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Liquid Crystals

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Liquid crystal mixtures for potential infrared applications

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Liquid crystals (LCs) with diazo linkages have high dielectric and optical anisotropy. Two newly synthesized liquid crystalline compounds were dissolved in room temperature LC hosts, E7 and PTTP-24/36, to assess their properties. It was found that these mixtures have higher birefringence, larger dielectric anisotropy, and better elastic properties than the hosts. Satisfactory viscoelastic coefficients were also obtained for these mixtures, showing that they are promising LC materials for applications in the near IR region.

1. Introduction

Currently, electro-optic liquid crystal (LC) devices are designed mainly for applications in the visible region of the spectrum, but some important industrial and military devices require operation in the near- and mid-IR range. However, most commercial liquid crystals and liquid crystal mixtures suffer from insufficient birefringence (Δn) and high optical loss when used in the IR region [1–5]. The importance of IR birefringence for liquid crystals has been recognized for some time [6, 7]. Compounds that have considerable IR birefringence include diphenylacetylenes (tolanes) [8–11], stilbenes [8], diphenyldiacetylenes [9, 12, 13], and bistolanes [14, 15]. Here we report another type of compound with high IR birefringence.

Molecules carrying electron donating and accepting (push–pull) groups connected by a conjugated system exhibit large molecular dipole moments, high birefringence and large dielectric anisotropy [16, 17]. They are used extensively as second order non-linear optics materials [16]. Diazo liquid crystal dyes carrying push–pull structures have been synthesized in this laboratory [17–21]. Because their melting points are above room temperature, they are usually used as dopants in room temperature LC mixtures. Liquid crystal dopants are more advantageous than dichroic dyes since they are not detrimental to the mesogenic properties of the LC hosts, and have higher order parameters. Therefore, liquid crystal mixtures can be utilized in TN or even STN mode; they are superior to normal dyes that can only be used in GH mode displays.

Most commercial liquid crystals do not have a conjugated mesogenic core, they therefore have low birefringence and are suitable for reflective mode display. The commercial mixture E7 is often used as a standard for measuring the electro-optic properties of liquid crystals. On the other hand, dialkyl diphenyl-diacetylene (PTTP) liquid crystals have an elongated conjugated core. They possess high birefringence, low melting temperatures, small fusion enthalpies, low viscosity, and reasonable nematic ranges [22–24]. A eutectic room temperature mixture, PTTP-24/36, has been formulated [22], and is a good candidate for direct view mode applications. However, the dielectric anisotropy ($\Delta\varepsilon$) of these LCs is very low (<1) and high threshold voltages are needed for displays using PTTP mixtures [22–25].

The goal of this study is to find room temperature liquid crystal mixtures for potential IR applications; the desired liquid crystal mixtures should therefore possess high birefringence in the IR region. For this purpose, we previously synthesized a number of diazo liquid crystals with push–pull groups and made preliminary tests on their electro-optic properties [21]. Now we have chosen the two most promising compounds for a more comprehensive study. Two room temperature liquid crystal solvents, E7 and PTTP-24/36, were used to evaluate the elastic and electro-optic properties.

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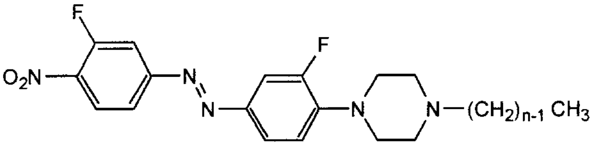
2. Experimental

Two series of diazo liquid crystals with the following structures were synthesized and studied. They were chosen for the present investigation because series **1** possesses rather large birefringence and series **2** exhibits large dielectric anisotropy. The synthesis of diazo liquid crystals **2** has been reported previously [21], and the procedure for the synthesis of **1** is very similar. For both series, the aliphatic chains contain 5–8 carbon atoms.



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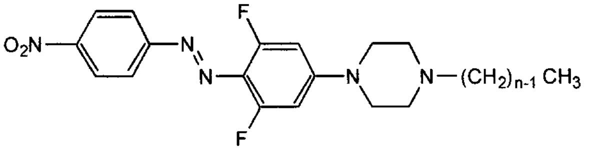

2

Phase transition temperatures were determined using a Perkin-Elmer DSC7 differential scanning calorimeter and the phases were checked using an Olympus BH-2 polarizing microscope.

Dielectric anisotropy measurements on the mixtures were made using a Displaytech APT III automatic property tester. Birefringence measurements were performed using a home-built optical path, as described in the literature [22]. The lamp, the monochromator and the photo-detector were purchased from the CVI instrument group and the polarizers in both the visible and the near-IR regions were purchased from GS Edmond Scientific Co. Viscoelastic coefficients were obtained based on the procedures reported by Wu and Wu [26].

3. Results and discussion

Many diazo liquid crystals have been synthesized in this laboratory and most have been found to possess broad mesogenic ranges and high birefringence [11]. Among them, the homologous series **1** and **2** were the most attractive. When 10 wt % mixtures of the liquid crystals in E7 were measured, series **1** had the highest birefringence and series **2** the highest dielectric anisotropy compared with other series of liquid crystals [21]. The phase transition temperatures of these compounds are moderate (table 1).

Since the melting points of both series of compounds are above room temperature, we used them as solutes in room temperature LC mixtures to study the dielectric, elastic, optic, and switching properties. Because the length of the alkyl chain is not expected to affect these properties substantially, we chose the compound with the lowest ΔH_{fus} in each series ($n=5$ for **1** and $n=6$ for **2**) for the measurements. This is because fusion enthalpy is of the same importance as melting point in forming eutectic mixtures [27]. The LC mixture E7 has a large $\Delta\varepsilon$, and the mixture PTTP-24/36 has a large Δn; they were therefore used as LC solvents in our study. The 20 wt % solution of **1** in PTTP-24/36 was waxy, and no measurements were made.

The dielectric, elastic, optic, and switching properties of the mixtures studied are listed in table 2. The data show that the push–pull compounds cause increases in $\varepsilon_{\|}$, $\varepsilon_{\perp}$ and $\Delta\varepsilon$, and decrease in K_{11}, K_{33}, and K_{33}/K_{11}. Because of the decrease in K_{11} and increase in $\Delta\varepsilon$, the threshold voltage became smaller when the push–pull compounds were added to the LC solvent. Using the equation [18, 22]

$$V_{\mathrm{th}}=\pi(K_{11}/\Delta\varepsilon)^{1/2} \tag{1}$$

the calculated values of V_{th} for the five entries in table 2 are 1.18, 2.48, 1.12, 1.02 and 1.49 V, respectively. They agree reasonably well with the experimental data, differing only by a factor of 1.3 for all values.

The largest changes in the properties listed in table 2 were those for **2** dissolved in PTTP-24/36. This LC solvent has a large birefringence and low viscosity, but very small $\Delta\varepsilon$ (0.87) because of its non-polar structure [18, 21, 22]. Therefore, it has a high threshold voltage. With 20 wt % of **2**, the dielectric anisotropy has improved to 9.05, and the elastic ratio K_{33}/K_{11} has decreased from 23.5 to 1.16. As a result, the threshold voltage has decreased from 3.27 to 1.96 V.

Table 1. Phase transition temperatures (°C) and melting enthalpies (kJ mol^{-1}) of liquid crystals of series **1** and **2**. *n* stands for the carbon atom numbers in the terminal chains.

	Series **1**								Series **2**							
n	Cr	→	SmA	→	N	→	I	ΔH_{fus}	Cr	→	SmA	→	N	→	I	ΔH_{fus}
5		—		69.9		160.6		21.7		—		115.2		175.2		24.3
6		—		75.4		150.6		25.6		101.9		133.0		170.4		18.3
7		—		88.8		152.1		36.7		100.2		153.1		175.9		39.6
8		76.0		138.0		150.0		30.0		100.2		164.8		175.4		28.6

Table 2. The dielectric, elastic, and switching properties of E7, PTTP-24/36, and solutions with 20 wt % of **1** ($n=5$) and **2** ($n=6$) in these LC mixtures. In the second column, d is the width of the cell. In the last column, the rise time is defined by the change of transmittance from 10% to 90%; a driving voltage of 8.0 V was used in our experiments.

Sample	$\frac{d}{10^{-6}\,\mathrm{m}}$	$\frac{V_{th}}{\mathrm{V}}$	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$	$\frac{K_{11}}{10^{-11}\,\mathrm{N}}$	$\frac{K_{33}}{10^{-11}\,\mathrm{N}}$	K_{33}/K_{11}	$\frac{\gamma_1/K_{11}}{10^{9}\,\mathrm{m}^{-2}\,\mathrm{s}}$	$\frac{\text{rise time}}{10^{-3}\,\mathrm{s}}$
E7	4.25	1.55	18.95	5.21	13.74	1.71	2.42	1.41	23.6	15
PTTP-24/36	3.69	3.27	3.25	2.38	0.87	0.479	11.2	23.5	23.6	500
1 in E7	4.13	1.47	20.58	5.90	14.67	1.64	1.77	1.08	36.3	15
2 in E7	3.77	1.35	22.81	6.40	16.41	1.54	1.64	1.06	29.9	14
2 in PTTP-24/36	4.33	1.96	12.41	3.36	9.05	1.80	2.08	1.16	16.2	20

The viscoelastic coefficient determines the decay time of the electro-optic response. Mixtures of compounds **1** and **2** with E7 have slightly higher γ_1/K_{11} values than that of E7. However, the mixture of **2** in PTTP-24/36 has smaller γ_1/K_{11} than PTTP-24/36, because the increase of rotational viscosity γ_1 is offset by the increase of splay elastic constant K_{11} (table 2). Since the K_{33}/K_{11} ratio of PTTP-24/36 is very high (23.5) and its $\Delta\varepsilon$ is small, the rise time for a PTTP-24/36 cell is very long (~500 ms). Therefore, although its viscoelastic coefficient is the same as E7, PTTP-24/36 by itself is unsuitable for practical applications. On the other hand, with **2** as a dopant, the rise time decreases by a factor of 25 at the same driving voltage. Although the rise time is dependent on cell parameters, this result shows that **2** provides a good dopant for improving the properties of LC mixtures.

The principle concern of this study is the birefringence of the liquid crystal mixture, especially in the infrared region. Birefringence is a function of temperature and wavelength [18, 28]. The birefringence of the mixtures was measured at room temperature at different wavelengths ranging from 600 to 1100 nm, and the results are presented in the figure. The gradual decrease of birefringence with increase in wavelength can be described by using equation [28]

$$\Delta n(\lambda, T) = G(T)\frac{\lambda^2(\lambda^{*2})}{\lambda^2 - \lambda^{*2}} \tag{2}$$

where $G(T)$ is a function which includes the effect of temperature, and λ^* is the mean resonance wavelength. Both $G(T)$ and λ^* can be obtained by fitting the Δn data as a function of λ to equation (2). The best fitting curves are also shown in the plots. The values of $G(T)$ are 2.03×10^{-6}, 2.15×10^{-6}, and $3.30\times10^{-6}\,\mathrm{nm}^{-2}$, respectively, for the mixtures **2** in E7, **1** in E7, and **2** in PTTP-24/36; the corresponding values of λ^* are 318, 297, and 300 nm at room temperature.

For $\lambda \gg \lambda^*$, equation (2) can be simplified to $\Delta n(\infty) = G(\lambda^*)^2$. This is the extrapolated birefringence value in the far infrared or even microwave region. For commercial liquid crystal mixtures, the values of $\Delta n(\infty)$ are 0.191 for E7, 0.123 for ZLI-1132, and 0.179 for NP-5 [27]. The $\Delta n(\infty)$ values for 20 wt % solutions of our compounds are: 0.205 for **1** in E7, 0.189 for **2** in E7, and 0.297 for **2** in PTTP-24/36.

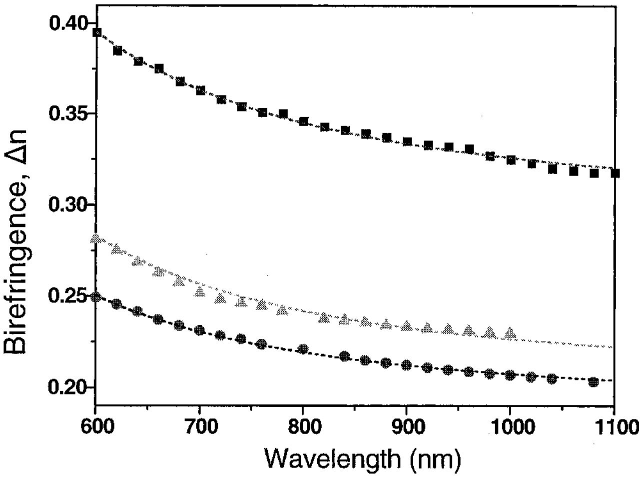

Figure 1. Wavelength dependence of birefringence of mixtures of 20 wt % **1** ($n=5$) in E7 (triangles), 20 wt % **2** ($n=6$) in PTTP-24/36 (squares) and 20 wt % **2** ($n=6$) in E7 (circles). The best fitting curves are presented as dashed lines.

In conclusion, three room temperature liquid crystal mixtures have been formulated by dissolving two new diazo liquid crystals in E7 and PTTP-24/36, and their physical properties have been measured. These mixtures have larger dielectric anisotropy and better elastic properties than the host liquid crystal mixtures. When compound **2** ($n=6$) is dissolved in PTTP-24/36, the dielectric anisotropy of the mixture improves substantially and the birefringence of the mixture stays high. The values of $\Delta n(\infty)$ for this mixture is 0.297, which is substantially larger than those for commercial liquid crystal mixtures in the visible range, and is comparable to or better than other compounds designed to have large IR birefringence [6–15]. Because its dielectric and switching properties are also quite good (table 2), this mixture is a good candidate for LC devices operating in the near IR region. Compounds with triple bonds or diazo linkage in the structures are known to be light sensitive, especially to UV irradiation. However, when the application is in the infrared region, the UV instability of the material is of less concern. Work continues on the synthesis and testing of compounds with further improved properties.

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