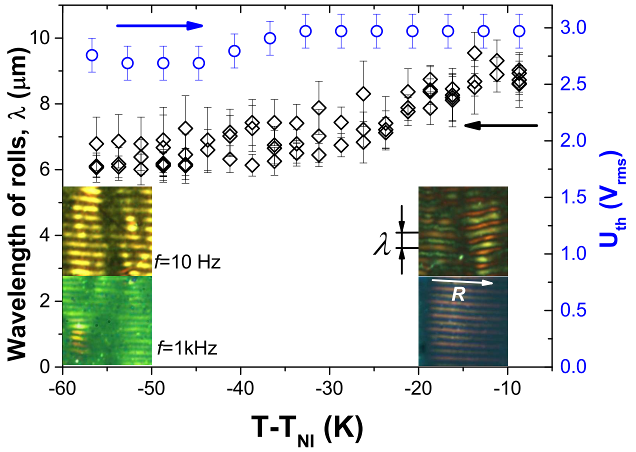

FIG. 1. (Color Online) The temperature dependence of the wavelength ($\diamond$) and threshold voltage ($\circ$) measured at a frequency of 10 Hz for C5-Ph-ODBP-Ph-OC12. The data are presented with respect to the temperature difference from the nematic to isotropic phase transition, T_{NI}. The insets: patterns of the flexodomains between crossed polarizers for $T-T_{NI}=-50K$ (left) and $T-T_{NI}=-15K$ (right) for 10 Hz (top) and of longitudinal rolls at 1 kHz (bottom); the images are 60μm wide.

$|\Delta\epsilon| < \frac{(e_1-e_3)^2}{\epsilon_0 K_{avg}}$.

The material under investigation in this work is the bent-core LC C5-Ph-ODBP-Ph-OC12 derived from a 1,3,4-oxadiazole-biphenyl core.[18–20] The phase transitions are measured as: Isotropic 239.6 °C Nematic 184.6 °C Dark Conglomerate phase and, importantly, the elastic constants and dielectric anisotropy are known across the entire nematic phase range.[19] The threshold voltage for the formation of flexodomains and their critical wave number are determined in 5 μm thick devices (details are given elsewhere[18,19]). Although the classical analysis of FDs uses DC voltage, in common with most similar experiments the FDs in our experiment have been observed at a low frequency of 10 Hz in order to avoid ionic conductivity contributions. For such a low frequency, we can neglect backflow effects, satisfying the requirement for the equilibrium deformation.[5] The FDs observed are shown in Figure 1 at low and high temperature regions in the nematic phase and it is important to note that they are stationary.

As can be seen from Eqns. (1), the (absolute) flexoelectric difference, $|e_1-e_3|$, can be deduced using either the critical voltage, U_{th}, or the wave number, q_c. These independent measurements allow us to confirm the accuracy of using parameters associated with FDs observed in our system to deduce the flexoelectric difference of the material. Figure 1 shows the temperature dependence of U_{th} and wavelength of the rolls, $\lambda = 2\pi/q_c$. The behaviour of U_{th} is almost temperature independent across the nematic regime. The measurement of λ depends on the visibility of the pattern which is poorer just above U_{th} and the scatter of λ is explained by the trade-off between measurements with relatively low visibility at threshold and patterns with better contrast but slightly altered periodicity just above U_{th}.

Figure. 2 shows the variation of (e_1-e_3) across the nematic temperature range, determined experimentally using U_{th}(filled squares) and assumed to take negative values, justified by the calculations described later. Ref.[18,19] provided the elastic constants and the high frequency data for $\Delta\epsilon$ from which values at 10 Hz were extrapolated. In using Eq. 1, K_{avg} is taken to be the average of K_{11} and K_{22} and this single constant approximation is the greatest source of error in determining (e_1-e_3). The extrapolate value of $\Delta\epsilon$ at 10 Hz is found to vary from 1.4±0.1 ($T-T_{NI}=-8.7$K) to 3.2±0.2 ($T-T_{NI}=-56.7$K). The flexoelectric difference (e_1-e_3) varies approximately linearly with temperature and more than doubles across the nematic regime, from -7.7±1.2pCm^{-1} ($T-T_{NI}=-8.7$K) to -20.1±2.5 pCm^{-1} ($T-T_{NI}=-56.7$K). For comparison (e_1-e_3) determined from q_c varies from -12.7 ± 0.8 ($T-T_{NI}=-8.7$K) to -20.1 ± 1.0 ($T-T_{NI}=-56.7$K), in excellent agreement (within 10-15%) of the values deduced from U_{th}. The absolute uncertainty in the measurement of $|e_1-e_3|$ using this technique is 15-20%. At all temperatures $|\mu|$ takes values <1 which satisfies the prerequisite for the existence of FDs.

It is worth mentioning that an earlier study of C5-Ph-ODBP-Ph-OC12, reported non-standard electroconvection at 1 kHz in the form of LRs and it was noted that flexoelectricity could potentially explain that observation. In fact, the linear behaviour of U_{th} with respect to frequency[18] together with the large change in q_c (by a factor of 0.6) with decreasing frequency (100 Hz - 1 kHz)[18] observed in C5-Ph-ODBP-Ph-OC12 is exactly what would be expected if the LRs were flexodomains. Similar frequency behaviour for U_{th} and qc reported for rolls in the rod-like nematic LC, 1OO8[21] led to the conclusion that the rolls were FDs. Wiant et al.[22] also suggested the possibility that the electroconvection pattern observed in the bent-core material ClPbis10BB could be caused by the flexoelectric effect. It would be unexpected for FDs to be observed at frequencies as high as 1 kHz, but such a possibility cannot be ruled out for the LRs observed in C5-Ph-ODBP-Ph-OC12. Indeed, the temperature dependence of (e_1-e_3) calculated using U_{th} for the LRs observed at 1 kHz is shown by open circles in Figure 2. In this case, the absolute uncertainty in the measurement of (e_1-e_3) is ~30%. Interestingly, within experimental error, the value determined for (e_1-e_3) using the assumption that the high frequency LRs are FDs is in good agreement with the values determined at 10 Hz.

The flexoelectric difference for C5-Ph-ODBP-Ph-OC12 is found to be 2-3 times higher than values reported for most calamitic nematic LCs,[10,21,23,24] in common with other bent-core nematic systems.

It is possible to make a comparative analysis of

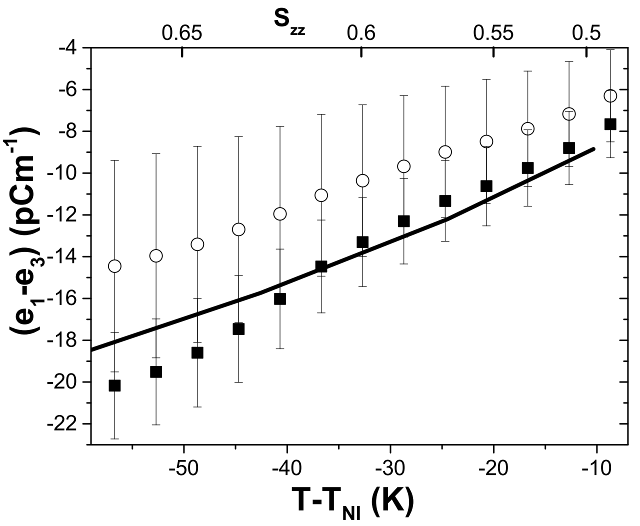

FIG. 2. The experimentally determined value of $(e_1 - e_3)$ at frequencies of 10 Hz(■) and 1 kHz (○) as a function of temperature (bottom axis) and order parameter (top axis). The solid line shows values for $(e_1 - e_3)$ calculated using atomistic modelling as a function of order parameter for the molecular axis passing through the carbon atoms of the oxadiazole ring (S_{zz}).The measurements of $(e_1 - e_3)$ are assumed to take a negative value, following calculations.

our experimentally determined flexoelectric coefficients with those calculated using a computational methodology. Such an approach has successfully been applied to the elastic constants of several different bent-core materials.[19,25,26] In this approach, expressions for the flexoelectric coefficients are obtained starting from the molecular orientational distribution in the nematic phase and the charge distribution in the molecule. The splay and bend coefficients are then expressed in terms of dipole (d) and quadrupole moments of the molecule and contain an implicit dependence on all the orientational order parameters, without restriction to quadratic terms in S. The dipolar contribution to the bend coefficient, $e_3(d)$, depends on the component of dipole moment perpendicular to the local director and hence parallel to the local bend, whereas the dipolar contribution to the splay coefficient, $e_1(d)$, depends on the component along the director. Conversely, the quadrupole contribution is identical for both e_1 and e_3. Therefore the difference $(e_1 - e_3)$ depends only on the molecular dipole and vanishes for non-polar molecules, while both dipole and quadrupole moments contribute to $(e_1 + e_3)$. This approach allows the prediction of both the magnitude and the sign of the flexoelectric coefficients of a LC material starting from the geometry and charge distribution of its constituent molecules. The effect of the conformational flexibility is easily included: the flexoelectric response of the material is obtained by averaging the contribution of the various molecular conformations, each weighted by the appropriate statistical weight. The latter takes into account the conformer's torsional potential energy and the fact that depending on their shape, conformers can be more or less accommodated in the nematic phase. As described in Ref.,[19] the rotational isomeric state (RIS) approximation was used to describe the conformational degrees of freedom of C5-Ph-ODBP-Ph-OC12, and two different conformations of the core were considered. Atomic charges were obtained using the restrained electrostatic potential method (RESP),[27] with the electrostatic potential computed by DFT at the B3LYP/6-311+G(d,p) level.[28] Charges equal to 70% of the RESP values were finally used to calculate the dipolar and quadrupolar moments and the flexoelectric coefficients.[16] The molecular transverse dipole moment predicted by the quantum mechanical calculations varies from ∼3.5 D to ∼4 D, depending on the molecular conformation. Figure 3 shows the individual flexoelectric coefficients and the dipolar contributions obtained from calculations as a function of the order parameter for the molecular axis passing through the carbon atoms of the oxadiazole ring of C5-Ph-ODBP-Ph-OC12 (S_{zz}). It is seen that the dipole contribution to e_3 is large and positive, as expected for a banana-shaped molecule with an inward pointing transverse dipole.[4] On the contrary, the dipole contribution to e_1 is very small, consistent with the small longitudinal dipole; in any case, the molecular shape would not allow an effective coupling of a longitudinal dipole to a splay deformation. The quadrupole contribution, which is identical for e_1 and e_3, is comparable in magnitude to the dipole contribution to e_3, but opposite in sign. This leads to a small e_3, lower than e_1, apparently in contrast to what one might expect for bent-core mesogens.

The calculated flexoelectric difference is shown by the thick line in Figure 2 allowing direct comparison with the experimentally determined values. The values are negative with $(e_1 - e_3) =\sim -e_3(d)$, since $e_1(d) \sim 0$. The trend of $(e_1 - e_3)$ as a function of the order parameter is in very good agreement with the experiment.

It is interesting to consider how our measurements of the bent-core LC C5-Ph-ODBP-Ph-OC12 compare with measurements of similar materials made using different techniques. A different bent-core mesogen, 4-cyanoresorcinol bisbenzoate, with an inwards pointing transverse dipole was studied using the ULH approach (such measurements are actually carried out on mixtures that include a chiral dopant).[13] Results qualitatively similar to those for C5-Ph-ODBP-Ph-OC12 are reported: a negative $(e_1 - e_3)$ which increases in magnitude from $\sim$ 10pCm^{-1} to $\sim$ 17pCm^{-1} with decreasing temperature. Although the magnitude $|e_1 - e_3|$ is comparable to the values for C5-Ph-ODBP-Ph-OC12, the temperature dependence is larger.[13] In Ref.[9] a value of $|e_3| \sim$ 4pCm^{-1} ($T - T_{NI} = -5$K) is reported for a 4-cyanoresorcinol derivate, determined using the converse flexoelectric effect. This is similar in magnitude to e_3 calculated for C5-Ph-ODBP-Ph-OC12, which we have found to result from the compensation between the quadrupolar and the dipolar contribution, but opposite in sign (Figure 3). The

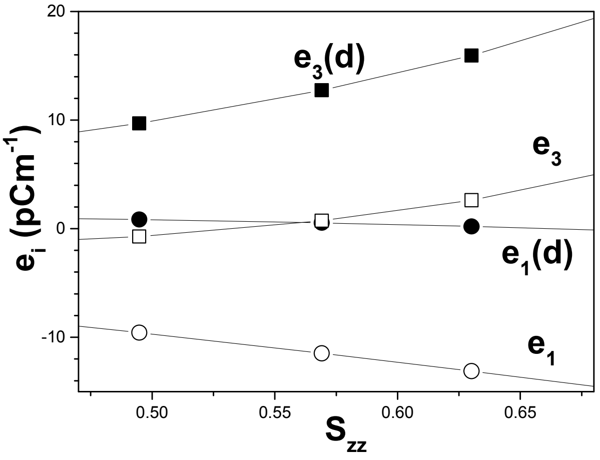

FIG. 3. The calculated flexoelectric coefficients, e_i as a function of the order parameter for the molecular axis passing through the carbon atoms of the oxadiazole ring (S_{zz}): splay (○), dipole contribution to the splay (●), bend (□), dipole contribution to the bend (■).

higher value, $|e_3| \sim 16\text{pCm}^{-1}$, found in Ref.[10] for another resorcinol derivative, is not necessarily in contradiction with Ref.[9] since in the former case the central ring bears a chlorine atom instead of a cyano group. As a consequence, a smaller dipolar contribution to e_3 is expected. High values of $|e_1 - e_3|$, even larger than 20pCm^{-1} at low reduced temperature, have been reported for odd mesogenic dimers, which have an average bent shape.[29,30] The behaviour of both $(e_1 - e_3)$ and of e_1 and e_3 individually[16] is similar to that found here for bent-core mesogens, provided all signs are reversed. This is explained by a change of sign of the transverse dipole which points outwards in the case of dimers with terminal cyano or fluorine groups.

In summary, we have experimentally determined $|e_1 - e_3|$ across the complete nematic regime of a bent-core oxadiazole nematic LC using two independent measurements of flexoelectric domains and utilizing known values for the elastic constants and dielectric anisotropy. Measurements of $|e_1 - e_3|$ are found to vary from ∼8 to $\sim 20\text{pCm}^{-1}$ across the nematic regime. These values are a factor of 2-3 higher than those reported in most calamitic nematic LCs, but are comparable to those obtained in other bent-core materials using similar experimental approaches. The flexoelectric coefficients, their differences and dipolar contributions are also calculated via atomistic modelling, giving results which are in excellent agreement (within 1-2 pCm^{-1}) with the experimental values. The calculations offer an important insight into the origin of the behaviour of the flexoelectric coefficients both in the material considered here and in other bent-core systems, which will be of use in the design of materials with specific flexoelectric behaviour.

The authors are grateful to Prof. J. C. Jones for very useful discussions. This work was supported by the Engineering and Physical Sciences Research Council (EP/G023093/1, EP/D055261/1 and EP/L012111/1). CG acknowledges the PhD School of Materials Science and Engineering (University of Padova) and Merck Chemicals Ltd for financial support. VG gratefully acknowledges the Royal Society for funding through a Dorothy Hodgkin Fellowship.

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