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Flexoelectricity of Wedge-Like Molecules in Nematic Mixtures

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We report on the observation of flexoelectricity of an asymmetric "swallow-tail" compound by dissolving it in a BMAOB nematic matrix and studying the thickness dependence of the period of longitudinal (2nd order) domains in planar layers under d.c. excitation. From the experimental data and Bobilev-Pikin theory we estimate the value of the flexocoefficient difference $|e^*| = |e_{1z} - e_{3x}|$ as a function of the evaluation about expected concentration and evaluate an extrapolated value of this difference for the "swallow-tail" compound.

Keywords: flexoelectricity; swallow-tail molecules; longitudinal (2nd order) domains

INTRODUCTION

Flexoelectricity provides a linear coupling between electric polarization $\boldsymbol{P}$ and orientational deformation in liquid crystals:

$$P = e_{1z} n(\mathrm{div} n) + e_{3x}(\mathrm{rot} n \times n), \tag{1}$$

where e_{1z} and e_{3x} are flexoelectric coefficients for splay and bend distortions, respectively. Elastic splay and bend deformations are connected with the appearance of a local polarization density in the liquid crystal. This phenomenon serves as a macroscopic manifestation of molecular asymmetry[1]. Accordingly, knowledge of the flexoelectric coefficients reveals important aspects of steric molecular interactions under external fields. In this respect, molecules of mesogens with

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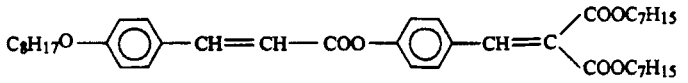
wedge-like asymmetry and especially "swallow-tail" mesogens (Figure 1) are of substantial interest[2].



$$Cr \xrightarrow{49^{\circ}C} (N38^{\circ}C)\ I$$

FIGURE 1 Typical representative of "swallow-tail" mesogens

We have chosen these molecules because of the theoretically expected strong flexoelectric properties related to their steric asymmetry. However, such mesogens are usually high temperature nematics, and are not easy to orient. To bypass such difficulties we have dissolved the swallow-tail compounds in a room temperature nematic matrix.

Assuming that the Frank elastic coefficients do not change substantially in the mixture, we may relate[1,3–9] the flexoelectric coefficients e_{1z}, e_{3x} of the mixture to those of the nematic matrix e^0_{1z}, e^0_{3x} and of the swallow tail dopant e^1_{1z}, e^1_{3x} by means of the simple approximation:

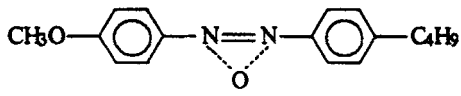
$$\begin{aligned} e_{1z} &\approx (1-\nu)e^0_{1z} + \nu e^1_{1z} \\ e_{3x} &\approx (1-\nu)e^0_{3x} + \nu e^1_{3x}. \end{aligned} \tag{2}$$

where ν is the dopant's concentration.

MATERIALS AND METHODS

The "swallow-tail" substance (Figure 1) was obtained from the Halle group. The nematic BMAOB (obtained from NIOPIC, Russia) was used as the room temperature, low conductivity nematic matrix showing 2nd order domains (Figure 2). Compared to Schiff base MBBA, which has the same end substituents but a less stable central bond, (-CH=N-), BMAOB has an advantage of being more stable because of the azoxy group.

The asymmetric mesogen has been dissolved in increasing concentrations in the well characterized nematic matrix and the evolution of the flexoelectricity of the mixture as a function of the concentration (1wt%, 2wt%, 5wt% and 10wt%, i.e. 0.54mole%, 1.09mole%, 2.21mole% and 4.55mole%) was followed.



$$Cr \xrightarrow{21^\circ C} N \xrightarrow{72^\circ C} I \quad ; \quad \varepsilon_a = -0.27$$

FIGURE 2 The chemical formula and transition temperature of the liquid crystal p-n-butyl-p-methoxyazoxybenzene (BMAOB)

The mixed material was placed between two conductive ITO coated glass substrates. Wedge-like cells (50mm long) with one 25 μm thick Mylar spacer were assembled in order to provide a varying layer thickness of the liquid crystal. The conductive surfaces were treated by rubbing for strong homogeneous planar anchoring of BMAOB. Diamond paste (DP – Paste, M, Sruers) was used as rubbing material. The cells were then filled by capillarity. Experiments were carried out at temperature 29°C in the nematic phase. The wedge cell thickness was calibrated interferometrically before every measurement at zero field by passing a laser beam through the liquid crystal cell between crossed polarizers directed at 45° to the rubbing direction. We assume that the refractive indices of the mixture do not differ substantially from those of the pure BMAOB[10].

The difference of splay-bend flexoelectric coefficients was measured by observing experimentally the appearance of 2nd order flexoelectric domains in the mixtures. These domains, discovered by Vistin[11] and interpreted theoretically as due to flexoelectricity by Bobilev-Pikin[12], can be well studied by laser light diffraction methods. The longitudinal domain formation is a two-dimensional flexoelectric instability with respect to director orientations and has no hydrodynamic nature. The second order longitudinal domains, which are directed parallel to the initial direction of the director, can be observed in thin films of some low conductivity liquid crystals. It seems that both small thickness and low conductivity suppress the hydrodynamic effects. The threshold voltage of the instability is independent of the electric conductivity and temperature and weakly depends on the thickness of the LC layer[13].

According to the Bobilev – Pikin theory developed for the rigid boundary conditions, small deformations and one-constant approximation, the following solutions hold for the threshold voltage U_c and the domain period ω_c at the threshold[12]:

$$U_c = \frac{2\pi K}{|e^*|(1+\mu)}; \quad \omega_c = d\left(\frac{1+\mu}{1-\mu}\right)^{1/2}, \tag{3}$$

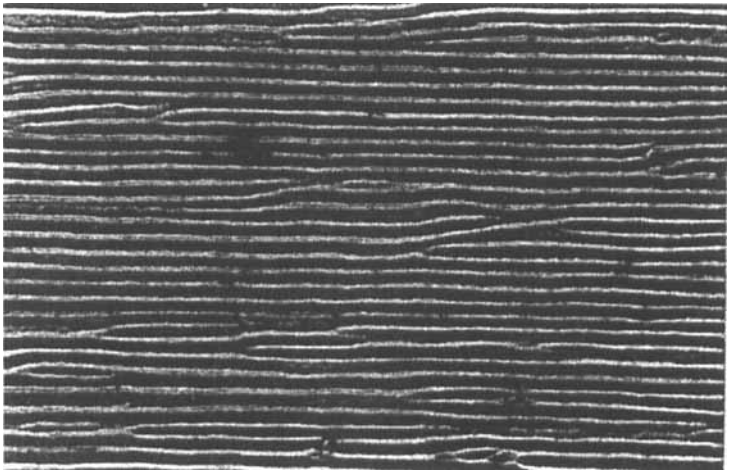


FIGURE 3 Longitudinal domains in a planar layer of "swallow-tail" compound (0.54 mole%) in BMAOB mixture; at the threshold voltage, 11.3V. Domains are **parallel** to the rubbing direction. Polarized light, analyzer normal to domain direction, polarizer slightly uncrossed. Layer thickness is 10 μm. Longitudinal domain period is 7 μm. Narrow side of the frame is 180 μm

where

$$\mu = \frac{\varepsilon_o \varepsilon_a K}{e^{*2}}; \quad e^* = e_{1z} - e_{3x}$$

ε_a is the dielectric anisotropy, ε_o is the dielectric constant of free space, d is the layer thickness and K is average elastic modulus. The domain period changes linearly with respect to the layer thickness. From the above equations we can find ε_a and the parameter μ, i.e., e^*, provided that independent data about K are available.

Upon reaching the threshold voltage a phase grating in the form of longitudinal domains is formed in the cell. A linearly polarized laser beam passing through the sample creates diffraction spots on a screen placed behind the cell. By measuring the distance to the first maximum and find out the angle θ the domain period ω was calculated from the relation: $\omega \sin\theta = n\lambda$, where λ is the laser wavelength.

RESULTS AND DISCUSSION

The measurements of the domain period at the threshold voltage as a function of the cell thickness for different mixture concentrations are shown in Figure 4. The

data points were taken in sequence at room temperature 29°C. Measurements at 4.55 mole% were limited for thicknesses below 12 μm, because above this thickness a striking anchoring transition from planar to homeotropic alignment takes place at this concentration of the "swallow-tail" compound. The unexpected appearance of this transition precluded further studies at higher concentrations.

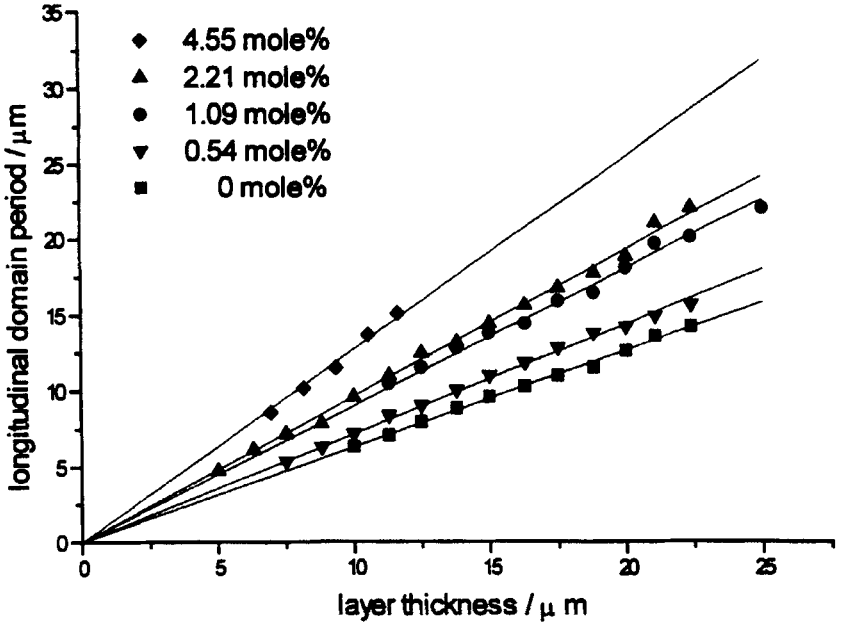


FIGURE 4 The 2nd order longitudinal domain period at the threshold voltage as a function of layer thickness. T = 29°C. The linear fits going through the origin is shown. The fit slope increases following the "swallow-tail" molar concentration in BMAOB liquid crystal: 0 mole%, 0.54 mole%, 1.09 mole%, 2.21 mole% and 4.55 mole%

All curves are nicely fitted by a straight line through the origin in accordance with Bobilev – Pikin theory[12] In the case of pure BMAOB it was confirmed that the dependence is essentially the same as that reported by Barnik et al.[13]. Good homogeneous orientation was also obtained after filling the cells with the prepared mixtures. No hydrodynamic effects were observed in the thickness range under consideration (5 – 25 μm) in any of the mixture concentrations (i.e., 0.54 mole%, 1.09 mole%, 2.21 mole% and 4.55 mole%). This fact suggests that the "swallow-tail" mesogen does not increase considerably the conductivity of the mixture even at higher concentration.

As it can be seen from Figure 4 the ω_c/d slope increases with increasing the "swallow- tail" molecule concentration. In order to extract the values $|e^*| = |e_{1z} -$

$e_{3x}|$ we assume that the average elastic constant remains at the value $K = 6.5x10^{-12}$ N[7] for all the dopant concentrations studied.

Using the experimental values of the threshold voltage and the fitted slopes ω_c/d at the threshold voltage by means of equations (3), we can calculate the flexoelectric coefficient difference $|e^*|$ and the dielectric anisotropy ε_a. It appears that ε_a varies in a roughly linear fashion from –0.21 to +0.10, i.e., it changes sign at about 2.62 mole%. This conclusion follows from the decrease of U_c with concentration (Figure 5). The positive sign of ε_a at 4.55 mole% was confirmed by separate experiments in planar cells, revealing a Freedericksz transition under a.c. excitation (1 KHz) with a Freedericksz threshold of 8.3 V_{rms}.

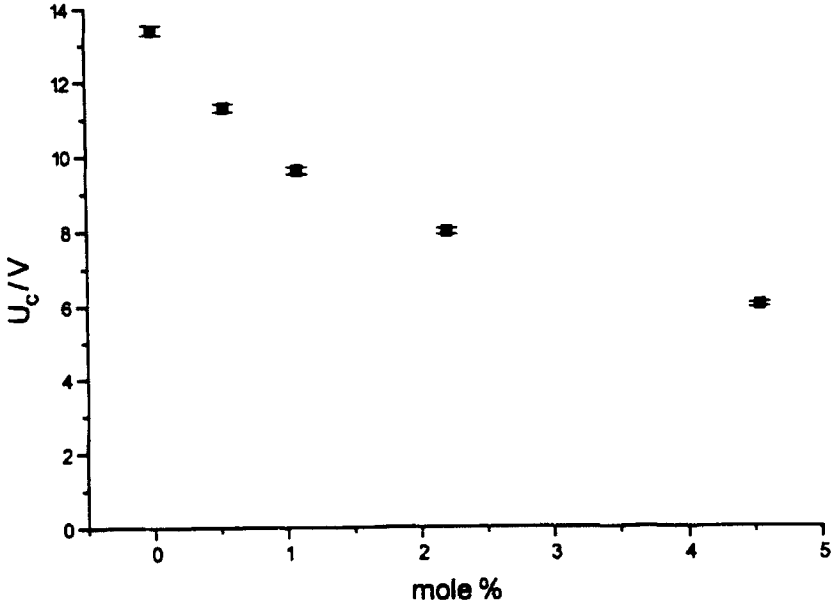


FIGURE 5 The threshold voltage U_c as a function of the "swallow-tail"/BMAOB molar concentration

The results for $|e^*|$ are shown in Figure 6. The relative error of our measurements is estimated to be ±5%. A shallow minimum at 1.09 mole% (not included in Figure 6) was found. However, such minimum is not predicted by the theory quoted above. Most probably, it is a computational artifact originating from the multiplication of an increasing dependence (ω_c/d vs. v) and a decreasing dependence (U_c vs. v). Apart from this "minimum" point a line with a positive slope of 0.0216 could nicely fit the rest of the points. This means that the extrapolated

value of $|e^*|$ for 100 mole% "swallow-tail", according to Eq. 2 is by $2.16 \cdot 10^{-12}$ C/m higher than that of the pure BMAOB, which is $5.3 \cdot 10^{-12}$ C/m. Such an 40% increment demonstrates the role of steric asymmetry of "swallow-tail" molecules.

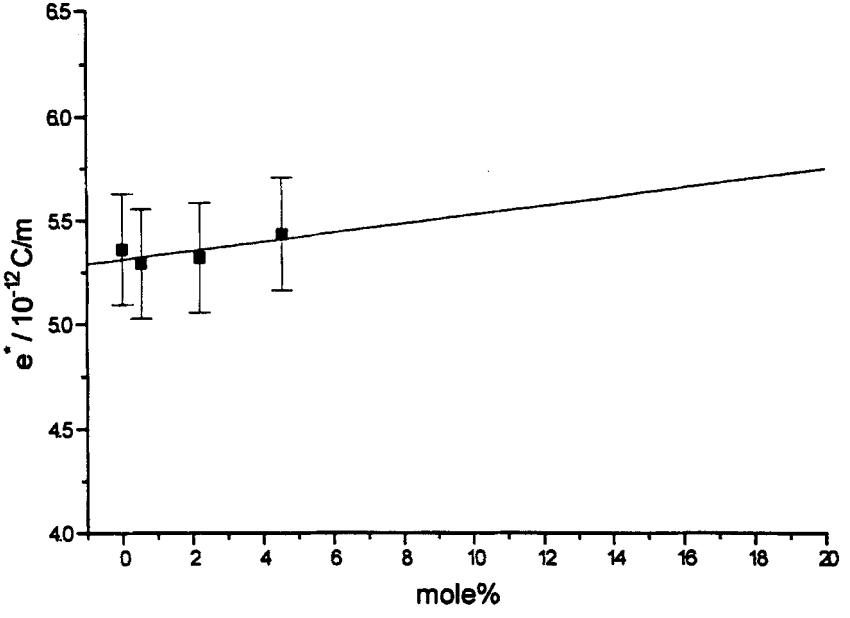


FIGURE 6 Flexoelectric coefficient difference $|e^*|$ as a function of "swallow-tail" concentration in BMAOB. T = 29°C

CONCLUSION

In this work we present the observation of flexoelectricity of a "swallow-tail" compound dissolved in BMAOB at room temperature. The flexoelectric coefficient difference $|e^*|$ is determined as a function of concentration by the method of 2nd order longitudinal domain formation in a case of strong anchoring of the molecules to the walls. The difference $|e^*|$ shows a measurable increase with concentration even in the relatively small range under investigated. This increase is attributed to the strong steric asymmetry of "swallow tail" molecules.

Acknowledgements

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