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Physical Properties of Polar Bis-Tolane Liquid Crystals

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Several cyano and fluoro bis-tolane liquid crystals were synthesized and their physical properties evaluated. Some of these highly conjugated liquid crystals possess birefringence larger than 0.5 in the visible region. Adding 10% of a binary bis-tolane mixture to a cholesteric display enhances the brightness by more than 20%.

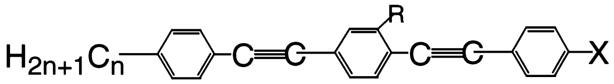
KEYWORDS: Polar bis-tolane liquid crystal, high birefringence, cholesteric display

1. Introduction

Bis-tolane liquid crystals (LCs)[1–7] possess birefringence (Δn) greater than 0.4 in the visible spectral region and are particularly attractive for reflective displays employing cholesterics[8] and polymer-dispersed LC.[9] However, most bis-tolanes reported so far are non-polar and their dielectric anisotropy is relatively small ($\Delta\varepsilon \sim 0.8$). As a result, the threshold voltage is too high ($V_{\mathrm{th}} \sim 4V_{\mathrm{rms}}$) for most display applications. There is an urgent need to develop polar compounds for reducing the operation voltage.

In this paper, we report five new series of polar bis-tolane liquid crystals. Both cyano and fluoro polar groups were investigated. The cyano polar compounds exhibit not only large $\Delta\varepsilon$, but also very high birefringence ($\Delta n > 0.5$) in the visible spectral region. Thus, it is desirable for high brightness cholesteric displays.

More than 20 cyano and fluoro bis-tolanes with molecular structures shown below were investigated:



The polar compounds we reported here have X=F or CN and R=methyl (CH_3), ethyl (C_2H_5) and fluoro (F) group. For simplicity, these lateral methyl and ethyl substituted fluoro and cyano bis- tolanes are abbreviated as [PTP(3-Me)TP-nF, PTP(3-Me)TP-nCN] and [PTP(3-Et)TP-nF, PTP(3-Et)TP-nCN], respectively. Here P stands for the phenyl ring, T for the carbon-carbon triple bond and P(3-Me) and P(3-Et) for the middle phenyl ring with a methyl or ethyl group substituted at the 3-position. For the lateral fluoro bis-tolanes, we have only studied X=F. These compounds are abbreviated as PTP(F)TP-nF. The synthesis procedures are similar to those of non-polar bis-tolanes.[10]

2. Phase Transitions

The phase transition temperatures and heat fusion enthalpy (ΔH) of the methyl-substituted fluoro and cyano bis-tolanes we synthesized are listed in Table I. Among the fluorine series, PTP(3-Me)TP-5F has the lowest melting point ($T_{\mathrm{m}} = 69.4$°C) and smallest ΔH value. Thus, it is most favorable for forming eutectic mixtures. From Schröder-van Laar equation,[11,12] a compound with low T_{m} and small ΔH would lead to a low melting temperature of the eutectic mixture. On the cyano series, the $n = 2$ and 3 homologues exhibit no nematic phase. In addition, their ΔH values are quite high which implies to a poor solubility in a mixture. Thus, the usefulness of these two homologues is limited. The $n = 5$ and 6 homologues have a reasonably wide nematic range although their melting point is still high. Owing to increased molecular conjugation, the polar compounds often have a higher melting point than their non-polar counterparts.

Table I. Phase transition temperatures (in °C) and heat fusion enthalpy (ΔH, in kcal/mol) of the methyl-substituted fluoro and cyano bis-tolane liquid crystals. The dashed lines indicate that these two compounds have no LC phase. Also included here for comparison are the phase behaviors of PTP(3-Me)TP-Fn, the fluoro and alkyl positions are exchanged.

PTP(3-Me)TP-	T_{m}	T_{c}	ΔH
2F	103.7	183.2	5.73
F2	122.2	191.5	5.50
3F	101.7	191.2	7.37
F3	130.2	196.4	5.74
5F	69.4	162.8	4.97
F5	88.1	174.0	5.78
6F	73.5	150.5	8.40
F6	82.7	157.4	8.14
2CN	142.9	—	7.64
3CN	125.8	—	13.2
5CN	114.0	203.0	5.46
6CN	100.7	215.2	7.10

Since the lateral methyl is in the 3-position, the above-mentioned molecular structure is not symmetric. Switching the axial fluorine and alkyl positions could make a noticeable difference in the phase transition temperature. Several methyl-substituted fluoro bis-tolanes with exchanged alkyl and fluorine positions, abbreviated as PTP(3-Me)TP-Fn, have been reported previously.[5] Some results are included in Table I for comparison. From Table I, the melting point of PTP(3-Me)TP-nF is about 20°C lower than the corresponding PTP(3-Me)TP-Fn. The electro-optical properties of these two isomers should be very similar. Thus, PTP(3-Me)TP-nF is preferred for practical applications from the viewpoint of lower melting temperature.

Table II lists the phase transition temperatures and heat fusion enthalpy of the ethyl-substituted fluoro and cyano bis-tolane compounds. Their melting and clearing points are both lower than the corresponding methyl derivatives. The molecular width of PTP(3-Et)TP homologues is larger than their methyl counterparts. Thus, their inter-molecular association is weaker and less thermal energy is needed to melt and clear the compounds. Among the fluoro series listed in Table II, all the four homologues have melting points below 70°C and modest ΔH values. For the cyano series, their melting point

Table II. Phase transition temperatures (in °C) and heat fusion enthalpy (ΔH, in kcal/mol) of the ethyl-substituted fluoro and cyano bis-tolane liquid crystals.

PTP(3-Et)TP-	T_m	T_c	ΔH
3F	65.0	112.9	5.10
4F	69.1	98.3	5.25
5F	60.9	103.2	5.20
6F	46.5	89.1	4.77
3CN	102.9	161.9	4.56
4CN	118.5	157.4	7.32
5CN	85.2	159.3	3.51
6CN	77.2	131.7	4.64

Table III. Phase transition temperatures (in °C) and heat fusion enthalpy (ΔH, in kcal/mol) of the lateral fluorine-substituted fluoro bis-tolane liquid crystals.

PTP(F)TP-	T_m	T_c	ΔH
2F	150.0	179.7	8.56
3F	154.1	185.4	8.27
4F	145.7	170.3	6.49
6F	123.2	163.6	4.84

is lowered by about 20°C as compared to the corresponding methyl homologues and the clearing point of the $n = 5$ and 6 homologues is decreased by more than 50°C. Although the ethyl substitution makes an important contribution to lower the phase transition temperatures, it also increases the viscosity dramatically, as to be discussed later.

Table III lists the phase transition temperatures and heat fusion enthalpy of the lateral fluorine-substituted fluoro bis-tolane compounds PTP(F)TP-nF. By comparison to the data listed in Table I, we find that the melting point of PTP(F)TP-nF is significantly (~50°C) higher than the corresponding methyl-substituted homologues PTP(3-Me)TP-nF. However, in comparison to the non-substituted fluoro bis-tolane,[7] the melting point of PTP(F)TP-4F is still ~25°C lower than that of PTPTP-4F. This sequence of phase transition temperature is mainly attributed to the fact that fluorine has a slightly larger size than hydrogen, but smaller than methyl.

3. Physical Properties

In addition to phase transition temperatures, birefringence (Δn), dielectric anisotropy ($\Delta\varepsilon$) and viscosity/elastic constant ratio (γ_1/K_{11}) are important for practical application. Due to the relatively high melting temperature of these polar bis-tolane compounds, it is inconvenient to characterize the physical properties of these compounds in their nematic phase. Instead, we have used the guest-host method. Four compounds with same alkyl chain length were chosen for studies: PTP(3-Me)TP-6F, PTP(3-Et)TP-6F, PTP(3-Me)TP-6CN and PTP(3-Et)TP-6CN. A Merck mixture E63 was used as host. In all the measurements, 10% of each selected compound was dissolved in E63. We measured the birefringence, dielectric anisotropy and visco-elastic coefficient of the mixture against host at room temperature ($T \sim 20$°C). Results of the guest compound under study are then extrapolated. Among the four compounds studied, the mixture containing 10% PTP(3-Me)TP-6F precipitates. Thus, its results were not obtained.

Table IV. The extrapolated results of PTP(3-Me)TP-6F, PTP(3-Et)TP-6CN and PTP(3-Me)TP-6CN. Host = E63. Δn was measured at three laser wavelengths, $\lambda = 633$, 514.5 and 488 nm. $T = 20$°C.

LC	$\Delta\varepsilon$ (1 kHz)	γ_1/K_{11} (ms/μm^2)	$\Delta n(\lambda)$ 633	515	488
E63	14.0	18	0.21	0.23	0.24
PTP(3-Et)TP-6F	8.3	73	0.33	0.37	0.41
PTP(3-Et)TP-6CN	13.0	129	0.42	0.51	0.54
PTP(3-Me)TP-6CN	15.6	62	0.44	0.53	0.57

To characterize $\Delta\varepsilon$, we measured the capacitance (C_o) of an empty cell with patterned electrodes.[13] The cell was then filled with the guest-host LC mixture. The capacitance at low and high voltage regimes lead to $\varepsilon_\perp$ and $\varepsilon_\parallel$, respectively. A HP-4274A multi-frequency LCR meter was used for such measurements. After the $(\Delta\varepsilon)_{gh}$ of the guest-host system was measured, we used the following equation $(\Delta\varepsilon)_{gh} = 0.9(\Delta\varepsilon)_h + 0.1(\Delta\varepsilon)_g$ to extrapolate the dielectric anisotropy $(\Delta\varepsilon)_g$ of the guest LC, where $(\Delta\varepsilon)_h$ is the dielectric anisotropy of the host E63.

To characterize birefringence, we have prepared a homogeneous cell with $d = 7$-μm and measured its voltage-dependent light transmittance under crossed polarizers.[13] Through this measurement, the total phase retardation ($\delta = 2\pi d\Delta n/\lambda$) of the cell is obtained. Knowing the cell gap and wavelength, the mixture's birefringence can be calculated. Three light sources were used for such measurements: an argon-ion ($\lambda = 488$ and 514.5 nm) laser and a HeNe ($\lambda = 633$ nm) laser. Similar extrapolation procedures were used to obtain the results of the compounds studied.

To characterize γ_1/K_{11}, we measured the transient phase decay time[13] of the 7-μm homogeneous cell at a voltage that is not too far above the threshold. A HeNe laser was used for such measurements.

The extrapolated results are listed in Table IV. We first discuss dielectric anisotropy. The CN group has a larger dipole moment[14] than F and as expected, the two cyano bis-tolanes we studied have a larger $\Delta\varepsilon$ than the fluoro compound. Among the two cyano compounds, PTP(3-Me)TP-6CN has a slightly larger $\Delta\varepsilon$ than PTP(3-Et)TP-6CN due to its more linear structure and denser molecular package. Regarding to birefringence, bis-tolanes possess a much higher Δn than E63. As the wavelength gets shorter, the Δn becomes larger.[15] At each wavelength, the Δn increases according to the order: PTP(3-Et)TP-6F < PTP(3-Et)TP-6CN < PTP(3-Me)TP-6CN. It is known that CN is an electron acceptor and F exhibits a strong electro-negativity. That means the electron conjugation of a CN compound is longer than its fluoro counterpart.[16] Therefore, the birefringence of a cyano bis-tolane is significantly higher than the corresponding fluoro compound. The reason that PTP(3-Me)TP-6CN has a larger Δn than PTP(3-Et)TP-6CN is because the methyl compound has a slightly higher molecular packing density.

Three key factors affecting the rotational viscosity of a LC compound are activation energy, moment of inertia (including molecular shape and mass), and temperature.[17,18] The three bis-tolanes studied exhibit a much larger γ_1/K_{11} than E63 due to their larger moment of inertia. Among the two ethyl-substituted LCs studied, PTP(3-Et)TP-6CN has a much

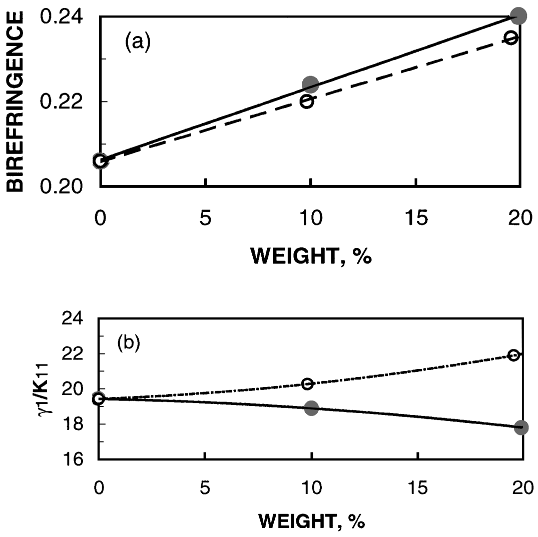


Fig. 1. Comparison of PTP(3-Me)TP-62 (filled circles) and PTP(3-Et)TP-62 (open circles) in (a) birefringence at $\lambda = 633$ nm and (b) visco-elastic coefficient (ms/μm^2). $T = 20$°C. Host: E63 mixture.

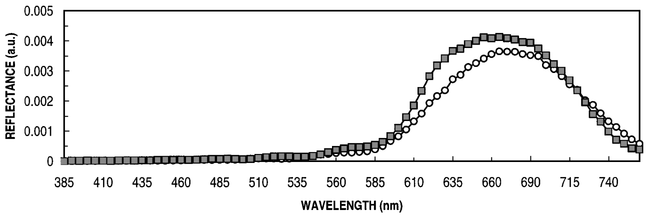


Fig. 2. Cholesteric display using ZLI-5400 alone (open circles) and ZLI-5400 + 10% binary bis-tolane mixture (15% PTP(3-Et)TP-5CN+ 85% PTP(3-Et)TP-53). Cell gap $d = 2\,\mu$m and pitch length $p = 0.35\,\mu$m.

larger γ_1/K_{11} than PTP(3-Et)TP-6F. The reasons are twofold: (1) the cyano compounds tend to form dimmers so that the inertia moment is increased, and (2) the cyano compounds generally have a larger activation energy of rotational viscosity.[17] Within the cyano family, the lateral alkyl group also makes a significant contribution to the visco-elastic coefficient. The γ_1/K_{11} of the PTP(3-Et)TP-6CN is about two times higher than PTP(3-Me)TP-6CN. Although the splay elastic constant (K_{11}) of these two LCs may be slightly different, the major difference originates from the rotational viscosity (γ_1).

To further examine the effect of lateral methyl and ethyl groups on viscosity, we have compared two non-polar bis-tolanes: PTP(3-Me)TP-62 and PTP(3-Et)TP-62 at 10 and 20% concentrations in E63 host. Both birefringence and visco-elastic coefficient were measured using a HeNe laser wavelength and $T \sim 20$°C. Results are depicted in Figs. 1(a) and 1(b), respectively. From Fig. 1(a), the extrapolated Δn for PTP(3-Me)TP-62 and PTP(3-Et)TP-62 is 0.38 and 0.35 at $\lambda = 633$ nm, respectively. And from Fig. 1(b), PTP(3-Me)TP-62 has a slightly lower γ_1/K_{11} than E63. This is consistent with the other homologue reported earlier. In contrast, PTP(3-Et)TP-62 has a higher γ_1/K_{11} than E63. Judged from birefringence and viscosity, the methyl-substituted bis-tolanes are more favorable than the ethyl for practical applications except that their melting points are higher.

4. Cholesteric Reflective Display

An important application of high birefringence LCs is reflective cholesteric display. In a cholesteric display, the reflectance spectral bandwidth ($\Delta\lambda$) is linearly proportional to the pitch length (p) and Δn of the LC employed. Thus, a high Δn LC is favorable for improving the display brightness. In addition, the use of high Δn LC could reduce the number of required helical pitches for the Bragg reflection to occur. That means the LC cell gap can be reduced. For a cholesteric display with uniform pitch length, the device operation voltage is inversely proportional to the cell gap.[19] As a result, a high Δn LC not only enhances display brightness but also reduces operation voltage.

We have formulated a binary eutectic mixture consisting of 15% PTP(3-Et)TP-5CN and 85% PTP(3-Et)TP-53. Its Δn was measured to be 0.407 at $\lambda = 633$ nm and $\Delta\varepsilon \sim 2.7$ at $T \sim 20$°C. In principle, we could use this mixture directly for cholesteric display. However, the dielectric anisotropy of this binary mixture is too small so that its driving voltage would be too high for practical application. In a preliminary experiment, we mixed 10% of this binary mixture with Merck ZLI-5400. A 2-μm cholesteric cell was prepared with pitch length of ~0.35 μm. Its peak reflection is designed to be at 675 nm.

The voltage-dependent reflectance of the cholesteric cell is depicted in Fig. 2. The open circles represent the measured reflectance of ZLI-5400 cell alone and squares are the data of the LC containing 10% binary bis-tolane mixture. From Fig. 2, the overall display brightness is increased by more than 20%.

High birefringence is not the only requirement for high brightness cholesteric displays. Other desirable properties of LC mixtures include wide nematic range, high $\Delta\varepsilon$, and low γ_1/K_{11}. More polar bis-tolanes with low melting temperature and low viscosity need to be developed.

5. Conclusion

We present the phase transition temperatures and physical properties of about 20 polar bis-tolane LC compounds. The lateral alkyl substitutions are found to make important contributions to melting temperature, birefringence and viscosity. Although a lateral ethyl substitution is favorable for lowering melting temperature, its negative effects on reducing birefringence and particularly boosting viscosity are undesirable. By contrast, a methyl compound exhibits an acceptable viscosity, but their melting points are higher. More methyl homologues and eutectic mixtures need to be developed before the high birefringence advantage can be fully utilized for cholesteric displays.

Acknowledgments

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