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Structure-flexoelastic properties of bimesogenic liquid crystals

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In this paper, we report on the flexoelastic and viscoelastic ratios for a number of bimesogens compounds with the same generic structure. Values are obtained indirectly by measuring the flexoelectro-optic response in the chiral nematic phase. By varying the molecular structure we alter the bend angle, transverse dipole moment, and length of the molecule. First, to examine the influence of the bend angle we use a homologous series whereby the only alteration in the molecular structure is the number of methylene units in the aliphatic spacer, n. Results show that the flexoelastic ratio, e/K, and the effective flexoelectric coefficient, e, both exhibit an odd-even effect with values for n=odd being greater than that for n=even. This is understood in terms of an increase in the bend angle of the molecule and an increase in the transverse dipole moment. Second, in order to investigate the impact of the dipole moment, we have altered the mesogenic units so as to vary the longitudinal dipole moment and used different linkages in the aliphatic spacer in an attempt to alter the transverse dipole moment. Qualitatively, the results demonstrate that the odd-spaced bimesogen with larger transverse dipole moments exhibit larger flexoelastic ratios.

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I. INTRODUCTION

Flexoelectricity in nematic liquid crystals has attracted significant interest since its discovery by Meyer in 1969 [1]. Specifically, asymmetry in the molecular shape can lead to a net local polarization due to an alignment of the dipole moments for splay and bend deformations of the local director field. The local polarization density, which results from the deformation, can be written in terms of the divergence and curl of the director field,

$$P = e_s\mathbf{n}(\boldsymbol{\nabla}\cdot\mathbf{n}) + e_b\mathbf{n}\times(\boldsymbol{\nabla}\times\mathbf{n}), \quad (1)$$

where e_s and e_b are the so-called flexoelectric coefficients. However, even though flexoelectricity may be observed for all nematic liquid crystals the effect, in general, is small due to very modest values of the flexoelectric coefficients.

There have been several reports dedicated to the theoretical treatment and modeling of the correlations between the molecular structure and flexoelectric properties [2–8]. According to dipolar theory, both the transverse dipole moment and the bend angle are expected to play a significant role in terms of the magnitude of the bend flexoelectric coefficient (e_b) [2,3]. Although the importance of molecular shape varies somewhat for each model, it is generally agreed that the bend flexoelectric coefficient depends upon the bend angle of the molecule; as a result there has been interest in banana-shaped liquid crystals. Dipolar and quadrupolar effects also vary for the different models: from Prost and Marcerou, quadrupolar effects are likely to be significant for rodlike molecules [8].

In recent years we have demonstrated that bimesogenic compounds that form nematic phases potentially have larger flexoelectric coefficients than conventional nematic liquid crystals using an indirect method of observing the magnitude of flexoelectro-optic switching in the chiral nematic phase [9–12]. In this case the chiral nematic phase is induced using low concentrations of a high twisting power chiral additive. Flexoelectricity in the chiral nematic phase is manifested as a rotation of the optic axis when the direction of the applied electric field is perpendicular to the helix axis [13–17]. In this case a periodic splay-bend deformation is formed which results in a macroscopic rotation of the optic axis in the plane of the device. As well as providing a means of gauging the magnitude of the flexoelectric coupling it also has potential as a technology. This is because the in-plane rotation of the optic is linear in the applied field and therefore leads to the possibility of a wide viewing angle and gray-scale capability, respectively [16,17]. Second, the time taken for the optic axis to switch can be of the order of ten to hundreds of microseconds.

The relationship between the collective rotation of the director planes or alternatively the tilt angle of the optic axis and the applied electric field strength was first obtained by Patel and Meyer [13]. Therein, the authors considered that the equilibrium helical distortion could be determined by assuming that for this condition the elastic energy compensates the energy due to flexoelectric coupling. By defining a suitable coordinate system so as to obtain an equation for the free-energy density in terms of the relevant angles, an expression for the tilt angle was then obtained by minimizing the free-energy density. The equation for the tilt angle can be written, in its simplest form, as

$$\tan\phi = \frac{e}{K}\frac{p}{2\pi}E, \quad (2)$$

where $e=(e_s+e_b)/2$, $K=(K_{11}+K_{33})/2$, and p is the pitch. Hereafter, the ratio of the effective flexoelectric coefficient to the effective elastic constant is referred to as the flexoelastic ratio. From this relationship it is apparent that the tilt angle

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depends not only on the strength of the applied electric field but also on its direction.

The dynamic behavior of the flexoelectro-optic effect depends upon the viscoelastic forces associated with the macroscopic deformation. Theoretically, it can be shown that, from a thermodynamics approach, the response time is given by [18]

$$\tau = \frac{\gamma}{K}\frac{p^2}{4\pi^2}, \tag{3}$$

where γ is the effective viscosity associated with the distortion of the helix. Therefore, for a given pitch the response time depends upon the viscoelastic ratio, γ/K.

By measuring both the tilt angle as a function of the applied electric field and the response time it is possible, to a first approximation, to determine the flexoelastic ratio (e/K) and the viscoelastic ratio (γ/K) provided that the pitch is known. The objective of this paper, therefore, is to determine the flexoelastic and viscoelastic ratios for a number of different bimesogenic compounds. Using a homologous bimesogenic series whereby the only change in the molecular structure is the number of methylene units in the flexible spacer, we consider how changes in the molecular shape affect both e/K and γ/K. It is found that those which contain an odd number of methylene units, and thus a bent-shape in the *all-trans* conformation of the flexible spacer, exhibit larger e/K ratios. Furthermore, we examine how e/K varies as one mesogenic subunit is changed so as to vary the dipole moment, both longitudinal and transverse.

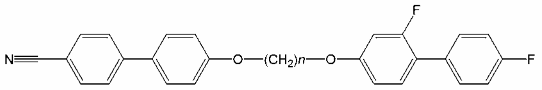
II. SAMPLE PREPARATION AND MATERIALS

All the compounds considered in this study were synthesized and purified in-house. Since none of the bimesogenic compounds contain chiral centers a high twisting power chiral dopant (BDH1281, Merck NB-C) had to be added to induce a chiral nematic phase. The concentration of chiral dopant was ~3.5 wt. %. Each sample was then heated into the isotropic phase for a period of >24 hours. Afterwards, the resulting mixtures were then capillary filled into 5 μm thick cells (EEV) which had a unidirectionally rubbed polyimide alignment layer and indium tin oxide (ITO) electrodes.

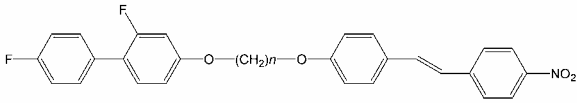
The generic structure of the bimesogen compounds studied herein is notably different to that of a monomesogen which, at the simplest level, consists of a central rigid core and a flexible terminal alkyl chain. For a bimesogenic compound these roles are reversed, the terminal components are instead the rigid aromatic cores and the central unit of the molecule is now the flexible alkyl chain containing an "odd" or "even" number of methylene units.

The homologous series α-(2′,4-difluorobiphenyl-4′-yloxy)-ω-(4-cyanobiphenyl-4′-yloxy)alkanes was used to study the effect of the bend angle on the flexoelastic properties. Hereafter, these bimesogens are designated FFO*n*OCB, where *n* is the number of methylene units in the flexible spacer. The members of this series that were synthesized were those for which the number of CH_2 groups ranged from $n=5$ to 12. The generic chemical structure for this series is shown in Fig. 1(a). The isotropic-nematic transition and the nematic-crystalline, T_{NK}, temperatures are shown in Table I and were determined from the optical textures when examined using a polarizing microscope. In addition, the width of the nematic phase on cooling, $\Delta T_{(N\text{cooling})}$ is also shown. At a shifted temperature ($T_s = T_c - T$) of 10 °C the dielectric anisotropy ($\Delta\varepsilon$), determined from capacitance measurements, was of the order of 2.5 for n=even and 3.5 for n=odd.

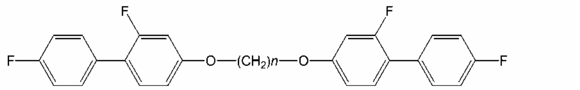
(a) Ether-linked non-symmetric bimesogen series FFOnOCB



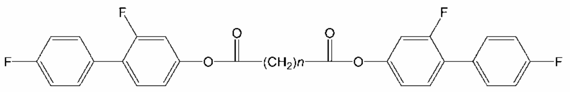
(b) Ether-linked non-symmetric nitrostilbene bimesogen (NSO9OFF)



(c) Ether-linked symmetric bimesogen series FFOnOFF



(d) Ester-linked symmetric bimesogen series FFEnEFF



(e) Ether-linked non-symmetric bent-core bimesogen, NSOnOphOnOCB

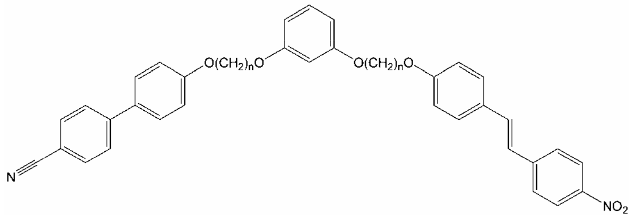


FIG. 1. Generic chemical structures of the different bimesogenic compounds. (a) nonsymmetric FFO*n*OCB homologous series [α-(2′,4-difluorobiphenyl-4′-yloxy)-ω-(4-cyanobiphenyl-4′-yloxy)alkanes], (b) nonsymmetric NSO9OFF bimesogen, (c) symmetric FFO*n*OFF homologous series [α-(2′,4-difluorobiphenyl-4′-yloxy)-ω-(4-difluorobiphenyl-4′-yloxy)alkanes], (d) the symmetric FFE*n*EFF homologues [α-(2′,4-difluorobiphenyl-4′-ester)-ω-(4-difluorobiphenyl-4′-ester)alkanes homologous series], and (e) bent-core nonsymmetric bimesogen NSO*n*OphO*n*OCB.

In order to alter the longitudinal dipole moment a nonsymmetric bimesogen containing a nitro-stilbene unit was synthesized. The chemical structure of this material is shown in Fig. 1(b) denoted NSO9OFF. It can be seen that the compound contains a nitro group (NO_2) at the terminal position of one of the mesogenic units and a stilbene unit which links the two phenyl rings together. The transition temperatures for this compound are also shown in Table I. From capacitance measurements the dielectric anisotropy was found to be 4.8 at $T_s = 10$ °C which is higher than that obtained for the FFO*n*OCB series.

To further alter the dipole moments, two types of symmetric bimesogen compounds were studied: these included

TABLE I. Transition temperatures for the different bimesogenic compounds. This table shows the isotropic-nematic temperatures, T_{IN}, and the nematic-crystalline, T_{KN}, the width of the nematic phase on cooling, $\Delta T_{(N\mathrm{cooling})}$ is also presented.

Compound/mixture	T_{IN}	T_{NK}	$\Delta T_{(N\mathrm{cooling})}$
FFO5OCB	105 °C	44 °C	61 °C
FFO6OCB	161 °C	99 °C	62 °C
FFO7OCB	113 °C	42 °C	72 °C
FFO8OCB	143 °C	83 °C	60 °C
FFO9OCB	112 °C	50 °C	62 °C
FFO10OCB	132 °C	85 °C	47 °C
FFO11OCB	111 °C	48 °C	63 °C
FFO12OCB	121 °C	80 °C	41 °C
FFO7OFF(50):FFO11OFF(50)	53 °C	<20 C	>33 °C
FFO9OFF(60):FFO11OFF(40)	55 °C	<20 C	>33 °C
NSO9OFF	127 °C	35 °C	92 °C

members from the α-(2′,4-difluorobiphenyl-4′-yloxy)-ω-(4-difluorobiphenyl-4′-yloxy)alkanes homologous series [Fig. 1(c)] and members from the α-(2′,4-difluorobiphenyl-4′-ester)-ω-(4-difluorobiphenyl-4′-ester)alkanes homologous series [Fig. 1(d)]. These are assigned the mnemonics FFO*n*OFF and FFE*n*EFF, respectively. The first symmetric bimesogenic series, like the nonsymmetrics, contain ether links (–O–) in the flexible chain which are replaced with ester linkages (–COO–) in the second series [cf. Fig. 1(d)]. Two-component mixtures of the odd members from this series were studied in this work due to the fact that as single compound materials these bimesogens exhibit monotropic nematic phases which supercool over a 20 °C temperature range. However, if left for a period of several hours the sample would eventually crystallize. The preparation of these two-component mixtures not only extended the temperature range but also increased the stability of the nematic phase. The transition temperatures for the mixtures are shown in Table I. For these compounds it was found from capacitance measurements that $\Delta\varepsilon \sim 0$: these compounds exhibited no Fréedericksz transition.

Bent-core bimesogenic structures were synthesized in an attempt to increase e_b by increasing the bend angle, θ. The generic chemical structure is shown in Fig. 1(e). In this case a central phenyl ring was connected at lateral positions to two flexible spacer chains which were then connected to separate mesogenic subunits. One mesogenic unit was the nitrostilbene group and the other was a cyanobiphenyl group. In this study, we examine the flexoelectro-optic properties of the compound for which $n=9$ denoted NSO9OphO9OCB. Although the mesogenic units are nonsymmetric the spacer chains are actually symmetric, i.e., they contain the same number of methylene units. The opening angle of this bent-core structure is ~120°. The dielectric anisotropy was found to be $\Delta\varepsilon=6.8$ at $T_s=10$ °C.

III. EXPERIMENTAL PROCEDURE

To observe the flexoelectro-optic effect an electric field must be applied perpendicular to the helix axis. However, in conventional cells the minimum free-energy configuration of a chiral nematic liquid crystal is the Grandjean texture whereby the helix axis is oriented perpendicular to the glass substrates. Consequently, if an electric field is applied across the cell for a standing helix geometry the direction of the applied field is then parallel to the helix axis. Therefore, to satisfy the condition of an orthogonal orientation of the external field with respect to the helix axis using conventional cells, a uniform lying helix (ULH) texture is then required. To achieve this, the sample was cooled rapidly from the isotropic phase to the chiral nematic phase under the influence of an applied electric field; a technique that was discovered some years ago [19]. Once in the chiral nematic phase, the sample was then subjected to mechanical stress, in the form of shearing, in a direction perpendicular to the rubbing direction until a ULH texture had formed.

Measurements of the rotation of the optic axis were carried out as follows. The following was carried out after the ULH texture had been achieved. First of all the sample was positioned on the hot-stage (THMS 600, Linkam controlled by TP94, Linkam) of the polarizing microscope (BH2, Olympus). Light transmitted through the sample was collected by the microscope objective which had a magnification of 20×. A bipolar electric field (square wave, $\nu=80$ Hz using a TG1304 signal generator, Thurlby Thandar) was then applied across the sample which forced the optic axis to deflect back and forth in-plane about its equilibrium position due to flexoelectric coupling. The continual switching of the optic axis generates a level-to-level response of the transmitted light intensity through the sample; this modulation was then monitored by a fast photodiode (PDA55, Thorlabs) and recorded by the digitizing oscilloscope (HP54503A, Hewlett-Packard). All measurements were carried out at field strengths below the onset of helix unwinding. Moreover, a constant pitch could be verified from the linear dependence of $\tan(\phi)$ as a function of the electric field strength [cf. Eq. (2)].

So as to ensure maximum contrast between the two switched states, the unperturbed optic axis was aligned at 22.5° to the transmission axis of one of the polarizers. Response times were measured as the time required for the intensity at the photodiode to increase from 10% to 90% once the polarity of the driving field was reversed. Note that the response is the time taken for the optic axis to undergo a complete switch (2ϕ) about its equilibrium position.

The pitch of each chiral nematic was determined from Cano wedge measurements. The dielectric permittivities, and consequently the dielectric anisotropy, were obtained in the nematic phase using planar aligned cells and a capacitance bridge. These cells consisted of unidrectionally rubbed polyimide alignment layers which gave a planar alignment of the director in the nematic phase. A single-cell method [20] was adopted to measure the dielectric permittivities because it was found that the bimesogens could not be homeotropically aligned with any conventional alignment layer. A single-cell method has also been used to measure the dielectric permittivities of bimesogens of a similar structure elsewhere [21] and the values obtained therein are comparable with those obtained in this study. The measurements were found to be in good agreement with those carried out at Merck NB-C for the same compounds using an alternative technique of doping into a nematic host and extrapolating to 100% concentration. The splay elastic constant (K_{11}) was then calculated from the Fréedericksz threshold voltage using the relationship,

$$K_{11} = \frac{V_{th}^2 \varepsilon_0 \Delta\varepsilon}{\pi^2}. \tag{4}$$

IV. RESULTS AND DISCUSSION

A. Importance of the molecular shape

To begin with we consider the variation in the flexoelectro-optic behavior for the homologous bimesogenic series FFO*n*OCB. In this case the only variation in the molecular structure is the number of spacer units in the flexible chain. The motivation behind synthesizing the nonsymmetric bimesogen series FFO*n*OCB was, first and foremost, to investigate the impact the molecular shape has on the flexoelectro-optic performance. The presence of the flexible spacer at the center of the molecule allows the opposing mesogenic units, which for all intents and purposes provide the source of the anisotropy, to assume different orientations relative to one another. There are, therefore, a range of potential molecular shapes, generally referred to as conformers, which a single bimesogen molecule can adopt. However, each conformer has different physical properties as a result of the different orientations of the mesogenic units. Consequently, by changing only the number of carbon atoms in the flexible chain the physical properties can be altered significantly giving rise to the so-called odd-even effect observed for the macroscopic properties. This provides a useful means of altering the shape of the molecule without drastically modifying the molecular structure.

In a generic model developed by Ferrarini, Luckhurst and co-workers [22], the continuous range of conformational states is replaced with just two possibilities: a linear conformer and a bent conformer. Here linear implies that the two mesogenic end groups are parallel to each other, i.e., at an angle of 0° or 180° whereas bent implies any other angle. The overall system can then be considered as a two-component mixture of linear and bent conformers which are free to interconvert as a result of the flexibility, see Fig. 2. The difference between "even" and "odd" spaced bimesogens is, therefore, the proportion of each conformer in the total system: even-spaced compounds consist of mainly linear conformers whereas odd-spaced compounds predominantly consist of bent conformers.

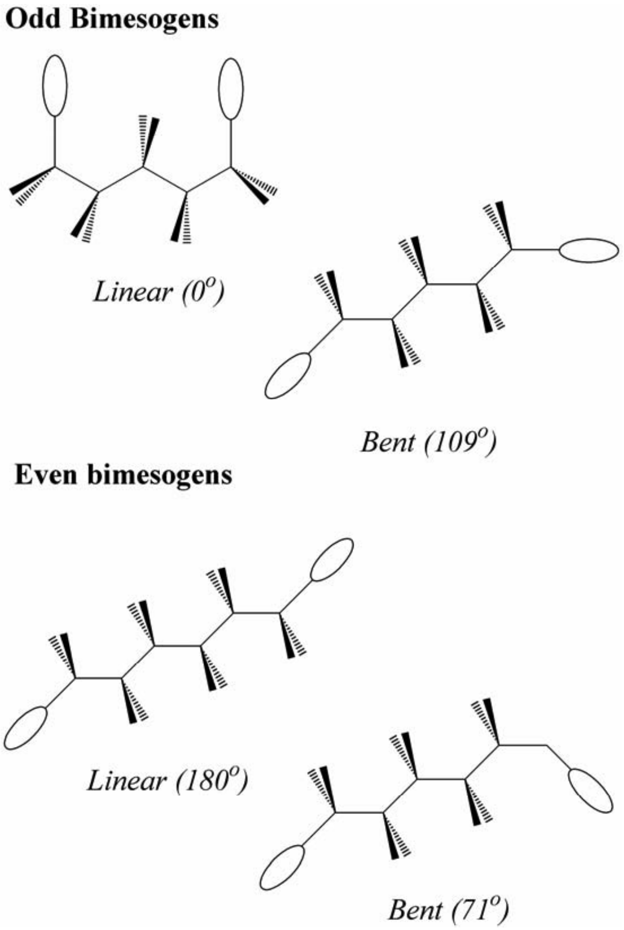


FIG. 2. Illustration of the linear and bent conformers for an odd- and even-spaced bimesogen.

As an example, the dependence of the tilt angle and response time on the electric field strength is shown for an odd- and even-spaced bimesogen in Fig. 3. For this exemplar case, results are presented for the bimesogen compounds FFO5OCB and FFO6OCB at the same reduced temperature of T_r=0.84 (T_r=T/T_{IN^*}). It can be seen that the tilt angles for a given field strength are higher for the odd-spaced bimesogen than the even-spaced bimesogen. For example, for an applied field of E=4 V μm^{-1}, the tilt angle of FFO5OCB is ϕ=16° compared with ϕ=7° for FFO6OCB. Measurements of the pitch, revealed that for the same concentration of chiral dopant the pitch was shorter for the odd-spaced bimesogen, i.e., p_{odd}=305 nm compared with p_{even}=440 nm. Therefore, from Eq. (1) the flexoelastic ratios were calculated to be $(e/K)_{\text{odd}}$=1.45 C N^{-1} m^{-1} and $(e/K)_{\text{even}}$=0.45 C N^{-1} m^{-1}. In this case the flexoelastic ratio is over a

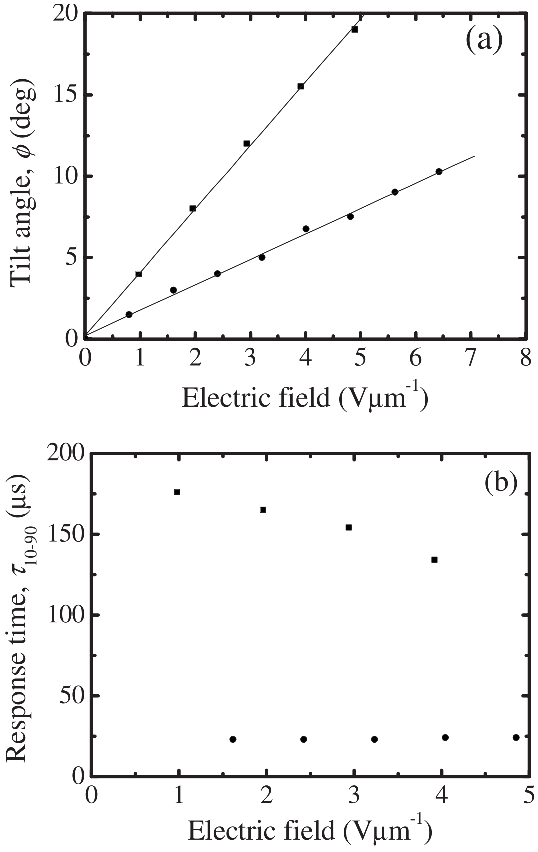


FIG. 3. The tilt angle, ϕ, and response time, τ_{10-90}, as a function of electric field strength for an odd- and even-spaced bimesogen at a reduced temperature of T_r=0.84. The compounds are FFO5OCB (■) and FFO6OCB (●).

factor of 2 greater for the odd-spaced bimesogen than that of the even-spaced compound. For the purposes of comparison, the same measurements were carried out using the monomesogen 7OCB doped with a low concentration of chiral additive. In this case the e/K ratio was found to be 0.5 C N^{-1} m^{-1} at the same reduced temperature of T_r=0.84.

In terms of response times, this is determined only by the viscoelastic ratio for a constant pitch, cf. Eq. (2). Results of the responses times for different field strengths are shown in Fig. 3(b). It should be noted that for these field strengths there is no unwinding of the helical structure: the critical field (E_{crit}), which represents complete unwinding of the helical structure, was found to be 14.2 V μm^{-1} for FFO5OCB and 12.2 V μm^{-1} for FFO6OCB. It can be seen that the even-spaced bimesogen (FFO6OCB) responds on a time scale of 20 μs and is virtually independent of the applied field strength. The response times of the odd-spaced bimesogen, on the other hand, are somewhat longer and do exhibit a field dependency. For example, at E=1 V μm^{-1}, τ_{10-90}=180 μs whereas for E=4 V μm^{-1}, τ_{10-90}=130 μs. The difference in response times is not due to different values for the pitch. From Eq. (2), it is shown that the time for the optic axis to respond is quadratic with the pitch and consequently a longer pitch results in a longer response time. Of the two materials, FFO6OCB has the longer pitch and yet exhibits a much faster response time. Inserting values for the pitch and the response time into Eq. (2) we find that the effective viscoelastic ratio for FFO6OCB is γ/K=4 $\times 10^9$ kg N^{-1} m^{-1} s^{-1} compared with γ/K=7.6 $\times 10^{10}$ kg N^{-1} m^{-1} s^{-1} for FFO5OCB. The viscoelastic ratio of the monomesogen 7OCB, determined by the same method, was found to be γ/K=9$\times 10^9$ kg N^{-1} m^{-1} s^{-1}.

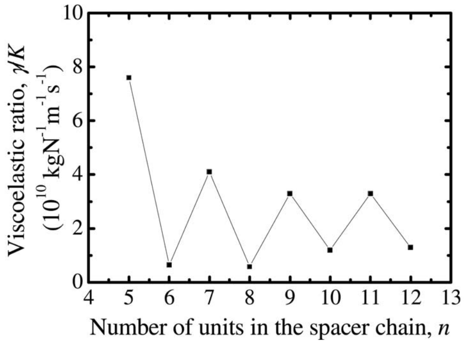


FIG. 4. The viscoelastic ratio (γ/K) as a function of the flexible spacer length, n, for the nonsymmetric homologous series FFOnOCB at a reduced temperature of T_r=0.84.

The viscoelastic ratios for the entire FFOnOCB homologous series are shown in Fig. 4 for a reduced temperature of T_r=0.84 where an odd-even effect is demonstrated. It can be seen that the viscoelastic ratio is larger for n=odd than for n=even and that it is largest for n=5 (γ/K=7.6 $\times 10^{10}$ kg N^{-1} m^{-1} s^{-1}). It is also apparent that the odd-even effect becomes less pronounced at longer spacer lengths.

To demonstrate how the flexoelastic ratio varies with spacer parity and spacer length for a specific homologous series, e/K is plotted as a function of the number of units in the spacer chain, n, for the FFOnOCB homologous series in Fig. 5. These values are all at the same reduced temperature of T_r=0.84. It can be seen that, to a first approximation, the ratio of e/K depends only upon the parity of the spacer, and is approximately 0.5 C N^{-1} m^{-1} for the even-spaced compounds compared with ~1.5 C N^{-1} m^{-1} for the opposite spacer parity. There is only a very weak dependence on the spacer length. Therefore, for a given electric field strength, and provided the pitch is the same, the tilt angle observed for the odd members of the FFOnOCB series will be higher than that for the even members.

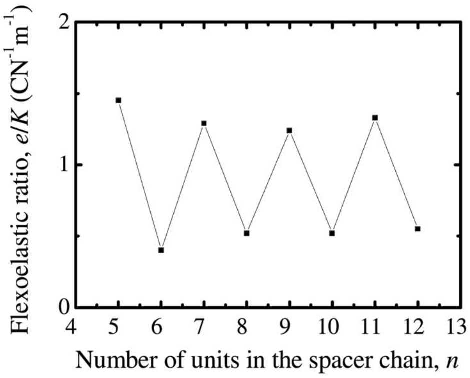


FIG. 5. Flexoelastic ratio (e/K) as a function of flexible spacer length, n, for the nonsymmetric homologous series FFOnOCB at a reduced temperature of T_r=0.84.

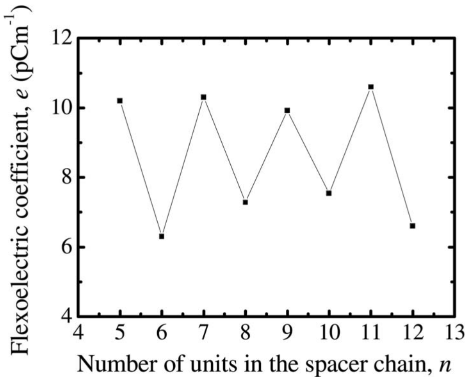


FIG. 6. The flexoelectric coefficient, e, as a function of the flexible spacer length, n for the homologous series FFOnOCB at a reduced temperature of T_r=0.84.

Using the same one-constant approximation as that used in Ref. [12] $[K_{11}=(K_{11}+K_{33})/2]$ we have estimated the flexoelectric coefficients. The dependence of the flexoelectric coefficient on the spacer length and parity are shown in Fig. 6 where it is apparent that e is larger for the odd-spaced bimesogens than their even-spaced counterparts. Values for the elastic constants are presented in Table II in the next section. The results clearly demonstrate an odd-even effect. The elastic constants also showed an odd-even effect and it was found that the even-spaced compounds were approximately a factor of 2 larger in terms of magnitude than the odd-spaced compounds, in accordance with the observations of DiLisi and co-workers [23]. Values of the flexoelectric coefficient for the odd- and even-spaced bimesogens are of the order of $e=10\pm0.5$ pC m^{-1} and $e=7\pm0.5$ pC m^{-1}, respectively. Therefore, the larger flexoelastic ratios observed for the odd-spaced compounds in comparison to the even-spaced compounds may be considered to be due to a combination of larger flexoelectric coefficients and smaller elastic constants.

The validity of the one-constant approximation requires further comment. Measurements of K_{33} have not yet been carried out for the entire homologous series. However, in a previous study DiLisi *et al.* examined the elastic constants for an odd and neighboring even dimer using dynamic light scattering [23]. At a shifted temperature (T-T_{NI}) of -15 °C, which corresponds approximately to a reduced temperature of T_r=0.89 for the odd dimer and T_r=0.90 for the even, $K_{11}(\text{odd})\sim 6$ pN and $K_{33}(\text{odd})\sim 7.5$ pN compared with $K_{11}(\text{even})\sim 10$ pN and $K_{33}(\text{even})\sim 17$ pN. From this, one finds that the average elastic constant, K $[=(K_{11}+K_{33})/2]$ is 6.75 pN and 13.5 pN for the odd and even dimers, respectively. Therefore, the ratio of $K_{\text{even}}/K_{\text{odd}}$ was approximately the same as that obtained herein, i.e., 2. As a result, the flexoelectric coefficients are indeed larger for the odd-spaced bimesogens than the even-spaced bimesogens, however, because the one-constant approximation has been used one must handle the absolute magnitudes with care as they may, in fact, be smaller than the values quoted herein.

Qualitatively, these results can be understood in the context of dipolar theory in that the bent configuration of the odd-spaced bimesogens result in a larger bend flexoelectric coefficient, e_b. On this basis, e_b can be considered to be proportional to the bend angle, θ, and the transverse dipole moment, μ_t, although the exact nature of this relationship differs somewhat in the literature. Specifically, the influence of the length-to-breadth ratio on e_b is debated; one example is Helfrich's theoretical treatment [2] which, using Meyer's dipolar model, found that $e_b \propto (b/a)^{2/3}$, where a is the molecular length and b is the breadth. Even though the dipole moment is along the longitudinal direction of the mesogenic units, for the bent conformation this would result in an increase in the component of the dipole moment in the transverse direction. This is supported by results obtained from shape models which have shown that the dipole moments are much larger for *cis* (bent) isomers than *trans* (linear) isomers [7]. These models also predict that the coefficients e_s, and in particular e_b, increase for *trans-cis* conformation change.

It is not possible from these results alone to delineate the contributions of μ_t and θ to e_b as both factors are likely to

TABLE II. Summary of the flexoelastic and viscoelastic ratios for all the bimesogenic compounds studied at a reduced temperature of T_r=0.84 (except for NSO9OphO9OCB which was obtained at T_r=0.91). Also included is the elastic constant used in the one-constant approximation and the corresponding effective flexoelectric coefficient. The table is arranged in order of increasing e/K.

Material	P (nm)	e/K (C N^{-1} m^{-1})	K (pN)	e (pC m^{-1})	γ/K (10^{10} kg N^{-1} m^{-1} s^{-1})
FFO6OCB	440	0.45	14	6.3	0.65
FFO8OCB	495	0.52	14	7.3	0.58
FFO10OCB	445	0.52	14.5	7.5	1.2
FFO12OCB	367	0.55	12	6.6	1.3
NSO9OphO9OCB	294	0.78	7.4	5.8	25
FFO9/11OFF	290	0.94	N/A	N/A	15.7
FFO9OCB	313	1.24	8	9.9	3.3
FFO7OCB	307	1.29	8	10.3	4.1
FFO11OCB	340	1.33	8	10.6	3.3
FFO5OCB	305	1.45	7	10.2	7.6
NSO9OFF	290	1.6	6.4	10.2	1.5
FFE9/11EFF	294	1.74	N/A	N/A	12.1

vary for the two different spacer parities. Moreover, by considering only e_b we are ignoring any changes in e_s. According to Osipov [3], the flexoelectric coefficients of banana-shaped molecules should only be represented by the bend flexoelectric coefficient, e_b. However, for the compounds studied herein it is unlikely that e_s tends to zero given the flexibility of the spacer chain; this is in contrast to conventional banana-shaped compounds which tend to be more rigid in terms of molecular structure. Nevertheless, it is believed that the dominant factor responsible for the change in e is due to a change in e_b.

For simplicity, we consider only the *all-trans* conformation of the flexible spacer for both the odd- and even-spaced bimesogens. In this case, the angle between the mesogenic units for the odd-spaced bimesogen is 1.9 rad compared to 0 rad for the even-spaced bimesogen. Consequently, $(\theta)_{\mathrm{odd}} = 0.95$ rad and $(\theta)_{\mathrm{even}} = 0$ rad. Here, $(e_b)_{\mathrm{even}}$ would be zero and the flexoelectric coefficient would reduce to just the splay coefficient. The value of the bend angle for the odd-spaced bimesogen is of a similar order of magnitude to that found in a previous study which showed that $\theta = 0.75$ rad for a similar bimesogen with a spacer chain length of $n = 7$ in the gaseous state.

The values for $(\theta)_{\mathrm{odd}}$ and $(\theta)_{\mathrm{even}}$ represent the extreme cases: according to the two-conformer model of Luckhurst and Ferrarini [22] each spacer-parity contains just two different species, the dominant species for the odd- and even-spaced compounds are bent and linear conformers, respectively. However, each compound also contains a proportion of the opposite type of conformer. Moreover, for real systems there are, by virtue of the flexible spacer, a range of conformers of differing concentrations and as a result $(e_b)_{\mathrm{even}} \neq 0$; this is evident from Ref. [22] where it was found that $(\theta)_{\mathrm{even}} = 0.5(\theta)_{\mathrm{odd}}$. In terms of the flexoelectric coefficient we find herein that $(e_b)_{\mathrm{even}} = 0.7(e_b)$odd and the smaller difference in the even and odd values may be the result of simultaneous changes in the dipole moment and the length-to-breadth ratio. In fact, in Ref. [22] it was also shown that the ratio of the transverse dipole moments for even—to odd-spaced bimesogens is of the order of 0.7. It is, therefore, difficult to elucidate the exact contributions of θ and μ_t to the increase of $(e_b)_{\mathrm{odd}}$ compared to $(e_b)_{\mathrm{even}}$. Having said this, the change in flexoelectric coefficient can be accounted for by dipolar theory as both components are known to be larger for the odd-spaced bimesogen than the even-spaced bimesogen and are in accordance with the results presented for the flexoelectric coefficient in this study.

B. Correlations between molecular structure and the flexoelastic ratio

Figure 7 shows the tilt angle and response time as a function of the applied electric field strength for compounds from each of the homologous series that were presented in Fig. 1. Specifically, data is presented for the two-component mixtures of the symmetric bimesogens FFO9OFF(50):FFO11OFF(50) and FFE9EFF(50):FFE11EFF(50), and the nonsymmetric bimesogens FFO5OCB and FFO6OCB. In each case, the results were obtained for a reduced temperature of $T_r = 0.84$. It can be seen that the tilt angle per unit field varies noticeably for the different compounds. Using measured values for the pitch in conjunction with the change in tilt angle per unit of applied field it is found that the nonsymmetric bimesogen FFO6OCB has the smallest e/K ratio ($0.45\ \mathrm{C\,N^{-1}\,m^{-1}}$). On the other hand, the largest flexoelastic ratio ($e/K = 1.74\ \mathrm{C\,N^{-1}\,m^{-1}}$) is found to be for the two-component mixture consisting of ester links (FFE*n*EFF). The two remaining compounds have values of $e/K = 0.94\ \mathrm{C\,N^{-1}\,m^{-1}}$ and $e/K = 1.45\ \mathrm{C\,N^{-1}\,m^{-1}}$ for the two-component mixture of FFO9OFF/FFO11OFF and FFO5OCB, respectively. Consequently, changing one mesogenic unit from a cyanobiphenyl (CB) to a difluorobiphenyl (FF) or replacing ether-links (O) with ester-links (E) the flexoelastic ratio can be altered significantly.

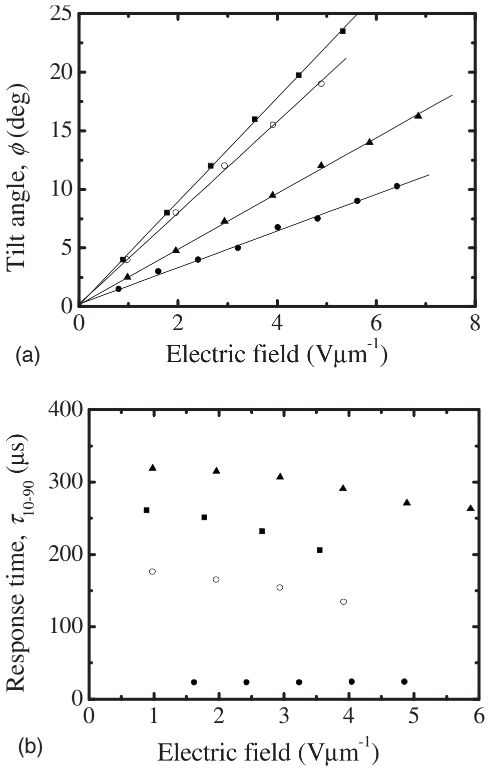


FIG. 7. The tilt angle, ϕ, and the response time, τ_{10-90}, as a function of electric field strength for the different bimesogenic compounds: FFO5OCB (○), FFO6OCB (●), FFO9/11OFF (▲), and FFE9/11EFF (■)at a reduced temperature of $T_r = 0.84$.

To some extent these results can be explained by considering the change in the dipole moment. Since they are all of a similar generic structure, and that they have an odd number of methylene units in the spacer, the bend angle and the length-to-breadth ratio are unlikely to vary significantly. By substituting a CB mesogenic unit for a FF unit the flexoelastic ratio is reduced and this is reflected in a decrease in the tilt angle for a given field strength. This is believed to be due to a decrease in the dipole moment and is supported by the fact that the dielectric anisotropy reduces from $\Delta\varepsilon \sim 3$ for the FFO*n*OCB compounds to $\Delta\varepsilon < 1$ for the FFO*n*OFF compounds. The increase in e/K on replacing the ether linkages (–O–) with ester linkages (–COO–) can be explained in that the presence of the ester links provides a significant increase in the transverse component of the dipole moment.

To summarize our findings for all the compounds studied, we present values for both the e/K and γ/K ratios for the different bimesogenic compounds at the same reduced temperature of $T_r=0.84$. These are shown in Table II. In addition, calculated values for the effective flexoelectric coefficient and the corresponding elastic constants used in the one-constant approximation are also included. For completeness, values of the pitch for a concentration of 3.5 wt. % chiral additive are also shown. It should be noted, however, that, due to the use of the one-constant approximation, the effective elastic constants are likely to be larger and the flexoelectric coefficients smaller as a result of the errors incurred using this approximation.

It can be seen that all the odd members have much higher e/K ratios ($e/K_{\text{odd}} \sim 2e/K_{\text{even}}$) than the alternative spacer parity and, as discussed previously, appears to be the result of a larger flexoelectric coefficient and a lower effective elastic constant. Both of these features result from the shape of the molecule as the mesogenic units remain the same. However, the contributions of the bend angle and the dipole moment to the increase in the flexoelectric coefficient are not yet known. If the CB in the FFO*n*OCB series or one of the FF mesogenic units in the FFO*n*OFF series are replaced with the nitro-stilbene (NS) mesogenic unit then the e/K ratio increases. Similarly, the larger values of $e/K = 1.6\ \text{C N}^{-1}\ \text{m}^{-1}$ and $e/K=1.74\ \text{C N}^{-1}\ \text{m}^{-1}$ for the NSO9OFF and FFE9/11EFF compounds, respectively, compared with the FFO*n*OCB and FFO9/11OFF compounds are also in accord with larger transverse dipole moments.

In terms of the viscoelastic ratios, these appear to be smaller for the even-spaced bimesogens ($\gamma/K=0.58-1.3 \times 10^{10}\ \text{kg N}^{-1}\ \text{m}^{-1}\ \text{s}^{-1}$) in comparison to the opposite parity bimesogens ($\gamma/K=3.3-7.6\times 10^{10}\ \text{kg N}^{-1}\ \text{m}^{-1}\ \text{s}^{-1}$). Moreover, the mixtures based on the symmetric difluorobiphenyl compounds (FFO9OFF/FFO11OFF and FFE9EFF/FFE11EFF) exhibit larger viscoelastic ratios than the nonsymmetric bimesogens.

The bent-core bimesogen, which contains a central nonsymmetrically substituted phenyl moiety (NSO9OphO9OCB), exhibits a flexoelastic ratio of $0.78\ \text{C N}^{-1}\ \text{m}^{-1}$ and therefore it lies between the even-spaced bimesogens and the odd-spaced bimesogens $[(e/K)_{\text{even}} < (e/K)_{\text{bent-core}} < (e/K)_{\text{odd}}]$. The viscoelastic ratio is also significantly higher than any of the other compounds ($\gamma/K \sim 25\times 10^{10}\ \text{kg N}^{-1}\ \text{m}^{-1}\ \text{s}^{-1}$). The reason for $(e/K)_{\text{bent-core}} < (e/K)_{\text{odd}}$ appears to be due to a smaller flexoelectric coefficient since the elastic constants were found to be of the same order of magnitude. It is not fully understood why the flexoelectric coefficient is lower for the bent-core compound as the dipole moments along the longitudinal direction of the mesogenic units are larger and for an *all-trans* conformation of the two flexible spacers, which results in a bent configuration, this should give rise to a larger component of the dipole moment in the transverse direction. A possible explanation may be that the contrasting behavior between the odd-spaced bimesogens and the bent-core bimesogen is due to the increased flexibility of the latter compound allowing for a range of different conformations that deviates from a true bent configuration.

The effects of doping banana-shaped liquid crystals into commercial nematic liquid crystals on the flexoelectric coefficients has been studied recently [24]. It was found that there was little correlation between the magnitude of the transverse dipole moment and the flexoelectric coefficient although the molecular length and bend angle did appear to have an influence. However, the observations were the opposite of that expected from dipolar theory in that the flexoelastic ratio was found to decrease with increasing bend angle. To some extent this correlates with our observations for the bent-core bimesogen but on the other hand the odd-spaced bimesogens clearly show an increase in e/K compared with the even-spaced counterparts. Moreover, there also appears to be a correlation between the magnitude of the dipole moment and e/K, albeit qualitatively.

V. CONCLUSIONS

In this paper, we have been concerned with the structure-flexoelectric property relationships of bimesogenic compounds. Our results show that bent-shaped molecules (odd-spaced bimesogens) exhibit larger flexoelastic ratios in accord with dipolar theory. The bent shape not only partially relieves the strain due to a bend deformation but also increases the effective flexoelectric coefficient, through a combination of the bend angle and the transverse dipole moment. Elongated bimesogens (even-spaced) possess lower flexoelastic ratios and consequently lower flexoelectric coefficients. The magnitudes of the viscoelastic ratios are also smaller than for the even-spaced bimesogens. Bent-core bimesogens, on the other hand, appear to have relatively low flexoelectric coefficients and much larger viscoelastic ratios. In terms of the molecular structure, the flexoelastic ratio is found to be largest for a two-component mixture of a symmetric difluorobiphenyl bimesogenic compound with ester linkages and an odd number of methylene units in the flexible spacer chain. This is suspected to be due to a combination of a bent shape and a large transverse dipole moment.

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[1] R. B. Meyer, Phys. Rev. Lett. **22**, 918 (1969).
[2] W. Z. Helfrich, Z. Naturforsch. A **26A**, 833 (1971).
[3] M. A. Osipov, Sov. Phys. JETP **58**, 1167 (1983).
[4] C. V. Brown and N. J. Mottram, Phys. Rev. E **68**, 031702 (2003).
[5] S. Ponti, P. Ziherl, C. Ferrero, and S. Zumer, Liq. Cryst. **26**, 1171 (1999).
[6] Y. Singh and U. P. Singh, Phys. Rev. A **39**, 4254 (1989).
[7] A. Ferrarini, Phys. Rev. E **64**, 021710 (2001).
[8] J. Prost and J. P. Marcerou, J. Phys. (Paris) **38**, 315 (1977).
[9] B. Musgrave, P. Lehmann, and H. J. Coles, Liq. Cryst. **26**, 1235 (1999).
[10] C. Noot, M. J. Coles, B. Musgrave, S. P. Perkins, and H. J. Coles, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **366**, 725 (2001).
[11] H. J. Coles, M. J. Clarke, S. M. Morris, B. J. Broughton, and A. E. Blatch, J. Appl. Phys. **99**, 034104 (2006).
[12] H. J. Coles, B. Musgrave, M. J. Coles, and J. Willmott, Chem. Mater. **11**, 2709 (2001).
[13] J. S. Patel and R. B. Meyer, Phys. Rev. Lett. **58**, 1538 (1987).
[14] L. Komitov, S. T. Lagerwall, B. Stebler, and A. Strigazzi, J. Appl. Phys. **76**, 3762 (1994).
[15] P. Rudquist, M. Buivydas, L. Komitov, and S. T. Lagerwall, J. Appl. Phys. **76**, 7778 (1994).
[16] P. Rudquist, T. Carlsson, L. Komitov, and S. T. Lagerwall, Liq. Cryst. **22**, 445 (1997).
[17] P. Rudquist, L. Komitov, and S. T. Lagerwall, Ferroelectrics **213**, 53 (1998).
[18] J. S. Patel and S.-D. Lee, J. Appl. Phys. **66**, 1879 (1989).
[19] S.-D. Lee and J. S. Patel, Phys. Rev. A **42**, 997 (1990).
[20] See, for example, I.-C. Khoo and S.-T. Wu, *Optics and Nonlinear Optics of Liquid Crystals* (World Scientific, Singapore, 1993), Vol. 1.
[21] D. Dunmur, G. R. Luckhurst, M. R. de la Fuente, S. Diez, and M. A. Perez Jubindo, J. Chem. Phys. **115**, 8681 (2001).
[22] A. Ferrarini, G. R. Luckhurst, P. L. Nordio, and S. J. Roskilly, Chem. Phys. Lett. **214**, 409 (1993).
[23] G. A. Dilisi, E. M. Terentjev, A. C. Griffin, and C. Rosenblatt, J. Phys. II **3**, 597 (1993).
[24] J. H. Wild, K. Bartle, N. T. Kirkman, S. M. Kelly, M. O'Neill, T. Stirner, and R. P. Tuffin, Chem. Mater. **17**, 6354 (2005).