

# High birefringence and wide nematic range bis-tolane liquid crystals

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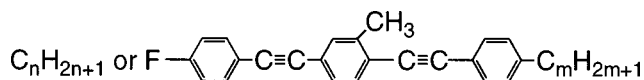
Several dialkyl and fluoro bis-tolane liquid crystals were synthesized and their physical properties evaluated. These highly conjugated liquid crystals exhibit a wide nematic range, small heat fusion enthalpy, high birefringence, and relatively low viscosity. Their excellent compatibility with commercial cyano mixtures makes these liquid crystals attractive for many electro-optic applications. © 1999 American Institute of Physics. [S0003-6951(99)02103-8]

Liquid crystals (LCs) with low melting and high clearing temperature are particularly attractive for automobile and outdoor display applications. Inside a car or at outdoor environment, temperature could vary wildly depending on the geographic locations. Generally speaking, the nematic range of a single LC substance is rather limited. Forming eutectic mixture is a common approach for lowering the melting point. From the Schroder–Van Laar equation,<sup>1,2</sup> the individual LC components possessing a low melting ( $T_{mp}$ ) and high clearing point, and small heat fusion enthalpy ( $\Delta H$ ) are better candidates for widening the nematic range of the eutectic mixture.

In addition to wide nematic range, high birefringence ( $\Delta n$ ) is also desirable for cholesteric LC displays<sup>3</sup> and optical phased arrays for laser beam steering.<sup>4</sup> For a cholesteric display using Bragg reflection,<sup>3</sup> high  $\Delta n$  widens the reflection bandwidth and improves the display brightness. For a LC-based optical phased arrays,<sup>4</sup> high  $\Delta n$  helps to shorten response time through thinner cell gap requirement. The birefringence of an LC is mainly determined by the  $\pi$ -electron conjugation, differential oscillator strength, molecular shape, and order parameter.<sup>5</sup> Thus, a more linearly conjugated LC would exhibit a larger optical anisotropy. A general problem of these highly conjugated molecules is that their melting temperature is usually very high.

Dialkyl diphenyl-diacetylene LCs<sup>6</sup> are found to possess a high  $\Delta n$ , low melting temperature, and small heat fusion enthalpy. They are excellent candidates for making eutectic mixtures, except their dielectric anisotropy is a little too small ( $\Delta\epsilon \sim 0.8$ ). To reduce operation voltage, some polar compounds need to be added. When these LCs are mixed with more than 10% cyano-biphenyls, they tend to form 1:1 complexes and limits the solubility of the polar compounds.<sup>7</sup>

Polytolane<sup>8–10</sup> is another interesting series of high birefringence LC. A major problem of polytolane is its high melting point. In this letter, we report a new series of bis-tolane LCs with wide nematic range, high  $\Delta n$ , low viscosity, and excellent compatibility with commercial cyano mixtures. More than 20 dialkyl and fluoro bis-tolanes with molecular structures shown below were synthesized.



For simplicity, these alkyl-alkyl and fluoro-alkyl compounds are abbreviated as PTP(3-Me)TP-nm and PTP(3-Me)TP-Fm, respectively; here P stands for the phenyl ring, T for the carbon–carbon triple bond, and P(3-Me) for the middle phenyl ring with a methyl group sticking out at the 3 position. The general synthesis schemes can be found in Refs. 8–10, and the detailed synthetic procedures for the described bis-tolanes will be published elsewhere.<sup>11</sup>

The phase transition temperature and heat fusion enthalpy of these bis-tolane LCs are listed in Table I. A compound (PTPTP-26) without the methyl group in the middle phenyl ring is also included for comparison. From Table I, we find several intriguing phase transition phenomena:

TABLE I. Phase transition temperatures (in °C), heat fusion enthalpy ( $\Delta H$ , in kcal/mol), and extrapolated (in E63 host) dielectric anisotropy ( $\Delta\epsilon$ ) of the dialkyl and fluoro PTP(3-Me)TP liquid crystals. Here, 26\* stands for PTPTP-26 LC; no methyl group in the middle phenyl group.

PTP(3-Me)TP-	$T_{mp}$	$T_c$	$\Delta H$	$\Delta\epsilon$
12	143.2	192.4	7.37	
13	139.1	187.4	6.64	
14	120.2	184.6	5.34	
15	111.3	185.7	5.38	
16	78.1	162.7	5.07	
21	136.5	189.6	7.12	
22	144.5	186.4	6.33	
32	115.3	190.0	5.38	
42	72.2	177.4	4.19	
52	61.6	173.5	3.54	
62	61.0	165.1	5.80	
33	123.4	200.4	5.03	
34	98.5	191.2	5.27	
35	86.2	182.8	3.61	
36	77.9	170.0	3.75	
25	97.8	179.9	4.52	
26	73.9	166.5	5.17	
26*	133.6	191.1	3.61	
63	57.3	168.7	3.28	~1
F3	130.2	196.4	5.74	
F5	88.1	174.0	5.78	~6
F6	82.7	157.4	8.14	

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- (1) These bis-tolane possess a very high clearing temperature ranging from 160 to 200 °C. Some homologues [e.g., PTP(3-Me)TP-52, 62, and 63] even exhibit a relatively low melting point ( $\sim 60$  °C) and small heat fusion enthalpy ( $< 4$  kcal/mol). Thus, these compounds are very useful for formulating eutectic mixtures with a wide nematic range.
- (2) The asymmetric compound generally shows a much lower melting point than the symmetric one. From Table I, the  $T_{mp}$  of PTP(3-Me)TP-33 is 123.4 °C. Keeping the total side-chain carbon number unchanged except breaking their symmetry leads to a much lower  $T_{mp}$ . For instance, the  $T_{mp}$  of PTP(3-Me)TP-42 is reduced to 72.2 °C. This effect was also clearly observed in the diphenyl diacetylene system as well.<sup>6</sup> However, if one side has a too short alkyl chain, such as in PTP(3-Me)TP-15, then the advantage is not obvious. Then  $T_{mp}$  of PTP(3-Me)TP-15 remains as high as 111.3 °C.
- (3) Since the methyl group is sticking out at the 3 position of the middle phenyl ring, it is more favorable to have a longer alkyl chain on the left-hand side than on the right. This is demonstrated in the [PTP(3-Me)TP-52 and -25], and [PTP(3-Me)TP-62 and -26] pairs. The  $T_{mp}$  of PTP(3-Me)TP-52 and -62 homologues is 36 and 13 °C lower than that of PTP(3-Me)TP-25, and -26 homologues, respectively.
- (4) The middle methyl group plays an important role in lowering the melting point. For example, the  $T_{mp}$  of PTPTP-26 is 133.6 °C while the  $T_{mp}$  of PTP(3-Me)TP-26 drops to 73.9 °C. This is because the methyl group slightly increases the width of the molecule and then decreases the molecular packing density. As a result, the required temperatures to melt and to clear the LC clusters are both lower. If we replace the methyl with an ethyl group, the melting point will further decrease. However, its viscosity will slightly increase.

The dialkyl bis-tolanes are nonpolar so that their dielectric anisotropy is small ( $\Delta\epsilon \sim 1$ ). A small  $\Delta\epsilon$  applies to a high operation voltage, as the Freedericksz transition threshold voltage<sup>12</sup> of a homogeneous cell is determined by the dielectric anisotropy and splay elastic constant ( $K_{11}$ ) of the LC as  $V_{th} = \pi[K_{11}/\epsilon_0\Delta\epsilon]^{1/2}$ . To lower  $V_{th}$ , one can either use fluoro compounds shown in Table I or mix the nonpolar bis-tolane compounds with commercial polar mixtures. The extrapolated  $\Delta\epsilon$  of fluoro bis-tolane is about 6. However, their melting temperature is relatively high so that their solubility in a dialkyl bis-tolane mixture is limited to  $\sim 10\%$ . For such a low concentration, its contribution to  $\Delta\epsilon$  enhancement is limited. Thus, we have selected to mix dialkyl bis-tolanes with a Merck cyano-biphenyl mixture, E63. The most impressive feature of E63 is that it does not freeze at  $-40$  °C. Its clearing temperature is  $\sim 87$  °C,  $\Delta n \sim 0.21$  at  $\lambda = 589$  nm and  $T = 22$  °C, and  $\Delta\epsilon \sim 14.6$  at  $f = 2$  kHz sine wave frequency.

In experiment, we have mixed 10%, 20%, and 30% of PTP(3-Me)TP-63 to the host E63 mixture and evaluated their clearing point, threshold voltage, visco-elastic coefficient, and birefringence. The phase transition temperatures of the mixtures were measured using a Mettler differential scanning calorimeter. Due to the high clearing point of PTP(3-Me)TP-

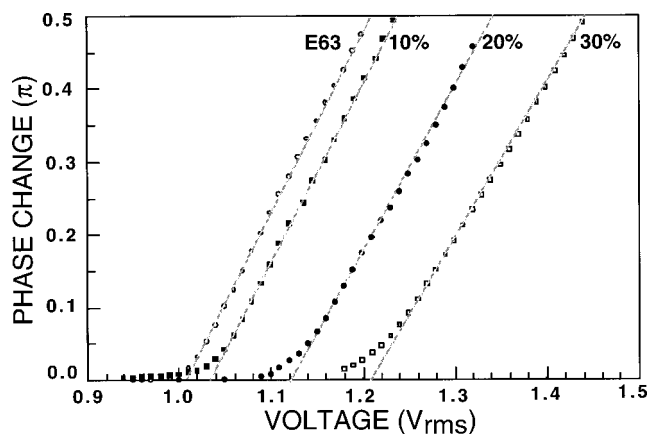


FIG. 1. The voltage-dependent phase change of four homogeneous LC cells: E63 alone, and E63 containing 10%, 20%, and 30% of PTP(3-Me)TP-63.  $\lambda = 633$  nm,  $f = 2$  kHz sine waves, and  $T = 22$  °C.

63, the mixture's clearing temperature increases in proportion to the dopant concentration. For example, adding a 30% of PTP(3-Me)TP-63 to E63 increases the mixture's clearing point to 103.3 °C while preserving the desirable low melting temperature.

To characterize the threshold voltage, we prepared a homogeneous cell and measured its voltage-dependent phase retardation at voltages slightly above the threshold. A HeNe laser with  $\lambda = 633$  nm was used for this study. The indium-tin-oxide coated glass substrates were evaporated with  $\text{SiO}_x$  layers to produce uniform homogeneous LC alignment with pretilt angle of  $\sim 2^\circ$ . The cell gap was controlled to be  $\sim 6$   $\mu\text{m}$ . Experimental data were collected at every 10 mV<sub>rms</sub>. The sine wave frequency of 2 kHz was set for all the measurements reported here. Results are depicted in Fig. 1 for E63 mixture alone, and E63 containing 10%, 20%, and 30% of PTP(3-Me)TP-63 dopant. In the vicinity of threshold, the phase retardation is linearly proportional to the applied voltage as expected from theory.<sup>13</sup> Through a linear extrapolation, the threshold voltage is determined as shown in Fig. 1. Since PTP(3-Me)TP-63 has a much smaller  $\Delta\epsilon$  than E63, the mixture's threshold voltage increases as the dopant concentration increases. As shown in Fig. 2, the  $V_{th}$  of E63 is 1.01 V<sub>rms</sub>. As the PTP(3-Me)TP-63 concentration increases to

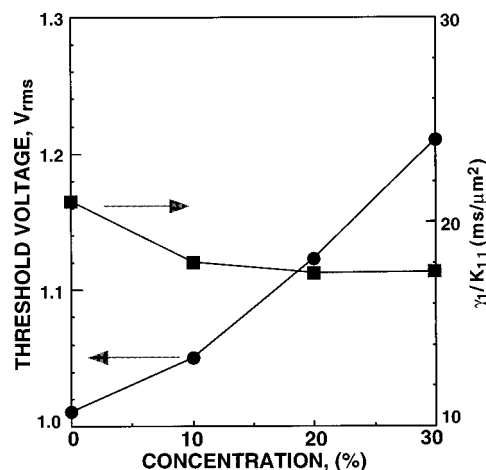


FIG. 2. Concentration effect of PTP(3-Me)TP-63 on the threshold voltage (left) and visco-elastic coefficient (right) of the E63 cells.

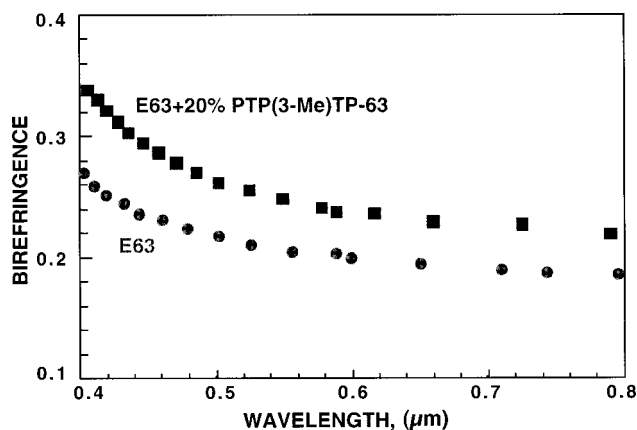


FIG. 3. Birefringence dispersion of E63 and E63+20% PTP(3-Me)TP-63.  $T=22^\circ\text{C}$ .

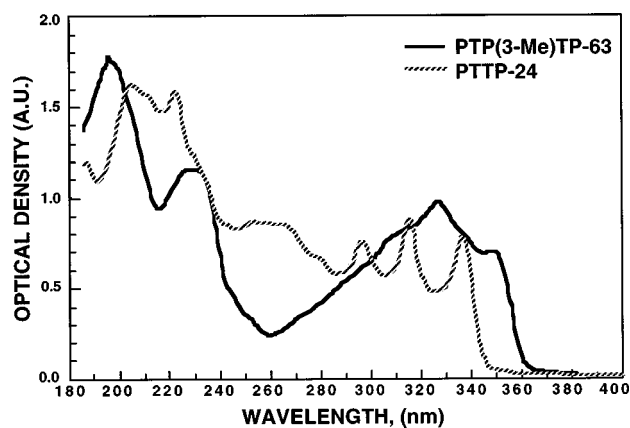


FIG. 4. The UV absorption spectra of PTP(3-Me)TP-63 and PTTP-24. LC host=ZLI-2359; Cell gap=6  $\mu\text{m}$  and dopant concentration=1%.

30%, the mixture's  $V_{\text{th}}$  increases to 1.21  $V_{\text{rms}}$ .

Using the same cell, we are able to measure the mixture's visco-elastic coefficient ( $\gamma_1/K_{11}$ ) through the time-dependent phase decay method.<sup>14</sup> Results are plotted in the right-hand side of Fig. 2. From Fig. 2, the visco-elastic coefficient of the mixtures is  $\sim 15\%$  lower than that of the E63 host indicating that the viscosity of PTP(3-Me)TP-63 is lower than that of E63. This result is encouraging because for such highly conjugated LC molecules, their viscosity would be normally quite high.<sup>15,16</sup> The observed low viscosity makes these compounds very attractive for many electro-optic applications.

The refractive indices of E63 and three mixtures containing 10%, 20%, and 30% of PTP(3-Me)TP-63 were measured using the Jelly-Leitz refractometer. The birefringence of such guest-host system can be approximated as:  $(n_{e,o})_{gh} = x(n_{e,o})_g + (1-x)(n_{e,o})_h$ ; where  $x$  is the concentration of the guest dopant, and  $n_e$  and  $n_o$  are the refractive indices for the extraordinary and ordinary rays, respectively. By measuring E63's refractive indices, the refractive indices of PTP(3-Me)TP-63 can be extrapolated. And the results are:  $n_e = 1.889$ ,  $n_o = 1.507$ , or  $\Delta n = 0.382$  at  $\lambda = 589$  nm and  $T = 22^\circ\text{C}$ . This high birefringence originates from the linear conjugation of the bis-tolane structure. We also measured the birefringence dispersion of a 20% PTP(3-Me)TP-63 in E63 over the entire visible region. Results are shown in Fig. 3. From Fig. 3, the  $\Delta n$  enhancement is more pronounced in the blue region than that in the near infrared (IR). This is because blue is closer to the PTP(3-Me)TP-63's electronic absorption wavelength.

The ultraviolet (UV) absorption spectra of PTP(3-Me)TP-63 was measured against a commonly employed diphenyl-diacetylene PTTP-24. In experiments, we mixed 1% of PTP(3-Me)TP-63 and PTTP-24 in a UV transparent LC mixture ZLI-2359. The mixture E63 absorbs strongly at wavelengths below  $\sim 350$  nm. So, ZLI-2359 is a better host. The computer-controlled Lambda 9 spectrophotometer was used for the absorption measurements. Two homogeneously aligned LC cells made of quartz substrates were prepared: the reference cell consists of a 6  $\mu\text{m}$  ZLI-2359 LC layer and the sample cell contains 1% dopant dissolved in ZLI-2359.

Figure 4 depicts the measured absorption spectra of PTP(3-Me)TP-63 and PTTP-24. From Fig. 4, PTP(3-

Me)TP-63 has a slightly longer absorption edge than PTTP-24 due to its longer molecular conjugation. The longer absorption alone is insufficient to explain the observed higher birefringence of bis-tolane. The molecular packing density and absorption anisotropy all play important roles.<sup>5</sup> In addition, the slightly longer absorption does not necessarily imply that bis-tolanes should have a poorer photostability than diacetylenes.

In conclusion, we have synthesized many asymmetric bis-tolane LC compounds which possess high birefringence, low viscosity, low melting and high clearing temperatures, and small heat of fusion enthalpy. These compounds are compatible with commercial cyan mixtures. Mixing PTP(3-Me)TP-63 LC to E63 mixture enhances the mixture's clearing temperature and birefringence while reducing its visco-elastic coefficient. The trade-off is in its slightly increased threshold voltage.

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