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To cite this article: Sebastian Gauza *et al* 2003 *Jpn. J. Appl. Phys.* **42** 3463

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High Birefringence Isothiocyanato Tolane Liquid Crystals

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(Received October 7, 2002; accepted for publication January 20, 2003)

The phase transition temperatures, birefringence and visco-elastic coefficient of several high birefringence isothiocyanato tolane compounds were evaluated. The polarizability of these compounds was calculated by the Austin Model 1 (AM1) and Modified Neglect of Diatomic Overlap (MNDO) methods. Using these compounds, we have formulated a eutectic mixture exhibiting a wide nematic range and high figure of merit. [DOI: 10.1143/JJAP.42.3463]

KEYWORDS: High birefringence, isothiocyanato tolanes, liquid crystals, polarizability

1. Introduction

High birefringence (Δn), low viscosity, small absorption and good stability polar liquid crystals are essential for both display and optical communication applications.¹⁾ For a cholesteric liquid crystal display (Ch-LCD), the reflection bandwidth ($\Delta\lambda$) is linearly proportional to the LC birefringence and pitch length (p) as: $\Delta\lambda = p\Delta n$.²⁾ In the visible spectral region, the pitch length is around 350 nm. Thus, if $\Delta n = 0.6$, then $\Delta\lambda \sim 210$ nm which would resemble a normally white Ch-LCD. For a Polymer Dispersed Liquid Crystals (PDLC)³⁾ or holographic PDLC,⁴⁾ high Δn enhances the light scattering efficiency and then improves the display contrast ratio. For fiber-optic light switches ($\lambda = 1.55 \mu\text{m}$) using optical phased arrays,⁵⁾ the required phase change ($\delta = 2\pi d\Delta n/\lambda$) is 2π . If we want to retain the cell gap $d \leq 4 \mu\text{m}$ for achieving fast response time, then the required Δn should be ~ 0.4 at $\lambda = 1.55 \mu\text{m}$ which implies to a $\Delta n \sim 0.5$ in the visible region.

To characterize the performance of liquid crystal materials, a figure-of-merit (*FoM*) which takes birefringence and response time into account has been defined as:⁶⁾

$$FoM = K_{11}\Delta n^2/\gamma_1 \quad (1)$$

In eq. (1), K_{11} is the splay elastic constant, Δn is the birefringence, γ_1 is the rotational viscosity. All of these parameters are temperature dependent. The birefringence of liquid crystals is mainly determined by the π -electron conjugation, differential oscillator strength, molecular shape and order parameter.⁷⁾ The rotational viscosity is dependent on the activation energy, molecular moment of inertia (including molecular shape and mass) and temperature. Thus, a linearly conjugated liquid crystal should exhibit a large optical anisotropy while retaining a relatively low rotational viscosity.

High melting temperature, increased viscosity and degraded photo and thermal stability are the major concerns for high Δn LCs. Eutectic mixture is a common approach for lowering the melting point. It is common for a commercial mixture to consist of 5–10 components in order to lower the melting temperature to -40°C . Elevated temperature operation is an efficient way for reducing viscosity. For every 10°C temperature increase, viscosity is decreased by $\sim 2\times$. To prevent LC material from interacting with moistures, a LC cell is hermetically sealed. An incoherent UV light is used to cure the glue lines before injecting LC mixture and

then plug the hole after vacuum filling the LC device. Thus, the LC material has to withstand UV exposure to certain extent, say $I \sim 100 \text{ mW/cm}^2$ for few minutes.

In this paper, we use the guest–host method to extrapolate the birefringence and visco-elastic coefficient of several isothiocyanato tolane compounds. Through this screening process, we have identified the LC compounds possessing the most promising *FoM*. Using these compounds, we have formulated a eutectic mixture with a relatively wide nematic range and high *FoM*.

2. Experimental

During experiments, we first measured the phase transition temperatures of the LC compounds. Since some high birefringence compounds are solid at room temperature, we mixed 10 wt% of the compounds in an LC host ZLI-1565 and extrapolated their birefringence and visco-elastic coefficient at $T \sim 23^\circ\text{C}$.

2.1 Thermal analyses

All the thermal analyses were performed using a high sensitivity differential scanning calorimeter (DSC, TA Instrument Model Q-100). Transition temperatures were measured using small samples ($\sim 1.5 \text{ mg}$) at 2°C/min scanning rate. The measured melting (T_{mp}) and clearing (T_c) temperatures of the compounds studied are listed in Table I for comparison.

2.2 Electro-optic measurements

In experiment, we mixed 10% of the high birefringence compounds (Table I) to the host ZLI-1565 nematic mixture and evaluated their birefringence and visco-elastic coefficient. The birefringence of such guest–host system can be approximated according to:

$$(\Delta n)_{\text{gh}} = x(\Delta n)_{\text{g}} + (1 - x)(\Delta n)_{\text{h}} \quad (2)$$

In eq. (2), the subscripts g, h, and gh denote guest, host and guest–host cells, respectively, and x is the concentration (in wt%) of the guest compound. By comparing the measured results for the guest–host mixtures to those of the host mixture, the birefringence of the guest compounds was extrapolated. Similarly, the figure-of-merit of each compound studied was extrapolated from the guest–host mixture.

For the electro-optic measurements, we prepared homogeneous cells with cell gap $d \sim 8 \mu\text{m}$. Figure 1 shows the schematic diagrams of the experimental setup. A HeNe laser

Table I. The phase transitions temperatures ($^{\circ}\text{C}$), extrapolated birefringence, visco-elastic coefficient, and FoM for the different rigid core LC compounds. Host LC mixture is ZLI-1565 and guest compound concentration is 10%.

No.	Compound	T_{mp}	T_c	γ_1/K_{11}	Δn	FoM
1	ZLI 1565	-20.0	85.0	8.58	0.12	1.75
2		39.0	41.3	8.81	0.17	2.77
3		76.5	248.7	10.24	0.24	1.98
4		149.2	238.8	9.64	0.30	4.65
5		110.5	192.9	9.97	0.34	5.28
6		129.0	207.0	9.62	0.35	6.35
7		137.3	265.5	10.49	0.35	6.68
8		97.1	97.1	8.24	0.38	11.02
9		125.3	125.3	9.15	0.41	9.28
10		138.6	186.0	11.00	0.45	6.32
11		112.8	126.3	10.79	0.46	6.89

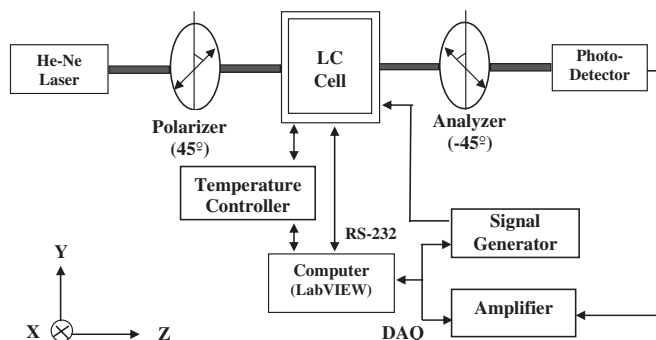


Fig. 1. The LabVIEW system for measuring the birefringence and visco-elastic coefficient of the LC mixtures. $\lambda = 632.8 \text{ nm}$.

($\lambda = 632.8 \text{ nm}$) is used as the light source. The linear polarizer is orientated at 45° with respect to the LC rubbing direction and the analyzer is crossed. The light transmittance is measured by a photodiode detector (New Focus Model 2031) and recorded digitally by a data acquisition system (DAQ, PCI 6110) using LabVIEW. The DAQ card can realize 5 MS/s, 12-bit, 4 analog input simultaneous samplings. An ac voltage with 1 kHz square waves is used to drive the LC cell whose inner sides are coated with indium-tin-oxide (ITO) electrodes. On top of the ITO, the substrate is covered with a thin polyimide alignment film. The buffing induced pretilt angle is about 3° . The cell is held in an oven

(INTEC STC-200D) with a temperature stability of 0.2°C . The extrapolated γ_1/K_{11} results at $T = 23^{\circ}\text{C}$ are listed in Table I.

2.3 Polarizability calculations

The polarizability of the compounds studied was calculated using HyperChem molecular modeling software with two semi-empirical AM1 and MNDO methods. The polarizability anisotropy was calculated according to:

$$\Delta\alpha = \alpha_x - (\alpha_y + \alpha_z)/2 \quad (3)$$

In eq. (3), α_x is the polarizability along the principal molecular axis, and α_y and α_z are the polarizabilities along the short molecular axes.⁸⁾

3. Results and Discussions

All the isothiocyanato compounds that were mixed in guest-host mixtures had ethylo- or ethyloxy-terminal chain. The phase transition temperatures, extrapolated birefringence, visco-elastic and FoM are compared in Table I.

3.1 Structural effects

To study the molecular structure effect on the physical properties, we have selected several compounds with different rigid core structures for comparison. All the compounds studied exhibit high melting temperatures. Only three compounds (2, 3 and 8) from our list have T_{mp} below 100°C . Compounds 8 and 9 do not exhibit an enantiotropic nematic phase. The compounds consisting of a cyclohexane ring (one or two rings) have clearing point exceeding 200°C (except compound 2 and 5).

The compounds 2–5 do not have multiple bonds between rings in the rigid core part of the molecules. Thus, the extrapolated birefringence is much smaller than that for compounds 6–11. It starts from 0.17 for the cyclohexyl-benzene core compound, to 0.30 for the compound with cyclohexyl-biphenyl core. The cyclohexane ring does not have π -electrons to enhance birefringence. Instead, it increases the rotational viscosity due to the increased moment of inertia. Therefore, the FoM of the cyclohexane compounds is not very impressive. However, the cyclohexane compounds are crucial for enhancing the clearing temperature of the mixture.

The tolane compounds (6–11) have a triple bond in the rigid core. The triple bond is an effective π -electron acceptor. In addition, its contribution to viscosity is not so significant. Thus, the rigid tolane core is favorable for achieving high figure-of-merit.^{9–11)} In the mean time, the NCS polar group extends the electron conjugation while retaining a relatively low viscosity and large dipole moment. The major challenges of the NCS tolanes are twofold: 1) they often exhibit smectic phase, and 2) the synthetic chemistry is harder. As shown in Table I, several compounds we studied exhibit an enantiotropic nematic phase. Especially the cyclohexane tolanes (6 and 7), their nematic range is quite wide.

From the comparison of compounds (4 and 5) with (6 and 7), we observe that the tolane compounds have a higher birefringence than the biphenyls while retaining a similar visco-elastic coefficient. As a result, the NCS tolanes have a larger FoM . A key factor contributing to the visco-elastic

coefficient is the linearity of the molecules. The cyclohexane ring usually lies in the plane perpendicular to the principal molecular axis. Therefore, the corresponding molecules without cyclohexane ring (8 and 9) have much lower viscoelastic coefficient and definitely higher birefringence. The alkilo and alkoxy NCS tolans exhibit the highest *FoM* among the compounds we investigated. The oxygen atom in the alkoxy chain of the compound 9 elongates the π -electron conjugation but also increasing the viscoelastic coefficient. Consequently, its extrapolated *FoM* is very high but lower than for alkilo NCS tolane (8).

Compounds 10 and 11 have a much different structure in the rigid core. The introduction of the naphthalene rings prominently increases the viscosity. The sulphur atom in the sulfalkilo chain in compound 11 increases the birefringence more effectively than the oxygen atom in alkoxy chain, although its viscosity is similar. Compound 11 has a higher *FoM* than compound 10. Overall speaking, its *FoM* is lower than that of simple tolane (8 and 9).

3.2 Material stability

Chemical, photo, and thermal stabilities are crucial for practical applications. All the 11 compounds we studied are chemically and thermally stable. However, their ultraviolet (UV) stability depends on the molecular conjugation and structures. For example, compounds 10 and 11 have longer conjugation than that of the rest compounds. As a result, their UV stability is worse. Detailed UV stability of these compounds has been investigated and results published.¹²⁾ Generally speaking, high birefringence LC compounds are aimed for near infrared applications (*e.g.*, telecom and laser beam steering at $\lambda = 1.55 \mu\text{m}$) where photostability is not a concern.

3.3 Polarizability

We also calculated the polarizability for all the compounds listed in Table I. Results are listed in Table II. The $\Delta\alpha$ was calculated using HyperChem v.7.0 software (AM1 and also MNDO method were used) for the isolated

Table II. The calculated polarizability of compounds 4, 7 and 8.

No. of the compound	$\Delta\alpha$	α	Components of the polarizability			
			X	Y	Z	
4	21.85	245.56	X	215.8	81.9	93.2
			Y	81.9	260.8	107.0
			Z	93.2	107.0	260.1
7	93.38	296.89	X	358.9	113.0	159.9
			Y	113.0	172.8	125.2
			Z	159.9	125.2	359.2
8	340.275	246.78	X	473.6	122.8	0.0
			Y	122.8	218.4	0.0
			Z	0.0	0.0	48.3

Table III. The calculated polarizability of compounds 10 and 11.

No. of the compound	$\Delta\alpha$	α	Components of the polarizability			
			X	Y	Z	
8	33.82	246.78	X	473.63	122.81	0
			Y	122.78	218.39	0
			Z	0	0	48.32
9	34.46	258.89	X	478.01	150.46	0
			Y	150.45	249.62	0
			Z	0	0	49.03
11	44.09	330.36	X	568.76	206.24	0
			Y	206.21	366.31	0
			Z	0	0	56.01

molecules. It is known that the calculated polarizability by using the AM1 method is useful for predicting the birefringence.¹³⁾ It is easy to see if we compare the compounds in the following way 4–7–8 (Table II). For the compounds with the highest Δn : 8, 9, 11 also we obtained the highest polarizability values along the long molecular axis (Table III).

4. Eutectic Mixture

Eutectic mixture is a useful method for lowering the melting temperature.¹⁴⁾ We have developed an in-house computer program for calculating the compositions of eutectic mixtures based on the Schröder–Van Laar equation.^{15,16)} Using some of the NCS tolane structures listed in Table I, we have formulated an eutectic mixture, designated as UCF-2, whose nematic range is from 10.3°C to 141°C. The measured birefringence of UCF-2 is $\Delta n = 0.45$ at $\lambda = 633 \text{ nm}$ and $T = 23^\circ\text{C}$.

Figure 2 plots the temperature-dependent figure of merit of UCF-2. From eq. (1), the *FoM* is defined as $K_{11}\Delta n^2/\gamma_1$ and its unit is $\mu\text{m}^2/\text{s}$. We use the following equation to fit the experimental data:⁶⁾

$$K_{11}\Delta n^2/\gamma_1 \sim \Delta n_o^2(1 - T/T_c)^{3\beta} \exp(-E/kT) \quad (4)$$

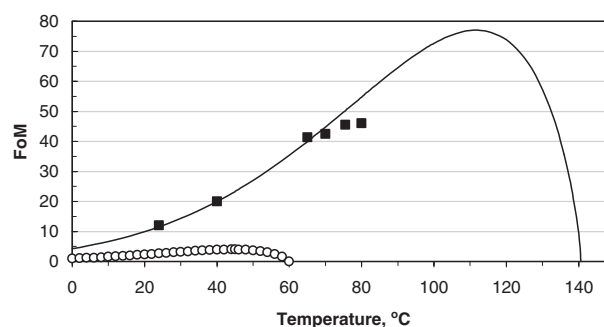


Fig. 2. Temperature dependent figure-of-merit of UCF-2 (squares) and E7 (circles). Solid lines are fittings to the experimental data of UCF-2 using $E = 340 \text{ meV}$, $\beta = 0.25$, and $T_c = 141^\circ\text{C}$. $\lambda = 633 \text{ nm}$.

where Δn_0 is the birefringence in completely ordered state ($S = 1$), E is activation energy of the liquid crystal and k is the Boltzmann constant. The value of the β parameter is around 0.25 and insensitive to liquid crystal structures.¹⁷⁾ As shown in Fig. 2, FoM increases as the operating temperature increases and then decreases rapidly as the temperature approaches the clearing point (T_c). Also included in Fig. 2 for comparison is a commercial E7 mixture. At 70°C, the UCF-2 mixture has 10X higher FoM than that of E7 at 48°C.

5. Conclusions

The measurements of the birefringence and visco-elastic coefficient by the electro-optic method for the alkyl isothiocyanato compounds with a different structure of the rigid core have been described. The compounds exhibited enantiotropic nematic phase and relatively high increases birefringence. The visco-elastic coefficient of these compounds increases when the rigid core contains one or more cyclohexane group as well as other rings than phenol. We observed that FoM is affected by the viscosity for high birefringence naphthalene compounds. But in this case high birefringence still keeps these compounds in the middle of the FoM range. The calculated polarizability is following the trend line of the birefringence values which were measured by electro-optic method.

Acknowledgment

We are indebted to the financial support from DARPA STAB program channeled through Raytheon Lexington

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