

## Flexoelectric and elastic coefficients of odd and even homologous bimesogens

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(Received 24 October 2011; published 3 January 2012)

It is known that bimesogenic liquid crystals exhibit a marked “odd-even” effect in the flexoelastic ratio (the effective flexoelectric coefficient to the average elastic coefficient), with the ratio being higher for the “odd-spaced” bimesogens (those with an odd number of alkyl groups in the spacer chain) than their neighboring even-spaced counterparts. To determine the contribution of each property to the flexoelastic ratio, we present experimental results on the flexoelectric and elastic coefficients of two homologous nonsymmetric bimesogens which possess odd and even alkyl spacers. Our results show that, although there are differences in the flexoelectric coefficients, there are substantially larger differences in the effective elastic coefficient. Specifically, the odd bimesogen is found to have both a low splay elastic coefficient and a very low bend elastic coefficient which, when combined, results in a significantly lower effective elastic coefficient and consequently a higher flexoelastic ratio.

DOI: [10.1103/PhysRevE.85.012701](https://doi.org/10.1103/PhysRevE.85.012701)

PACS number(s): 42.70.Df

Bimesogenic liquid crystals (LCs) comprise two mesogenic units that are attached by a flexible spacer chain. They are of technological interest for next-generation LC displays since they have been shown to be a major candidate for the flexoelectro-optic effect in chiral nematic LCs [1–4]. This is a fast switching in-plane deflection of the optic axis upon application of an electric field orthogonal to the helicoidal axis. Bimesogens exhibit higher flexoelastic ratios than conventional monomesogens, leading to larger tilt angles of the optic axis for a given applied electric field strength [2]. Furthermore, they possess lower dielectric anisotropies,  $\Delta\epsilon$  ( $<3$ ), which extends flexoelectro-optic switching to high electric field amplitudes. Conventional materials, with greater  $\Delta\epsilon$ , exhibit unwinding of the chiral nematic helicoidal axis at lower fields, which limits the application of such materials in the flexoelectro-optic effect.

The important parameter that determines the effectiveness of a material for use in flexoelectro-optic switching is the flexoelastic ratio  $e/K$ . Here,  $e = (e_s + e_b)/2$ , where  $e_s$  and  $e_b$  are the splay and bend flexoelectric coefficients, respectively (using the notation of Ref. [4]) and  $K = (K_1 + K_3)/2$ , where  $K_1$  and  $K_3$  are the splay and bend elastic coefficients, respectively. To maximize the electro-optic effect, materials with large  $e$  and low  $K$  are required. Toward this end, mixtures of bimesogenic compounds with high tilt angles for flexoelectro-optic switching have been developed [5]. Similar mixtures have also been shown to exhibit unusually wide temperature range blue phases [6,7].

The macroscopic properties of the bimesogens are sensitive to molecular structure. Changing the number of carbon atoms in the flexible alkyl spacer chain gives rise to a strong odd-even effect [8]. In particular, it was demonstrated experimentally that the flexoelastic ratios are significantly higher for the odd-spaced bimesogens than their even-spaced counterparts for a particular homologous series. In this study, it was estimated that the flexoelectric coefficients of the odd bimesogens were higher than those of even bimesogens and, consequently, the

high  $e/K$  values of the former were considered to be the result of a combination of larger flexoelectric coefficients and slightly lower elasticity [8]. However, these estimations were based on values of the effective elastic coefficient,  $K$ , that were calculated using a one-constant approximation (i.e.,  $K = K_1$ ).

More recently Cestari *et al.* [9] predicted the individual flexoelectric coefficients and elastic coefficients, using a molecular field theory with atomistic modeling, for members of the same homologous series as that presented in Ref. [8]. The authors calculated that, although the flexoelectric coefficients are slightly higher for odd bimesogens, compared with even bimesogens, this was insufficient to predict the strong dependence of the flexoelastic ratio on the odd-even nature of the molecules. Calculations suggested that odd bimesogens have unusually low bend elastic coefficients, which causes the particularly high  $e/K$  values of odd bimesogens.

The purpose of this Brief Report is to present experimentally determined values of the individual flexoelectric coefficients and elastic coefficients for two, odd-even homologs as a function of temperature in order to investigate the cause of the high  $e/K$  values of odd-spaced bimesogens. This is of significant importance for the development of LC structures for both flexoelectro-optic switching and flexoelectricity, in general. The two compounds that are studied in this work are the nonsymmetric bimesogens:  $\alpha$ -(2',4-difluorobiphenyl-4'-yloxy)- $\omega$ -(4-cyanobiphenyl-4'-yloxy)nonane (FFO9OCB) and the neighboring compound with an even alkyl spacer  $\alpha$ -(2',4-difluorobiphenyl-4'-yloxy)- $\omega$ -(4-cyanobiphenyl-4'-yloxy)octane (FFO8OCB). The chemical structures of these compounds, along with the molecular shape in the *all-trans* conformation of the spacer chain, are shown in Fig. 1.

The synthetic route of these bimesogens has been reported elsewhere [10]. Transition temperatures were determined using a polarizing optical microscope (BH2, Olympus) that was fitted with a hot stage (THMS 600, Linkam) and a temperature controller (TP94, Linkam) at a heating rate of 1 °C/min. Both bimesogens have enantiotropic nematic phases. For FFO8OCB, the melting temperature,  $T_m$ , is 123 °C

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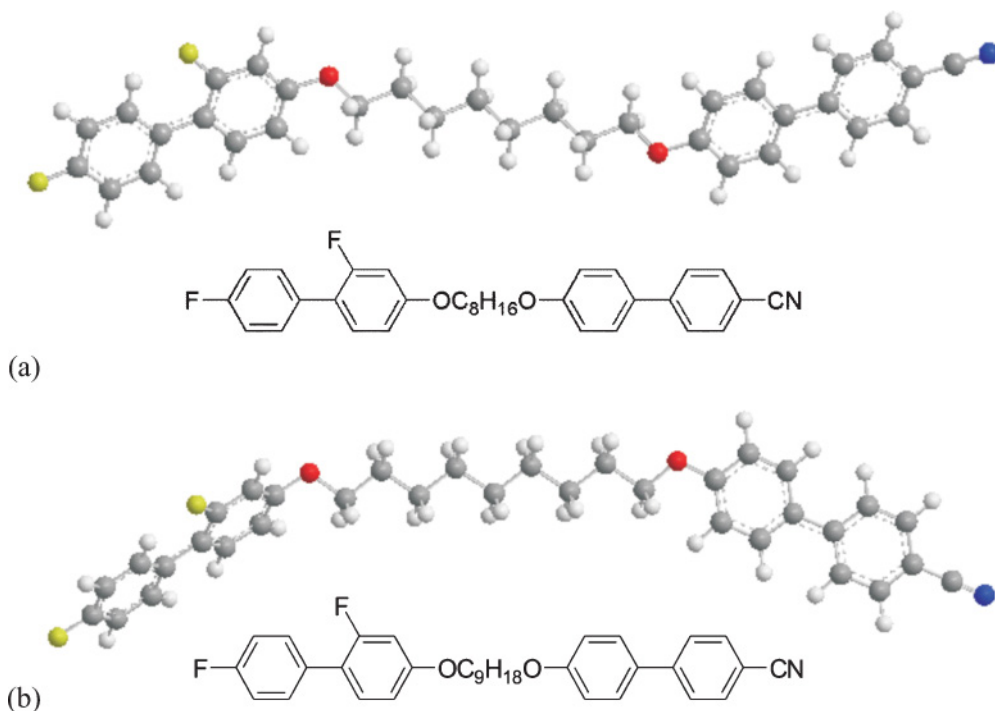


FIG. 1. (Color online) Chemical structure of neighboring even and odd bimesogens: (a)  $\alpha$ -(2',4-difluorobiphenyl-4'-yloxy)- $\omega$ -(2',4-cyanobiphenyl-4'-yloxy)octane (FFO8OCB) and (b)  $\alpha$ -(2',4-difluorobiphenyl-4'-yloxy)- $\omega$ -(4-cyanobiphenyl-4'-yloxy)nonane (FFO9OCB).

and the clearing temperature,  $T_c$ , is 147 °C. On the other hand, for FFO9OCB, formed by the addition of an extra methylene group in the spacer chain, the melting temperature and the clearing temperature are  $T_m = 60$  °C and  $T_c = 109$  °C, respectively, which are significantly lower than that found for the even compound.

The elastic coefficients were determined using the standard capacitance technique [11–13]. Measurements were carried out using 20  $\mu\text{m}$  antiparallel planar aligned cells and a precision component analyzer (6440A, WK Electronics) at a frequency of 10 kHz.  $K_1$  and  $K_3$  were deduced from the measurements using a computational curve fitting method based on the Oseen-Frank free energy. It has previously been argued that the possible effects of flexoelectricity may be ignored for frequencies of 1 kHz and above [14].

Chiral nematic mixtures were prepared for flexoelectro-optic measurements by adding approximately 3.5 wt% of a chiral dopant (BDH1281, Merck KGaA). The samples were heated above the clearing point and left in the isotropic phase for 1 h, before being left in the chiral nematic phase for >24 h. They were then capillary filled into cells, coated with indium tin oxide (ITO) electrodes, to enable an electric field to be applied orthogonal to the plane of the cells. The dimensions of the cell gap, defined by spacer beads, were measured to be 3.3  $\mu\text{m}$  using optical interference measurements. The inner substrates of the cells were coated with antiparallel rubbed polyimide alignment layers, which resulted in a “Grandjean” texture whereby the helicoidal axis was parallel to the normal of the substrates. The procedure for measuring the flexoelectro-optic response has been described in previous studies [8]. The pitch  $P$  of the chiral nematic samples was measured using both the Cano wedge method and the width of the reflection band ( $\Delta\lambda$ ) combined with the birefringence ( $\Delta\lambda = P\Delta n$ ) [15–17].

Values of the pitch were then used to determine the flexoelectric ratios from the flexoelectro-optic measurements.

Figure 2 shows the flexoelectric ratio as a function of temperature for the FFO8OCB and FFO9OCB compounds. Clearly, over the measured temperature range, the flexoelectric ratio is approximately a factor of 2 greater for the odd bimesogen, which is in good agreement with previously published values at a fixed reduced temperature [8]. As an example, at a reduced temperature of  $T_r = 0.96$  ( $T_r = T/T_c$ ) the flexoelectric ratio for the odd-spaced bimesogen is  $e/K = 1.1 \text{ C N}^{-1} \text{ m}^{-1}$ , whereas for its even-spaced neighbor,  $e/K = 0.5 \text{ C N}^{-1} \text{ m}^{-1}$ . Theoretically calculated values for bimesogens

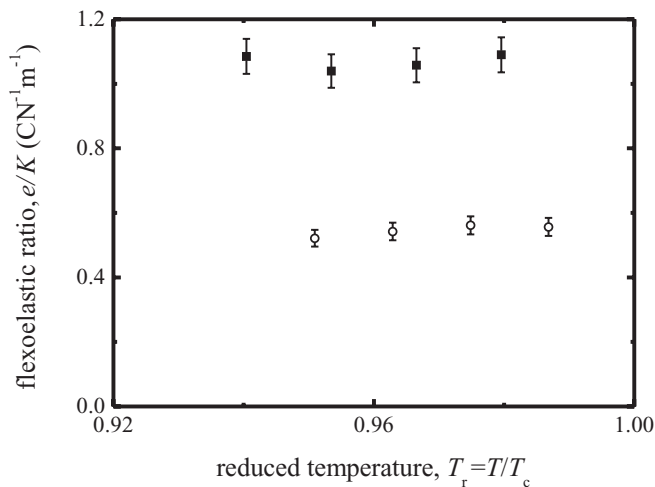


FIG. 2. The flexoelectric ratio  $e/K$  as a function of reduced temperature for FFO9OCB (closed squares) and FFO8OCB (open circles).

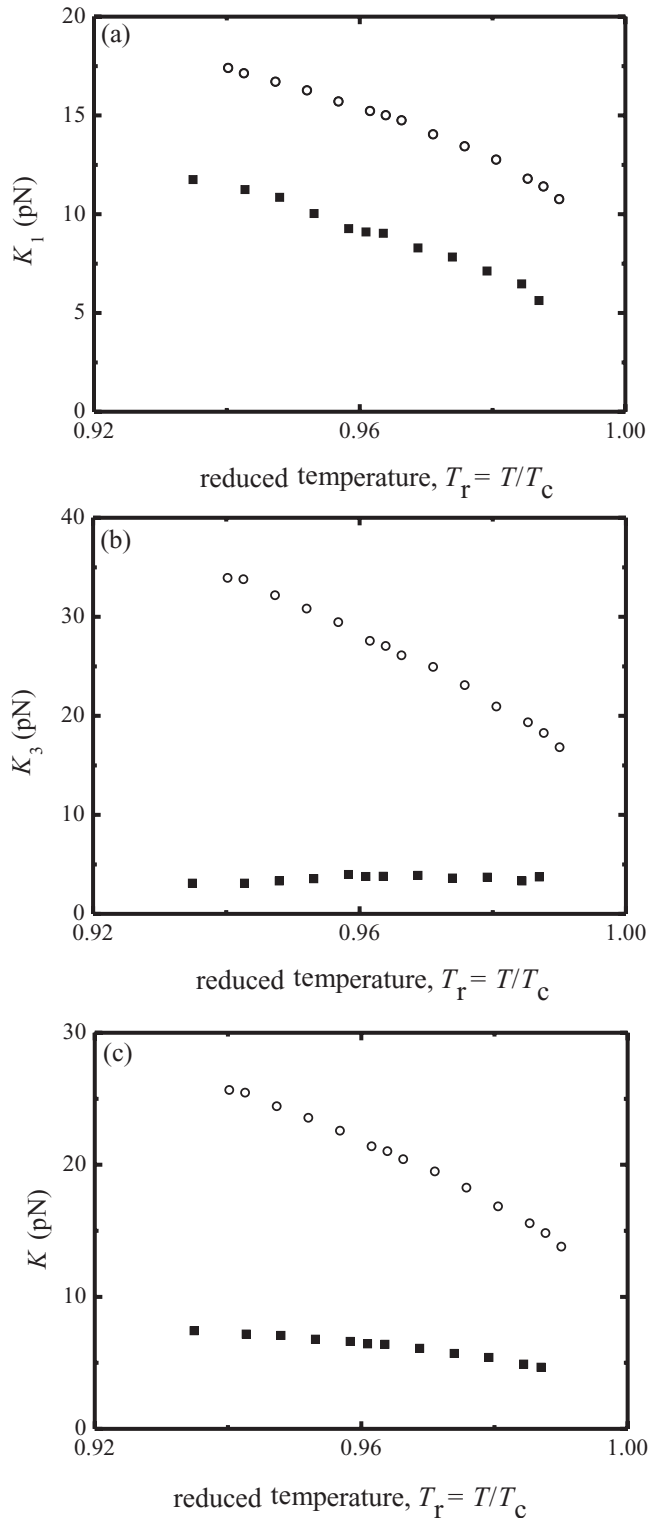


FIG. 3. The elastic coefficients for the FFO8OCB (open circles) and FFO9OCB (closed squares) as a function of reduced temperature. (a) The splay ( $K_1$ ) elastic coefficients, (b) the bend ( $K_3$ ) elastic coefficients, and (c) the effective elastic coefficients.

from the same FFO $n$ OCB homologous series were  $e/K \approx 2-3 \text{ CN}^{-1} \text{ m}^{-1}$  for the odd-spaced compound compared with  $e/K \approx 0.5 \text{ CN}^{-1} \text{ m}^{-1}$  for an even bimesogen [9]. The agreement with the even-spaced compound is good although simulated values for the odd compound are slightly higher

than we find experimentally. The alkyl chain length of the odd bimesogen we have investigated herein (FFO9OCB) is slightly longer than that considered in the atomistic simulations [9], however, both previous experimental investigations and modeled values have shown that, for similar spacer lengths of the same parity, there are only small differences in the flexoelectric and elastic coefficients [8,9].

Figure 3 presents the splay, bend, and effective elasticity plotted as a function of reduced temperature for both FFO8OCB and FFO9OCB. The results show that  $K_1$  is lower for the odd bimesogen over a wide range of reduced temperatures. Values for the odd-spaced bimesogen are found to range from  $K_1 \approx 5-12 \text{ pN}$  for the temperatures studied in this work compared with  $K_1 \approx 12-18 \text{ pN}$  for FFO8OCB. Here, the ratio of odd to even elasticity at  $T_r = 0.96$  is  $K_{1(\text{odd})}/K_{1(\text{even})} = 0.60$  and there is little variation over the measured temperature range. The bend elastic coefficient of FFO8OCB, Fig. 3(b), shows similar behavior to conventional monomesogens, with  $K_3 > K_1$ . This ordering of the elastic coefficients is consistent with theoretical results for rod-shaped molecules that take into account only the hard-core repulsion [18]. We find that  $K_{3(\text{even})} \approx 16-35 \text{ pN}$  over the temperature range, which is of a similar magnitude to that predicted in simulations [9]. On the other hand, for FFO9OCB the bend elastic coefficient behaves very differently. Not only does it take particularly low values, up to an order of magnitude less than the even homolog ( $K_{3(\text{odd})} \approx 3-4 \text{ pN}$  for this temperature range) but it is almost temperature independent. As an example, at  $T_r = 0.96$ ,  $K_{3(\text{odd})}/K_{3(\text{even})} = 0.14$ . This is in good qualitative agreement with calculated values of  $K_3$  for the odd bimesogens (FFO7OCB and FFO5OCB) reported in Ref. [9]. Predicted values were in the range of  $K_{3(\text{odd})}/K_{3(\text{even})} \approx 0.13-0.17$ .

The temperature dependency of  $K$ , which is important for the flexoelastic ratio, is shown for both FFO9OCB and FFO8OCB in Fig. 3(c). It is apparent that  $K$  is substantially lower for the odd homolog than for the even compound. As Figs. 3(a) and 3(b) show, this is due in the most part to low

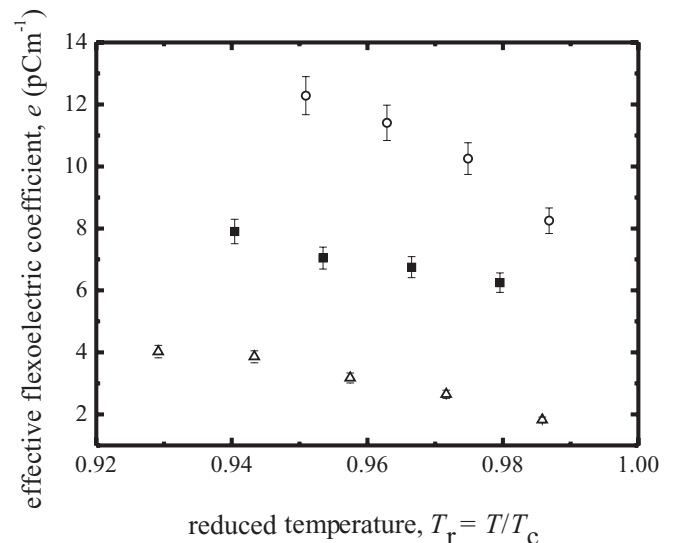


FIG. 4. The effective flexoelectric coefficient as a function of reduced temperature for FFO8OCB (open circles), FFO9OCB (closed squares), and 7OCB (open triangles).

$K_3$ , although there is also a contribution from  $K_1$ . To give an idea of the difference, at  $T_r = 0.96$  the ratio  $K_{(\text{odd})}/K_{(\text{even})} = 0.30$ . For FFO9OCB, the increase in the elastic coefficient with decreasing reduced temperature is much more gradual than for FFO8OCB, due to the persistently low values of  $K_3$  over this temperature range.

The flexoelectric coefficients, calculated from the effective elastic coefficients and the flexoelastic ratio, are shown as a function of reduced temperature in Fig. 4. Here  $e_{(\text{odd})} \approx 6\text{--}8 \text{ pC m}^{-1}$  and  $e_{(\text{even})} \approx 7\text{--}12 \text{ pC m}^{-1}$ . These results show that the flexoelectric coefficients are actually slightly lower for the odd bimesogen (FFO9OCB) than the even (FFO8OCB) bimesogen ( $e_{(\text{odd})}/e_{(\text{even})} = 0.6$  at  $T_r = 0.95$ ), which is in contrast to the estimated values in Ref. [8] and the simulated results in Ref. [9]. The effective flexoelectric coefficient appears to be less dependent upon temperature for the odd compound. The flexoelectric coefficients for the monomesogen, 7OCB, measured using the same experimental technique, are also shown in Fig. 4 for comparison. Despite the lower value for FFO9OCB, both the odd- and the even-spaced bimesogens exhibit larger values of the flexoelectric coefficients than 7OCB: for example, for 7OCB,  $e = 2.7 \text{ pC m}^{-1}$  at  $T_r = 0.97$ .

The effective elastic coefficient also influences the response time ( $\tau$ ) through the viscoelastic ratio ( $\gamma/K$ ) whereby  $\tau \propto \gamma/K$ . At similar electric field strengths and reduced temperatures, measurements of the response times for both compounds showed that it was considerably longer for the odd bimesogen

( $\tau \approx 100 \mu\text{s}$ ) compared with that of the even compound ( $\tau \approx 40 \mu\text{s}$ ). These results are consistent with the smaller elastic coefficient of the FFO9OCB, which leads to a larger viscoelastic ratio.

In summary, all these combined results indicate that the improvement observed in the flexoelastic ratio, and consequently flexoelectro-optic switching, on replacing a monomesogen with an even-spaced bimesogen is due to an enhancement of the flexoelectric coefficient. However, when changing from an even-spaced bimesogen to an odd-spaced bimesogen the increase in the flexoelastic ratio is the result of a dramatic reduction in the effective elastic coefficient. Earlier studies using values of the effective elastic coefficient based on the one-constant approximation overestimated the effective elastic coefficients of the odd bimesogens, resulting in estimates of the flexoelectric coefficients higher than the measured values presented in this study. The one-constant approximation, used widely in LC modeling and experimentation, should therefore be used with caution when investigating bimesogenic materials.

#### ACKNOWLEDGMENTS

The authors gratefully acknowledge the Engineering and Physical Sciences Research Council (UK) and LG Display for financial support. One of the authors (K.A.) also acknowledges Merck UK for a CASE studentship. One of the authors (S.M.M.) gratefully acknowledges The Royal Society for financial support.

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