

## 16.3: Conjugation Effects on High Birefringence Liquid Crystals

**Carmen Otilia Catanescu, Soon Nam Lee and L. C. Chien**  
Liquid Crystal Institute, Kent State University, Kent, OH 44242, USA

### Abstract

We report several difluoro isothiocyanato tolane-based liquid crystal (LC) singles having a high optical birefringence. Several eutectic mixtures are formulated using these LC singles exhibiting a wide nematic phase range and high birefringence. We will report the physical properties of and photochemical stability of these new eutectic mixtures.

### 1. Introduction

Recently, there is a strong demand to develop LC materials with fast response time for liquid crystal displays (LCDs) used for large-size direct-view television display systems, because of their iridescent color, high brightness, low power consumption and light weight as well as having the high optical contrast and wide viewing cone characteristics.<sup>1,2</sup> However, the state-of-the-art LC mixtures and LCD technologies still not yet satisfy the required response time for LCD-TV applications.<sup>3-5</sup> An effective way to achieve the fast response time is to reduce the cell thickness in combination with the use of high birefringence liquid crystal with low rotational viscosity. For almost all display applications, the response time is proportional to the rotational viscosity and the square of the cell thickness,  $d$  and inversely proportional to the elastic constant. As the product of cell thickness  $d$  and the birefringence  $\Delta n$  is fixed for a certain set of cell parameters improved response time can be achieved by increasing the  $\Delta n$  value of the mixtures.

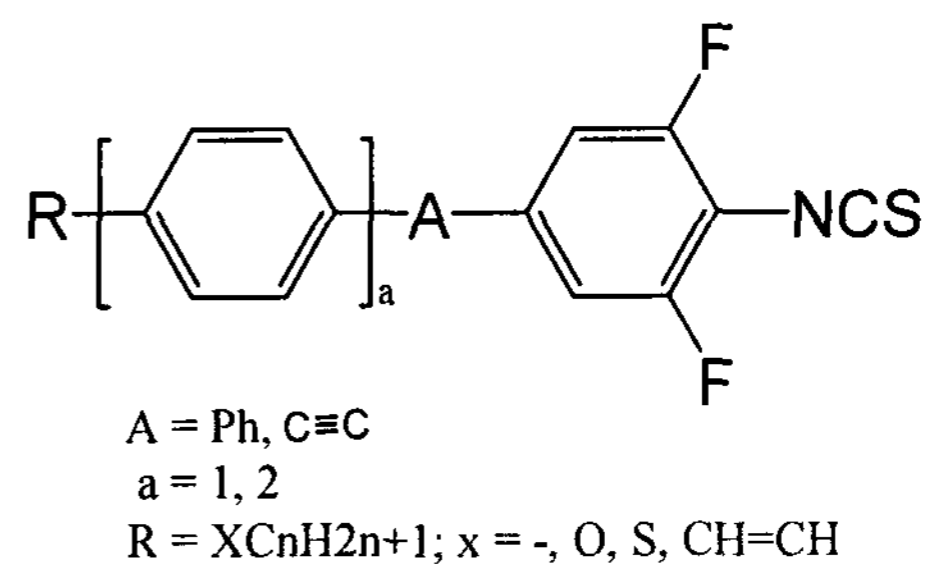
Conventional liquid crystal (LC) materials with high birefringence tend to exhibit large rotational viscosity. Extensive efforts also have been made in the development of fast-switching liquid crystals. Yet there are few reports on the optimization of high birefringence liquid crystal, especially very few reported high birefringence liquid crystals with the low viscosity. Asymmetric diphenyldiacetylene based liquid crystals having high birefringence and low rotational viscosity have been reported.<sup>6</sup> However, the diacetylene group of these compounds has environmental stability problems, such as, for example, susceptibility to heat and light, which make the compounds become yellow and degrade their physical properties. Therefore, there is a need for alternative LC materials with high birefringence, low rotational viscosity and fast response time.

In this paper we describe the synthesis of difluoro

isothiocyanato tolane LC singles and optical properties of high birefringence materials containing a terminally isothiocyanato group and fluorine atoms. The introduction of fluorine atoms can lead to a high dielectric anisotropy  $\Delta\epsilon$ , while an appropriate selection of their position can lower the viscosity, reduce melting points, depress the temperature of smectic phase formation and improve solubility and stability. High birefringence ( $\Delta n$ ), another important physical property, can be achieved by introducing permanent dipoles at one end of the rigid core, such as isothiocyanato group, but usually high  $\Delta n$  is closely associated with high viscosity. To achieve fast switching times a low viscosity is required, and in general shorter molecules are less viscous than longer molecules. We systematically vary and increase the length of the rigid core which contributes greatly in electronic conjugation and thus, gives large optical anisotropy.

### 2. Experimental

In the search for new materials with improved properties several tolanes having fluorine atoms and NCS terminal group were synthesized based on the representative molecular structure listed below.



The terminal group of the molecules is selected from saturated alkyl, alkyl chain linked with the rigid core through oxygen or sulfur atom, or an olefin to enhance the conjugation effect. The phase transition temperatures of the compounds and mixtures were determined by using a differential scanning calorimeter and 2°C/min scanning rate. The dielectric anisotropies ( $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$ ) of compounds were measured by the capacitance method at a frequency of 1 kHz ( $\lambda = 633 \text{ nm}$ ) using a computer-controlled APT III instrument (manufactured by Displaytech). The measurements were carried out at a fixed temperature of  $T = 295.9 \text{ K}$ , 10% of the compound being dissolved in a

Merck LC mixture (ZLI-3086 with  $\Delta\epsilon\sim 0$ , or ZLI-5100-100 with  $\Delta\epsilon=11.5$ ) as a host. The birefringence  $\Delta n=n_e-n_o$  of the same compound was measured using a Abbe refractometer equipped with a sodium lamp ( $\lambda=589\text{ nm}$ ) at  $T=295.9\text{ K}$  using 10% of a LC single in a low birefringence LC host (ZLI-14600-100 or ZLI-5100-100 with  $\Delta n=0.1716$ ). In both cases, the  $\Delta\epsilon$  and  $\Delta n$  values were extrapolated to 100% concentration. The UV stability of the NCS based tolans (15% of compound in a LC host) in the test cells was illuminated using a metal halide lamp,  $8\text{ mW/cm}^2$  for 600 sec ( $4.8\text{ J/cm}^2$  dosage).

### 3. Results and Discussion

#### 3.1. Mesomorphic and physical properties of LC singles

Several series of nematic LC materials tolane-based having the difluoro thioisocyanate polar group were prepared with the aim to exhibit a superior physical properties such as, high optical birefringence, low viscosity, and large dielectric anisotropy. The phase transition temperatures and physical properties of representative LCs of different series were listed in Table 1. The birefringence and dielectric anisotropy of compounds was measured using the guest-host method to extrapolate its  $\Delta n$  value, 10% of the compound being dissolved in LC host. Compound 1 exhibit a large optical birefringence due to the presence of a tolane rigid core and a push-pull alkoxy, NCS and difluoro terminal groups. The exchange of oxygen atom with sulfur one led to a decrease in transition temperatures of all homologues, in some case with even  $22^\circ\text{C}$  (compound 2). This effect appears due to the change in the L/D ratio of the compounds containing sulfur atom because of its bigger volume compared with the oxygen atom. Yet the mecapto terminal group enhances both the optical birefringence and dielectric anisotropy. Replacing the triple bond of compound 3 with a phenylene ring leads to an increase in transition temperatures as well as the optical birefringence. Extending the rigid core with an additional phenylene, the biphenyltolane, compound 4 exhibits a wider nematic range and a larger optical birefringence because of the increase in molecular polarizability, compared with those of compound 3. By introducing a short olefin terminal group to the tolane-based LC single, aimed to have a lower viscosity, we obtained the compound 5 with a higher optical birefringence because of the higher electronic conjugation from the extended rigid core. The dielectric anisotropies of these nematic singles vary from 18 to 21, depending on the nature of their molecular structures.

Table 1. Transition temperatures and physical properties of LC singles.

No.	n	X	A	Phase Transition ( $^\circ\text{C}$ )	Physical property $\Delta n$
1	4	O	T	K 61.6 I (N 59.7)	$\Delta n=0.33$
2	4	S	T	K 58.4 I	$\Delta n=0.37$
3	5	O	Ph	K 157.5 N 219.3 I	$\Delta n=0.39$
4	3	-	PT	K 101 N 222.5 I	$\Delta n=0.42$
5	1	D	T	K 111.8 N 130 I	$\Delta n=0.53$

O: oxygen; S: thio; D: C=C; T: c-triple bond-C; Ph: phenyl; PT: phenyl-c-triple bond-C

#### 3.2 Mesomorphic and physical properties of LC mixtures

These high optical birefringence nematic singles are enviable for forming LC mixtures because of their widely scattered nematic temperature ranges. Their nematic behavior was predicted using a computer program based on the Schroder van Laar equation and compared with DSC thermograms of the mixtures as presented in Table 2. All mixtures are enantiotropic liquid crystals; the last three mixtures exhibit the sub-ambient crystallization temperature. The nematic mesophase ranges ( $\Delta T_{C-I}$ ) for the mixtures are quite large ranging from  $30^\circ\text{C}$  to  $75^\circ\text{C}$ . The observed nematic ranges of the eutectic mixtures fromed from the nematic singles are in general in agreement with those of the predict ones. The eutectic mixtures studied here exhibit very similar optical birefringence and dielectric anisotropy.

Table 2. Transition temperatures and physical properties of LC eutectic mixtures (EM).

No.	$T_{cn}/^\circ\text{C}$ The.	$T_{cn}/^\circ\text{C}$ Exp.	$T_{ni}/^\circ\text{C}$ The.	$T_{ni}/^\circ\text{C}$ Exp.	$\Delta n$
EM <sub>1</sub>	39.2	39.7	106.3	104.4	0.35
EM <sub>2</sub>	35.6	34.5	110.8	109.2	0.36
EM <sub>3</sub>	23.4	27.8	85.5	66.1	0.36
EM <sub>4</sub>	14.0	13.2	83.1	68.9	0.35
EM <sub>5</sub>	19.8	17.8	49.4	32.5	0.36
EM <sub>6</sub>	12.1	8.9	87.3	71.8	0.37

$T_{cn}$ : crystal-nematic transition temp.;  $T_{ni}$ : nematic-isotropic transition temp.; The: theoretic; Exp.: experimental.

#### 4. Conclusion

We developed several difluoro isocyanato tolane LC single compounds that exhibit a high birefringence. Using the LC singles we formulated several eutectic mixtures that exhibit a wide nematic phase ranging from 30 to 75°C. Other physical properties and the photochemical stability of these LC singles and mixtures will also be evaluated and presented.

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