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Physical Properties of Some Novel Nematic Bimesogens for the Flexoelectric Effect

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In a chiral nematic liquid crystal, the flexoelectric effect consists of a fast and linear coupling with an applied electric field. One difficulty to overcome is the unwinding of the helix that occurs at higher fields due to dielectric coupling. The use of bimesogens, which possess very low molecular dielectric anisotropy can improve flexoelectric characteristics. New bimesogen compounds have recently been synthesised that exhibit switching angles of 45° for applied fields of about 9 $V.\mu m^{-1}$. In this paper, results from dielectric, electro-optic and dynamic light scattering measurements are reported for the new bimesogenic mixture. The dielectric anisotropy $\Delta\varepsilon$ changes sign with temperature and its values range between −0.2 and 0.3 for the temperature range studied. For $\Delta\varepsilon$ weakly positive, no electric field Freedericksz transition could be induced but Williams domains are observed instead. The large decrease in the bend elastic constant to viscosity coefficient ratio is attributed to a large increase in the bend viscosity coefficient.

Keywords: bimesogens; dielectric anisotropy; Williams domains; dynamic light scattering; visco-elastic properties

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INTRODUCTION

In short pitch chiral nematic materials, the flexoelectric switching effect can be temperature independent and is linear with applied field amplitude E. In a uniform lying helix texture cell, the application of an electric field can induce an in-plane switch of the optic axis [1]. The rotation angle ϕ can be expressed as:

$$\tan \phi = (eEP)/(2\pi K), \quad (1)$$

where P represents the pitch of the helix, $K=(K_{11}+K_{33})/2$ and $e=(e_s+e_b)/2$ are respectively the effective elastic constant and effective flexoelectric coefficient of the chiral nematic phase. K_{11} and e_s are associated with the splay distortion while K_{33} and e_b are related to the bend deformation [2, 3]. The response time τ ($\tau<100\mu s$) characteristic of the flexoelectric switching is given by:

$$\tau = (P^2\gamma)/(4\pi^2 K), \quad (2)$$

where γ is the effective viscosity coefficient corresponding to the helix distortion [3].

The optimisation of the flexoelectric effect requires short and temperature independent helical pitch, large flexoelectric coefficients, fast response times and small dielectric anisotropy $\Delta\varepsilon$ [3]. In fact, the dielectric coupling mechanism is quadratic in applied electric field amplitude [1]. Thus, it becomes predominant at higher fields and causes the helix to unwind.

Enhanced flexoelectric behaviour can be obtained by using symmetric dimer molecules with low molecular dielectric anisotropy [4, 5]. A novel non-chiral bimesogenic mixture doped with a low concentration of a suitable chiral agent can display interesting flexoelectric properties such as switch angles ϕ of 45° for applied fields of about 9 $V.\mu m^{-1}$ [4].

It is necessary to determine the Franck elastic constants K_{11} and K_{33} in order to calculate the effective flexoelectric coefficient from Eq. 1. In achiral nematic liquid crystals, dynamic light scattering (DLS) is a widely used technique to measure visco-elastic constants [6-8]. The Orsay theory predicts that the Lorentzian frequency broadening is due to quasi-elastic scattering from two overdamped director fluctuation modes: mode 1 corresponds to splay-bend deformations while mode 2

consists of twist-bend contributions [6]. Using a well-aligned homeotropic or planar sample in specific scattering geometries with appropriate input and scattered light polarisations, it is possible to isolate the splay, twist and bend mode. Thus, the associated visco-elastic parameters can be derived from the measurement of the linewidth corresponding to each mode [6-8].

The main difficulty encountered when performing DLS on achiral bimesogenic mixtures is that only planar alignment can be achieved for these systems. Several surface treatment agents were tried to induce homeotropic alignment (such as lecithin in chloroform or CTAB in methanol) without any success.

We report here on the measurement of the pure bend mode in planar samples. In this case, the linewidth obtained with mode 1 or 2 is given by:

$$\Gamma_{1,2}=K_{33}q_{\parallel}^{2}/\eta_{bend}, \qquad (3)$$

where η_{bend} is the bend viscosity coefficient and $q_{\parallel}$ is the component of the scattering wavevector $\mathbf{q}$ parallel to the nematic director $\mathbf{n}$.
In principle, it is possible to deconvolute the visco-elastic ratios by applying an electric field to quench the director fluctuations [7, 8]. The field has to be along $\varepsilon_{\parallel}$ for materials with $\Delta\varepsilon = \varepsilon_{\parallel}-\varepsilon_{\perp}>0$ and along $\varepsilon_{\perp}$ for materials with $\Delta\varepsilon<0$. $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are respectively components of the dielectric constant parallel and perpendicular to the molecular long axis.

To understand the flexoelectric coupling occurring in this new bimesogenic system, dielectric anisotropy measurements were carried out in the chiral-induced sample. Electro-optic experiments and dynamic light scattering studies were performed in the achiral mixture.

RESULTS AND DISCUSSION

Materials

A novel series of non-chiral symmetric bimesogens with various spacer lengths have recently been synthesised and selected eutectic mixtures have been prepared [9]. The generic structure of these compounds is represented on Figure 1.

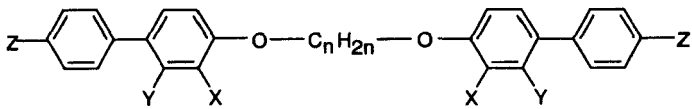

FIGURE 1: Chemical structure of the novel bimesogenic liquid crystal investigated (n is the number of carbon atoms in the spacer chain and X, Y, Z are functional groups).

The achiral mixture investigated in this paper is composed of several bimesogens containing an odd number of carbon atoms in their spacer. It exhibits a wide nematic phase at relatively low temperatures (T_{NI}<60°C) compared to other dimers. The following transition temperatures were measured using differential scanning calorimetry:

Cr –30.5°C N 56.4°C I.

Dielectric Constant Measurements

The measurements were carried out on a Wayne-Kerr 6425 multi-bridge. The chiral sample was obtained by doping the original achiral bimesogenic mixture with low concentration (<3%) of suitable chiral molecules. The pitch of this system is ≈2μm. A uniform lying helix texture forms *spontaneously* when the mixture is cooled from the isotropic phase. However, it is necessary to apply a voltage of about 5 Vrms at a frequency of 500 Hz to maintain this texture in the $\Delta\varepsilon>0$ regime. In this configuration, $\varepsilon_{ave} = (\varepsilon_{\parallel}+\varepsilon_{\perp})/2$ is measured. $\varepsilon_{\perp}$ is determined in the standing helix texture that reappears when no external aligning field is applied.

Figure 2 shows the dielectric anisotropy as a function of reduced temperature T_{NI}-T for the chiral-induced bimesogen sample. It can be seen that $\Delta\varepsilon = \varepsilon_{\parallel}-\varepsilon_{\perp}$ changes sign at T_{NI}-T=15.5°C. At low concentrations, the chiral additive is not expected to strongly influence the dielectric properties of the bimesogenic host. We measured $\Delta\varepsilon$ for a well-known non-chiral mesogen 5CB and for the same compound doped with 6% of chiral molecules. The dielectric anisotropy was found to be identical in both systems. Thus, the $\Delta\varepsilon$ values obtained for the chiral system are extrapolated to the pure dimeric mixture at the same reduced temperature.

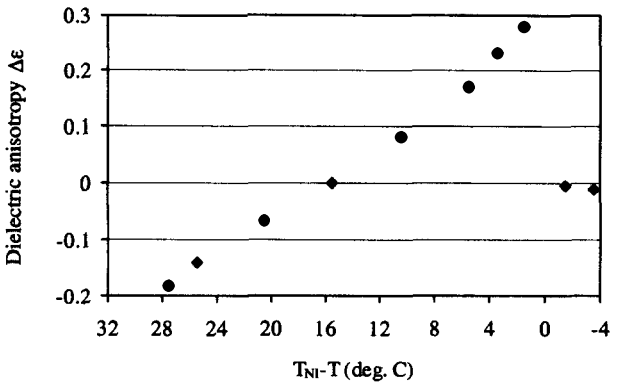

FIGURE 2: Dielectric anisotropy $\Delta\varepsilon$ against reduced temperature (data obtained at 10kHz with a 6μm planar cell).

Similar behaviour of the dielectric anisotropy was found in the chiral mixture TM216; $\Delta\varepsilon$ is positive above 31°C-32°C and becomes negative below this critical temperature [2]. In TM216, $-0.11<\Delta\varepsilon<0.08$ was measured for T=28°C-39°C. These values are of the same order of magnitude as those obtained for our sample. However, the tilt angles ϕ that have been measured in TM216 are much lower and require much higher fields than our materials [2, 4] ($\phi \approx 30°$ obtained with applied fields of 120 $V.\mu m^{-1}$).

For the achiral bimesogens, conformational changes may explain the evolution of $\Delta\varepsilon$ against temperature [10]. For odd dimers, the energy ground state of the nematic phase is associated with the bent conformers. Thus, as the temperature decreases, the population of bent conformers is increased resulting in $\Delta\varepsilon<0$ at lower temperatures.

The increase of $\Delta\varepsilon$ with temperature plus the fact that it is positive near the chiral nematic-to-isotropic transition is an advantage for the flexoelectric effect. A good lying helix texture alignment is obtained just below the clearing point by applying an electric field. Then at lower temperatures for which $\Delta\varepsilon\approx0$, large tilt angles can be measured at higher fields.

Electro-optic Experiments

Since no homeotropic alignment could be achieved for the achiral bimesogenic mixture by treating the glass surface with various surfactants, electric fields were applied to a planar cell of thickness 44.7 μm at T>42.6°C (for $\Delta\varepsilon>0$) to induce a Freedericksz transition.

No such transition was observed; instead Williams domains started to appear at a certain threshold voltage V_{th}. Stationary Williams domains are electrohydrodynamic distortions arising from the coupling between a low frequency ac field and the anisotropy of electrical conductivity [11]. Though these effects are generally associated with materials of negative dielectric anisotropy, they also occur in weakly positive nematics if the applied field is perpendicular to the initial director alignment [11]. V_{th} is almost independent of the frequency of applied field in the range 100 Hz-10 kHz investigated. The evolution of the Williams domains as a function of applied rms voltage can be seen on figure 3. The domains disappear at higher fields. No Freedericksz transition from planar to homeotropic orientation was observed. When $\Delta\varepsilon<0$, at similar frequencies, the effect of the field was to align the sample and to suppress any disclinations present. No Williams domains are formed at maximum applied voltages of 130 Vrms.

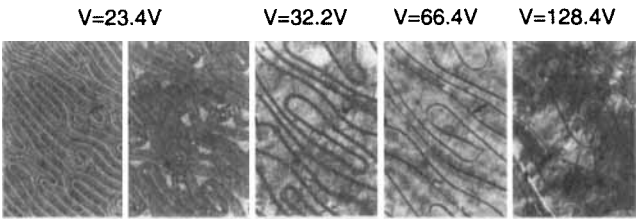

FIGURE 3: Williams domains observed between crossed polarisers (director initially at 45°) with an ac square wave signal of 1 kHz at T=45°C at different voltages in the achiral bimesogenic mixture. See Color Plate XII at the back of this issue.

Dynamic Light Scattering

Photon correlation experiments were performed with a 30 mW He-Ne laser (λ=632.8 nm) using a 10 μm thick planar cell filled with the achiral bimesogenic mixture The apparatus is described in detail elsewhere [8]. Time-dependent autocorrelation functions of the scattered light intensity are measured and the associated linewidths deduced.

The scattering plane is defined as (**n**, **q**). The initial director orientation is planar and perpendicular to the incident beam. There are several possible geometries to isolate the pure bend contributions to mode 1 or mode 2:

- Mode 1: Both input and scattered light polarisations are in the (**n**, **q**) plane (E-E configuration) at low scattering angles θ_{lab} in the laboratory frame [6, 7]. For $\theta \leq 10°$, the scattered light beats with the intense unshifted light in the $\theta_{lab}=0°$ direction and full heterodyning occurs.
- Mode 2: The incident and scattered light polarisations are respectively perpendicular and parallel to the (**n**, **q**) plane (O-E configuration) at sufficiently large θ_{lab} [7, 8]. In this case, the measured signal is purely homodyne and by recombining the scattered beam with a portion of unscattered light derived from the same laser source, heterodyne detection could be employed.

In this work, mode 2 geometry was used. The bend mode can be isolated at a certain scattering angle θ_{bend} that is dependent on the refractive indices of the material [8]. The linewidth was measured for a wide range of scattering angles θ_{lab} in order to determine the appropriate values for θ_{bend} ($\theta_{bend} \approx 29°$-$26°$ for T=28°C-54°C). Figure 4 shows the bend elastic constant to viscosity coefficient ratio as a function of reduced temperature for the achiral bimesogenic mixture.

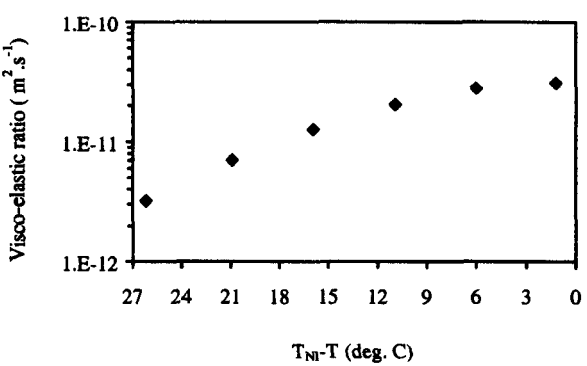

FIGURE 4: Bend visco-elastic ratio K_{33}/η_{bend} against T_{NI}-T.

DiLisi et al. measured the splay, twist and bend visco-elastic constants of a series of achiral dimers based on the monomer unit 5005 and containing an even and odd number of carbon atoms n in the spacer chain (respectively, n=10 and n=9) [12, 13]. They showed that the weak flexibility of the spacer linking the two monomers has a major influence on the visco-elastic parameters. Values of bend visco-elastic ratios are given in Table 1 for our bimesogenic mixture as well as for the monomer and both even and odd dimers [12, 13] examined by DiLisi et al..

Materials	T_{NI}-T (deg. C)	K_{33}/η_{bend} ($m^2.s^{-1}$)	K_{33} ($x10^{-12}N$)	η_{bend} (Pa.s)
5005 monomer	10	$5.8x10^{-10}$	7	$1.2x10^{-2}$
5005 even dimer	10	$1.1x10^{-10}$	11	$1.0x10^{-1}$
5005 odd dimer	10	$3.9x10^{-11}$	4.7	$1.2x10^{-1}$
New bimesogenic mixture	10.9	$2.0x10^{-11}$	N/A	N/A

TABLE 1: Values of bend visco-elastic ratios extracted from published data [12, 13] for the 5005 samples and measured for the new bimesogens.

The bend visco-elastic ratio of our sample is of the same order of magnitude as for the 5005 odd dimer. In the case of the odd dimer, the bend elastic constant K_{33} is just less than half that of the even dimer and less than that of the 5005 monomer; this is expected considering that the odd dimer will adopt a bent shape in the all-trans conformation [10, 13]. For our odd bimesogenic mixture, it may be possible that lower bend elastic constants are associated with lower values of K_{33}/η_{bend}.

The bend viscosity of the 5005 dimers is an order of magnitude greater than for the 5005 monomer. In our system, the visco-elastic ratio K_{33}/η_{bend} is reduced by almost an order of magnitude on cooling the mixture to 30°C below the N-I transition (see Figure 4). Thus for the novel mixtures reported herein, the low values of K_{33}/η_{bend} appears to be dominated by large increase in the bend viscosity coefficient. It is then interesting to note that the response times, c.f. Equation 2, are in the microsecond regime (for instance, at 9 $V.\mu m^{-1}$, $\tau \approx 400$ µs at T=42°C [14]). Considering that a conventional nematic monomesogen exhibits switching times of about 10-100 ms under the same conditions, this raises interesting questions about the role of the effective viscosity coefficient γ in the flexoelectro-optic switching.

Martinand and Durand [7] studied a nematic material with $\Delta\varepsilon<0$, namely MBBA, by dynamic light scattering in the presence of an ac electric field to dampen the director fluctuations. When an electric field is applied, a quenching of the scattered light is observed in the mode 1 configuration but not in the case of mode 2. The authors were able to deduce values for the bend elastic constant and viscosity coefficient K_{33} and η_{bend} from the following equation:

$$\Gamma_1 = \frac{K_{33}}{\eta_{bend}} q_{\parallel}^2 + \frac{(-\Delta\varepsilon)\,\varepsilon_{\perp}}{4\pi\varepsilon_{\parallel}\eta_{bend}} E^2. \qquad (4)$$

For the achiral bimesogenic mixture, no damping of the scattered light intensity could be observed in either mode configuration when $\Delta\varepsilon<0$. This may be explained by some intrinsic properties of the dimers. As mentioned previously, the values of the bend visco-elastic ratio are quite low. Since $\Gamma_{1,2} \propto \sin^2\theta_{lab}$, the linewidth decreases with scattering angles. Thus, in mode 1, at $\theta_{lab}=10°$ the measured frequency broadening Γ_1 is about 20 Hz at T=34°C. At such low linewidths, the mechanical and electrical noise becomes significant and distorts the scattered light correlation function resulting in inaccurate values for the linewidth [8]. Furthermore, the low negative dielectric anisotropy requires the application of very high fields (> 10 $V.\mu m^{-1}$) in order to detect any quenching of the director fluctuations.

CONCLUSION

The novel bimesogenic compounds present promising features for flexoelectric coupling. Their dielectric anisotropy is low and exhibits a sign reversal with temperature. Further investigation is required to understand the visco-elastic behaviour of this system. The bend visco-elastic ratio ranges from 3.2×10^{-12} to 3.1×10^{-11} $m^2.s^{-1}$ in the temperature interval investigated. These low values result from a combination of high viscosity coefficients and lower elastic constants with the former effect predominant.

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