

## Wedge-Like Asymmetry Contribution to Flexoelectricity in Nematic Mixtures\*

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**Abstract.** Experimental values of the flexocoefficient difference  $|e^*| = |e_{1z} - e_{3x}|$  of a BMAOB/“swallow-tail” mixture as a function of the concentration of a “swallow-tail” compound are analysed. The fact that the extrapolated value of this difference is somewhat lower than originally expected is explained by a theory showing that the strong steric asymmetry of “swallow-tail” molecules gives a comparable contribution to *both* flexocoefficients.

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### 1 Introduction

In previous paper [1] we reported the observation of flexoelectricity of an asymmetric “swallow-tail” compound dissolved in a BMAOB nematic matrix. Flexoelectricity consists in the appearance of a local polarization density in the liquid crystal subjected to elastic splay or bend deformations [2]. As far as stronger steric molecular interactions predict stronger flexoelectric properties the so-called “swallow-tail” mesogens are of substantial interest [3]. The “swallow-tail” substance under consideration is shown in Figure 1. The nematic matrix is BMAOB. The substance details are described elsewhere [1]. The “swallow-tail” compound was dissolved in BMAOB by heating to isotropic phase. Subsequently the mixed material was placed between two conductive ITO coated glass substrates forming wedge-like cells. Further the thickness dependence of the period of longitudinal (2nd order) domains [4,5] in planar layers under d.c. excitation has been studied. According Bobilev-Pikin theory [6], the flexoelectric coefficient difference  $|e^*| = |e_{1z} - e_{3x}|$  has been determined as a function of concentration by quantitative observations of the 2nd order longitudinal domain formation, described in [1]. However the concentration dependence observed

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\*This work is dedicated to Professor Alexander Derzhanski, DSc, Corresponding Member of the Bulgarian Academy of Sciences, on the occasion of his 70<sup>th</sup> anniversary.

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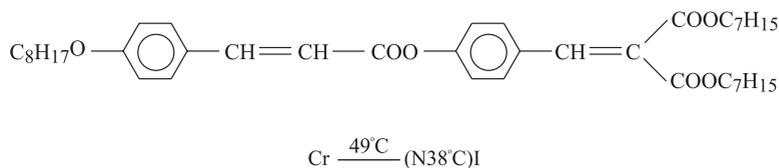


Figure 1. Typical representative of “swallow-tail” mesogens

by us, although in a quite narrow range: 0–4.55 mole%, was not terribly steep. The major finding of that work was that the effect of a marked wedge shape molecule upon flexoelectricity is not dramatic, as originally expected! This is now theoretically explained by the fact that wedge-like asymmetry gives comparable contributions to both flexocoefficients, thus their difference is weakly influenced.

## 2 Theoretical remarks

We shall consider flexoelectric polarization originating from the combination [3] of steric and electric asymmetry of a mixture of mesogenic molecules. Imagine an elongated molecule, having an electric dipole with two components:  $\mu_3$  (longitudinal) and  $\mu_1$  (transversal), and a steric dipole [7,8] with two components (Figure 2):  $s_0 = \alpha/a$  (wedge-like asymmetry) and  $b_0 = \Omega/c$  (banana-like asymmetry), while  $\mu_1$  lies in the plane of banana-like asymmetry. Define  $\mu_3$  as positive, if pointing towards the thicker end of the pear-shaped molecule and  $\mu_1$  as positive if pointing towards the center of banana-like curvature. Ascribe to

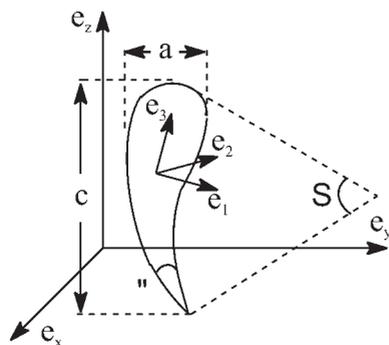


Figure 2. A schematic model of an asymmetric molecule with both wedge-like and banana-like asymmetry

the molecule a local frame  $\{e_1, e_2, e_3\}$ , where  $e_3$  points along the longitudinal molecular axis (as above), and to the nematic a laboratory frame  $\{e_x, e_y, e_z\}$ , where  $e_z$  points along the director  $\mathbf{n}$  (Figure 2). As shown earlier [9-11], any induced (*e.g.*, electrically induced) polarity in molecular ordering, expressed by non-zero values of the ensemble averages  $\langle e_3 \cdot e_z \rangle$ , *etc.*, leads to steric stresses. These may eventually relax to macroscopic director field deformations, thus giving rise to converse flexoelectric effect

$$\begin{aligned} n_{x,x} + n_{y,y} &= 2s_0 \langle e_3 \cdot e_z \rangle_E - b_0 \langle e_1 \cdot e_z \rangle_E, \\ n_{x,z} &= s_0 \langle e_3 \cdot e_x \rangle_E + b_0 \langle e_1 \cdot e_x \rangle_E. \end{aligned} \quad (1)$$

Notice that in Eq. (1) both components of the steric dipole,  $s_0$  and  $b_0$ , give a contribution to the macroscopic splay, respectively bend ([11], cf. also [12]). On the other hand, according to the phenomenological definition of splay ( $e_{1z}$ ) and bend ( $e_{3x}$ ) flexocoefficients [9]

$$\begin{aligned} n_{x,x} + n_{y,y} &= e_{1z} E_z (2K_{11} - K_{22} - K_{24})^{-1}, \\ n_{x,z} &= e_{3x} E_x (K_{33})^{-1}. \end{aligned} \quad (2)$$

In this manner Eqs (1) and (2) permit to express flexocoefficients by molecular asymmetry parameters in the one-component case [11]. Note that the Frank elastic coefficient  $K_{22} + K_{24}$  enters the expression for splay flexocoefficient because of the non-planar splay deformation,  $n_{x,x} + n_{y,y}$ . In the case of mixtures Eq. (1) must be generalized. For a weak solution, where the molar part of the solute is  $\nu \ll 1$  the generalization (assuming additivity) is straightforward (solvent, superscript 0; solute, superscript 1)

$$\begin{aligned} n_{x,x} + n_{y,y} &= (1 - \nu) [2s_0^0 \langle e_3^0 \cdot e_z \rangle_E - b_0^0 \langle e_1^0 \cdot e_z \rangle_E] \\ &\quad + \nu [2s_0^1 \langle e_3^1 \cdot e_z \rangle_E - b_0^1 \langle e_1^1 \cdot e_z \rangle_E], \\ n_{x,z} &= (1 - \nu) [s_0^0 \langle e_3^0 \cdot e_x \rangle_E + b_0^0 \langle e_1^0 \cdot e_x \rangle_E] \\ &\quad + \nu [s_0^1 \langle e_3^1 \cdot e_x \rangle_E + b_0^1 \langle e_1^1 \cdot e_x \rangle_E]. \end{aligned} \quad (3)$$

Then, performing the ensemble averages in electric field by using Boltzmann distribution from the ellipsoidal model of dielectric permittivity [10,13] and the nematic Maier-Saupe distribution function, we can easily obtain from (2) and (3)

$$\begin{aligned} e_{1z} &= (1 - \nu) (2K_{11} - K_{22} - K_{24}) \left[ \frac{s_0^0 \mu_3^{0*}}{3k_B T} (2S + 1) - \frac{b_0^0 \mu_1^{0*}}{3k_B T} (1 - S) \right] \\ &\quad + \nu (2K_{11} - K_{22} - K_{24}) \left[ \frac{s_0^1 \mu_3^{1*}}{3k_B T} (2S + 1) - \frac{b_0^1 \mu_1^{10*}}{3k_B T} (1 - S) \right] \\ e_{3x} &= (1 - \nu) K_{33} \left[ \frac{s_0^0 \mu_3^{0*}}{3k_B T} (1 - S) + \frac{b_0^0 \mu_1^{0*}}{3k_B T} \left( 1 + \frac{S}{2} \right) \right] \\ &\quad + \nu K_{33} \left[ \frac{s_0^1 \mu_3^{1*}}{3k_B T} (1 - S) + \frac{b_0^1 \mu_1^{10*}}{3k_B T} \left( 1 + \frac{S}{2} \right) \right] \end{aligned} \quad (4)$$

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where Frank elastic coefficients take their values for the mixture, and it is assumed that all molecules in the mixture have a common degree of uniaxial ordering  $S$ . In (4)  $\mu_i^* = g_i F_i \mu_i$ ,  $i = 1, 3$  are the corrected electric dipole components, where  $g_i$  are the corresponding cavity field factors and  $F_i$  are the reaction field factors from the ellipsoidal model [10,13].

To a good approximation then (assuming that Frank elastic coefficients do not change substantially in the mixture) we can write

$$\begin{aligned} e_{1z} &\approx (1 - \nu)e_{1z}^0 + \nu e_{1z}^1, \\ e_{3x} &\approx (1 - \nu)e_{3x}^0 + \nu e_{3x}^1. \end{aligned} \quad (5)$$

### 3 Experimental Results and Comparison to Theory

An 40% increment of value of  $|e^*|$  for 100 mole% was reported in [1]. Namely, value of  $|e^*|$  is by  $2.16 \times 10^{-12}$  C/m higher than that of the pure BMAOB, which is  $5.3 \times 10^{-12}$  C/m.

Apart from the fact that the concentration range of the swallow-tail additive, [0–4.55 mol%], in which it was still possible to perform our experimental programme (*i.e.*, to observe 2nd order domains) is quite narrow, the principal result of the previous paper was that there is no drastic effect of the steric asymmetry of the additive upon the mixture's difference of flexocoefficients. In view of the marked wedge-like shape of swallow-tail molecules such result is rather strange.

On the other hand, the theory developed above, gives a clue for its understanding: Let us neglect banana-like asymmetry of the additive and consider only its wedge-like asymmetry. Then, when taking the difference of the two Eqs. (4), we observe that  $s_0$  participates in both of them [11,12], so that its effect upon the difference is greatly reduced

$$e_{1z} - e_{3x} = \nu \frac{s_0^1 \mu_3^{1*}}{3k_B T} [(2K_{11} - K_{22} - K_{24})(2S + 1) - K_{33}(1 - S)]. \quad (6)$$

Since  $K_{24}$  is generally unavailable, we could further use a Cauchy type relation [14]  $K_{24} = (K_{11} - K_{22})/2$ , *i.e.*, the extrapolated difference for 100% will be

$$e_{1z} - e_{3x} = \nu \frac{s_0^1 \mu_3^{1*}}{6k_B T} [(3K_{11} - K_{22})(2S + 1) - K_{33}(1 - S)]. \quad (7)$$

Now, taking from [15] elastic constants:  $K_{11} = 8.5$  pN,  $K_{22} = 6.8$  pN,  $K_{33} = 9.7$  pN, and assuming  $S = 0.5$ ,  $s_0 = 5 \times 10^8$  m and  $\mu_3^1 = 4 \times 10^{-30}$  C/m (cf.[16]), we obtain from (7)

$$e^* = 2 \times 10^{-12} \text{ C/m},$$

to be in good agreement with our extrapolated value mentioned above.

#### 4 Conclusion

In this work we attempted a molecular theory that is able to explain why the concentration dependence observed earlier by us is not steep. The theory gives a good agreement to the extrapolated value of the flexoelectric coefficient difference  $|e^*|$ . The relatively small increase of the flexocoefficients' difference is explained by a theory showing that the strong steric asymmetry of "swallow-tail" molecules gives a comparable contribution to *both* flexocoefficients.

#### Acknowledgements

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