

Fluoro diphenyldiacetylene and tolane liquid crystals for display application

Shin-Tson Wu
Hughes Research Laboratories
3011 Malibu Canyon Road
Malibu, California 90265

Chain-Shu Hsu
Yee-Nan Chen
Show-Ru Wang
Shu-Hua Lung
National Chiao Tung University
Department of Applied Chemistry
1001 Ta Hsueh Road
Hsinchu, Taiwan 30050

Abstract. Several fluorinated diphenyldiacetylene and tolane liquid crystals are synthesized and their physical properties evaluated. These liquid crystals exhibit a high resistivity, high birefringence, low viscosity, and modest dielectric anisotropy. Some difluoro compounds show a relatively low melting temperature and small heat fusion enthalpy and are useful for formulating eutectic mixtures. The mixtures consisting of these fluorinated compounds are particularly useful for active matrix, photoactivated light valve, and polymer-dispersed liquid crystal displays.

Subject terms: display technologies; fluoro diphenyldiacetylenes; tolanes; liquid crystal displays.

Optical Engineering 32(8), 1792–1797 (August 1993).

1 Introduction

Nematic liquid crystals (LCs) with high birefringence, high resistivity, low viscosity, low threshold voltage, and wide nematic range are particularly attractive for direct-view displays using a thin-film transistor (TFT) active matrix,¹ large screen projection displays using photoactivated light valves,² and polymer-dispersed LC (PDLC)³ display devices. High birefringence improves the light modulation efficiency; this feature is particularly attractive for infrared and PDLC applications. High resistivity keeps the voltage holding ratio constant, which is essential for TFT-based display devices. Low viscosity shortens the response times, which is desirable for almost every LC device. Finally, low threshold voltage simplifies the driving electronics, which, in turn, leads to lower costs. Low threshold voltage is especially important for PDLC devices where the applied voltage is partially shielded by the polymer matrix⁴ so that the voltage dropped across the LC droplets is far less than the applied voltage. As a result, the operation voltage increases considerably.

Asymmetric dialkyl diphenyldiacetylene LC compounds⁵ possess a high birefringence, low viscosity, low melting temperature T_m , wide nematic range, and low heat fusion enthalpy ΔH . From the Schröder-van Laar equation,⁶ the low T_m and small ΔH of a LC component play equally important roles in lowering the melting point of the eutectic mixture. How-

ever, these two parameters are difficult to predict before the compound is actually synthesized. The major drawback of these asymmetric diphenyldiacetylenes is in their small dielectric anisotropy ($\Delta\epsilon \sim 1$). As a result, the threshold voltage becomes relatively high ($V_{th} \sim 3.5 V_{rms}$).

Low threshold voltage can be achieved by enhancing the dielectric anisotropy, reducing the elastic constant, or a combination of both. To improve the dielectric anisotropy, polar groups with a large dipole moment [such as cyano (CN) (Refs. 5 and 7) and chloro (Ref. 5)] have been investigated. However, their melting points are so high ($> 120^\circ\text{C}$) and heat fusion enthalpy ΔH so large that their usefulness is quite limited. To reduce the elastic constant, alkenyl or alkenyloxy side chains are useful.^{8–10}

The fluorinated LC compounds^{11–14} are known for their modest dielectric anisotropy, low viscosity, high resistivity, and excellent photostability. The dielectric anisotropy of a fluoro LC is, generally speaking, in the three to eight range, which is about two to three times smaller than the corresponding cyano compound. This is because the dipole moment of the CN group ($\mu \sim 4.0$ D) is nearly three times larger¹⁵ than the fluoro group ($\mu \sim 1.4$ D). The rotational viscosity of a LC compound is mainly determined by its molecular shape, moment of inertia, intermolecular association, activation energy, and temperature.^{16,17} In general, the viscosity of a fluoro compound is about two to three times lower than the corresponding cyano mesogen.

On the optical properties, the cyano is an electron donor that contributes its four π electrons to enhance the birefringence of the compound. On the contrary, the axial fluoro (which is an electron acceptor) substitution causes a blue

Invited paper DPT-06 received Feb. 3, 1993; accepted for publication April 7, 1993. This paper is a revision of a paper presented at the SPIE conference on Display Technologies, Dec. 1992, Taiwan. The paper presented there appears (unrefereed) in SPIE Proceedings Vol. 1815.
© 1993 Society of Photo-Optical Instrumentation Engineers. 0091-3286/93/\$5.00.

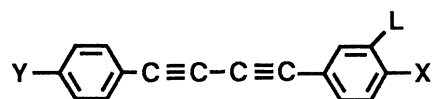
shift in the π electron resonance wavelengths resulting in a reduced birefringence.¹⁸ The major advantage of this blue shift is that the photostability is greatly enhanced because of the smaller absorption in the visible region. Photostability determines the lifetime of a LC device, which is crucial for practical display applications. The resistivity of an entirely fluorinated mixture can be as high as 10^{14} Ω cm, compared to 10^{10} Ω cm for the cyano compounds. In spite of the attractive features mentioned previously, the fluoro compounds do pose a serious problem: Many fluorinated compounds either exhibit no mesogenic phase or possess a wide smectic phase, which is undesirable for forming nematic mixtures.

In this paper, we report the physical properties of several novel fluoro diphenyldiacetylene and tolane LCs. Three types of polar groups and three different side chains are investigated. The three polar groups studied are (1) single fluoro (F) in the axial (or 4) position, (2) difluoro (FF) in the (3,4) positions, and (3) trifluoromethyl (CF₃) in the axial position. The three side chains studied are (1) alkyl (C_nH_{2n+1}), (2) alkoxy (C_nH_{2n+1}O), and (3) alkenyloxy (C_nH_{2n-1}O; alkoxy containing a carbon-carbon double bond). A more specific structure of the alkenyloxy group is expressed as C_xH_{2x+1}CH=CH-(CH₂)_{n-2-x}-O and is abbreviated as xd_{n-1-x}, where d stands for the double bond position.^{8,9}

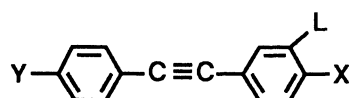
2 Liquid Crystal Structures

The structures and codes of the diphenyldiacetylene and tolane compounds we synthesized are shown here. For simplicity, we use the abbreviations P for a phenyl ring and T for a triple bond:

Diphenyldiacetylene series (PTTP)



Tolane series (PTP)



where X = F or CF₃, L = H or F, and Y = alkyl, alkoxy, or alkenyloxy group.

3 Physical Properties

3.1 4-Fluoro Alkyl PTTPs and PTPs

The phase transition temperatures, heat fusion enthalpy, refractive indices, and dielectric constants of several 4-fluoro alkyl PTTPs and PTPs are shown in Table 1. From Table 1, the fluorinated alkyl diphenyldiacetylene compounds we synthesized all exhibit an enantiotropic nematic phase. The melting temperature T_m decreases; however, their nematic range gets narrower as the side chain length increases. Narrow nematic range implies a high reduced temperature ($T_r = T/T_c$), which makes the physical characterization of a single substance difficult. The dielectric constants, refractive indices, elastic constants, and viscosity are all very sensitive to the reduced temperature. Thus, we use the guest-host method to extrapolate the dielectric constants and refractive indices at room temperature ($T = 22^\circ\text{C}$ or $T_r \sim 0.86$). In the

Table 1 Physical properties of some fluorinated alkyl (C_nH_{2n+1}) diphenyldiacetylene (PTTP-*n*F) and tolane (PTP-*n*F) homologs; T_m = melting temperature, T_c = clearing temperature, $n_{e,o}$ = refractive indices, $\epsilon_{\parallel,\perp}$ = dielectric constants, ΔH = heat fusion enthalpy, and two dashes indicate no mesogenic phase. Both refractive indices and dielectric constants are obtained by extrapolating the results from 10% samples mixed with 90% ZLI-1132 (Merck, Germany).

LCs	T_m	T_c	n_e	n_o	ϵ_{\parallel}	ϵ_{\perp}	ΔH
	($^\circ\text{C}$)						
PTTP-3F	94.4	102.2					4.85
PTTP-4F	85.4	87.7	1.843	1.534	8.5	3.3	4.57
PTTP-5F	85.7	89.3					6.23
PTTP-6F	76.0	80.1					7.43
PTP-3F	50.8	--					5.77
PTP-4F	56.7	--	1.707	1.527	8.0	3.0	4.43
PTP-5F	64.2	--					6.12
PTP-6F	45.8	--					5.33

measurement, 10% of the guest LC is mixed with a 90% host nematic mixture (ZLI-1132, from Merck). From Table 1, the extrapolated dielectric anisotropy of PTTP-4F is about 5.2 and $\Delta n \sim 0.31$. Under the same conditions, the $\Delta\epsilon$ and Δn of a dialkyl PTTP are about 1 and 0.36, respectively. The improvement in $\Delta\epsilon$ and the decrease in Δn originate from the dipole moment and blue shift of the fluoro group, respectively. Although PTTP-6F has the lowest melting point among its homologs, its high ΔH makes it less attractive than PTTP-4F from the eutectic mixture standpoint.

On the fluoro tolane series shown in Table 1, all the 4-fluoro alkyl tolane compounds we synthesized exhibit no mesogenic phase. The extrapolated birefringence and dielectric anisotropy of these compounds are all lower than the corresponding PTTPs. This is because the differential molecular polarizability of tolanes is smaller than the corresponding diphenyldiacetylenes with the same chain length. However, the shorter conjugation length of tolanes also leads to two desirable features: (1) better photostability and (2) lower melting temperature, which are important for display application in the visible wavelengths. The better photostability of tolanes results from their weaker absorption in the visible region. The melting temperature of the fluoro tolanes is about 20 to 40 deg lower than the diphenyldiacetylenes. Although some fluoro tolanes exhibit no LC phase, they are still useful in the mixtures.

3.2 Difluoro PTTPs and PTPs

In this category, the difluoro substitutions take place at the third and fourth hydrogen positions of a phenyl ring. The phase transition temperatures, heat fusion enthalpy, refractive indices, and dielectric constants of several 3,4-fluoro PTTPs and PTPs are shown in Table 2. Among the difluoro alkyl PTTPs and tolanes we synthesized, only PTTP-6FF exhibits a narrow monotropic nematic phase (from 48.5 to 36.2 $^\circ\text{C}$). The dielectric anisotropy of PTTP-6FF is extrapolated to be about 7.8 at $T \sim 22^\circ\text{C}$. The melting temperature of the difluoro compounds is, on the average, 10 deg lower than the corresponding single fluoro compounds shown in Table 1. The lateral fluoro substitution increases the width of the molecule

Table 2 Physical properties of some 3,4-difluoro diphenyl-diacyetylene and tolane homologs. Both refractive indices and dielectric constants are obtained by extrapolating the results from 10% samples mixed in ZLI-1132.

LCs	T_m	T_c	n_e	n_o	ϵ_{\parallel}	ϵ_{\perp}	ΔH
	($^{\circ}\text{C}$)	($^{\circ}\text{C}$)	(22 $^{\circ}\text{C}$, 589 nm)	(22 $^{\circ}\text{C}$, 589 nm)	(22 $^{\circ}\text{C}$, 1kHz)	(22 $^{\circ}\text{C}$, 1kHz)	(kcal/mol)
PTTP-2FF	89.9	--					8.14
PTTP-3FF	70.5	--					5.25
PTTP-4FF	67.6	--					5.82
PTTP-5FF	81.9	--					7.35
PTTP-6FF	65.3	(48.5)	1.779	1.515	12.0	4.2	5.95
PTTP-60FF	96.8	--					8.96
0d ₅ PTTP-60FF	91.2	--					8.45
1d ₄ PTTP-60FF	91.4	--					7.41
PTP-2FF	28.0	--					3.98
PTP-3FF	37.8	--					4.83
PTP-4FF	50.3	--					6.05
PTP-5FF	49.9	--	1.672	1.512	9.8	3.8	5.29
PTP-6FF	41.7	--					5.82

so that the separation between the neighboring molecules is increased. Less heat is needed to overcome the intermolecular attractions and, thus, the melting point drops. This looser molecular packing also leads to a slightly lower birefringence.

Note that the melting temperature of several difluoro tolanes is very low and ΔH is small. PTP-2FF, PTP-3FF, and 1d₄PTP-60FF remain liquid for days at room temperature due to the supercooling effect. Although these difluoro tolanes exhibit no mesogenic phase, they can still be used in the eutectic mixtures for enhancing the dielectric anisotropy.

To evaluate the contribution of dipole moments to the dielectric constants of a LC compound, Maier and Meier¹⁹ derived the following expressions:

$$\epsilon_{\parallel} = NhF\{\langle\alpha_{\parallel}\rangle + (F\mu^2/3kT)[1 - (1 - 3 \cos^2\theta)S]\}, \quad (1)$$

$$\epsilon_{\perp} = NhF\{\langle\alpha_{\perp}\rangle + (F\mu^2/3kT)[1 + (1/2)(1 - 3 \cos^2\theta)S]\}, \quad (2)$$

$$\Delta\epsilon = NhF\{\langle\alpha_{\parallel} - \alpha_{\perp}\rangle - (F\mu^2/2kT)(1 - 3 \cos^2\theta)S\}, \quad (3)$$

where N is the molecular packing density, $h = 3\epsilon/(2\epsilon + 1)$ is the cavity field factor, $\epsilon = (\epsilon_{\parallel} + 2\epsilon_{\perp})/3$ is the averaged dielectric constant, F is the Onsager reaction field, α_{\parallel} and α_{\perp} are the principal elements of the molecular polarizability tensor, θ is the angle between the dipole moment μ and the principal molecular axis, and S is the order parameter of the second rank. From Eq. (3), the dielectric anisotropy of an anisotropic LC is influenced by the molecular structure, temperature, and the applied frequency. For a polar compound with its dipole at $\theta < 55$ deg, $\Delta\epsilon$ is positive. On the other hand, $\Delta\epsilon$ becomes negative if $\theta > 55$ deg. As temperature increases, $\Delta\epsilon$ decreases in proportion to S/T . In addition, at a sufficiently high frequency (~ 10 MHz for the cyanobiphenyls²⁰), dielectric relaxation occurs and the dielectric anisotropy changes sign.

The effective dipole moment of a molecule having two dipole groups (with dipole moments μ_1 and μ_2) can be cal-

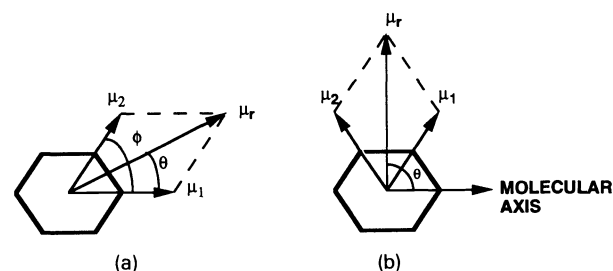


Fig. 1 Illustration on how dipole moments affect the dielectric anisotropy of a LC compound. The two dipoles μ_1 and μ_2 are at an angle ϕ . The resultant dipole μ_r is at an angle θ to the principal molecular axis. (a) Two dipoles are in the (3,4) positions. The dielectric anisotropy is strongly positive. (b) Two dipoles are in the (2,3) positions. The dielectric anisotropy is strongly negative.

culated by the vector addition method, as illustrated in Fig. 1. In Fig. 1(a), μ_1 is along the principal molecular axis and μ_2 is at an angle ϕ with respect to μ_1 . The resultant dipole moment μ_r can be calculated from the following equation:

$$\mu_r = (\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\phi)^{1/2}. \quad (4)$$

From Eqs. (3) and (4), the following frequently encountered special cases can be calculated easily:

Single polar group (μ_1):

1. If μ_1 is in the 4 (axial) position, then $\theta = 0$ deg and $\Delta\epsilon$ is strongly positive.
2. If μ_1 is in the 3 position and we assume the axial group has a negligible dipole moment, then $\theta = 60$ deg and $\Delta\epsilon$ is weakly negative.
3. If μ_1 is in the 2 position and we assume the axial group has a negligible dipole moment, then $\theta = 120$ deg and $\Delta\epsilon$ is weakly negative, identical to case 2.

Two polar groups (assume $\mu_1 = \mu_2$ for simplicity):

1. If μ_1 and μ_2 are in the (3,4) positions, then $\phi = 60$ deg, $\mu_r = \sqrt{3}\mu_1$, and $\theta = 30$ deg, so that $\Delta\epsilon$ is strongly positive.
2. If μ_1 and μ_2 are in the (2,4) positions, then $\phi = 120$ deg, $\mu_r = \mu_1$, and $\theta = 60$ deg, so that $\Delta\epsilon$ is weakly negative.
3. If μ_1 and μ_2 are in the (2,3) positions, then $\phi = 60$ deg, $\mu_r = \sqrt{3}\mu_1$, and $\theta = 90$ deg, so that $\Delta\epsilon$ is strongly negative.

From the preceding analyses, the (3,4) difluoro substitutions should exhibit about 80% larger dielectric anisotropy than the single axial fluoro substitution at the same reduced temperature. This prediction is confirmed in the chloro ($\mu \sim 1.55$ D) and fluoro compounds²¹ where dielectric constants of single substances were measured directly, rather than the currently extrapolated results from the guest-host mixtures. The (3,4) difluoro substitution enhances both ϵ_{\parallel} and ϵ_{\perp} , but the contribution to ϵ_{\parallel} is greater than ϵ_{\perp} , resulting in an improvement in $\Delta\epsilon$. If the difluoro substitutions occur at the (2,3) lateral positions as shown in Fig. 1(b), then the effective dipole is perpendicular to the principal molecular axis ($\theta = 90$ deg), and $\Delta\epsilon$ becomes strongly negative, according to Eq. (3).

LCs with positive $\Delta\epsilon$ are necessary for realizing the useful electro-optic effects employing a twist or parallel-aligned cell. On the other hand, LCs with negative $\Delta\epsilon$ are useful for the tilted-perpendicular alignment.²² Perpendicular alignment is known to display an excellent contrast ratio that is independent of the LC birefringence, cell thickness, wavelength, and temperature.

For a nonpolar LC compound, $\mu \sim 0$ and the dielectric anisotropy is generally very small. In this case, $\Delta\epsilon$ is determined entirely by the differential molecular polarizability, i.e., the first term in Eq. (3). The molecules with a larger differential polarizability in the low-frequency (kilohertz) regime often exhibit a larger birefringence in the optical frequency regime. Thus, the $\Delta\epsilon$ of a nonpolar PTTP compound is expected to be slightly larger than the corresponding PTP with the same chain length. Within the same homologs, the one with a shorter side chain will generally exhibit a slightly larger $\Delta\epsilon$ due to the molecular packing density (N) effect. As indicated in Eq. (3), $\Delta\epsilon$ is linearly proportional to N .

3.3 Trifluoromethyl Alkoxy PTTPs

Table 3 shows the phase transition temperatures of four trifluoromethyl alkoxy PTTP compounds we synthesized. No mesogenic phase is found in any homolog. Although their dielectric anisotropy is expected to be about 10 (the dipole moment of CF_3 is about 2.5 D), the melting temperature of these compounds is too high. Thus, their practical usefulness is limited. To lower the melting temperature, an alkyl rather than an alkoxy side chain could be considered.

3.4 Fluoro Alkoxy and Alkenyloxy PTTPs and PTPs

Table 4 shows the phase transition temperature and heat fusion enthalpy of several fluoro alkoxy and alkenyloxy PTTPs and PTPs. In the 4-fluoro PTTP homologs we synthesized, all exhibit an enantiotropic nematic phase, except PTTP-20F because of its short side chain. Generally speaking, the double bond makes three important contributions to the physical properties of a LC compound: (1) It lowers the melting temperature, (2) it reduces the heat fusion enthalpy, and (3) it reduces the splay elastic constant significantly.¹⁰ The detailed effects depend on the double bond position, as indicated in Table 4. On the other hand, in the fluoro tolane (PTP- n 0F; $n = 2$ to 6) homologs, only PTP-60F possesses a narrow but monotropic (from 52.3 to 47.3°C) nematic phase. The rest show no mesogenic phase at all. Replacing the alkoxy side chain of PTP-60F with an alkenyloxy group suppresses the nematic phase completely. However, the melting temperature of 1d₄ PTP-60F drops to 24°C and ΔH decreases to 3.36 kcal/mol. Thus, this homolog contributes effectively to the lowering of the melting temperature and enhances the dielectric anisotropy of the eutectic mixtures.

The compounds with no mesogenic phase may be added to the mixtures and become useful. One example is illustrated in Table 5. Here, binary mixtures of PTP-60F and PTP-20F are formulated. Note that PTP-60F exhibits a monotropic phase and PTP-20F shows no mesogenic phase at all. However, their mixtures may exhibit an enantiotropic, a monotropic, or nonmesogenic phase, depending on the percentage of PTP-20F employed. At low PTP-20F concentration, the mixtures possess an enantiotropic phase with a nematic range of about 10 to 15 deg. We can convert a monotropic phase

Table 3 Phase transition behavior of the trifluoromethyl alkoxy ($\text{C}_n\text{H}_{2n+1}\text{O}$) diphenyldiacetylene (PTTP- n 0CF₃) homologs; T_m =melting temperature, T_c =clearing temperature, ΔH =heat fusion enthalpy in kilocalories per mole, and two dashes indicate no mesogenic phase.

Compounds	T_m (°C)	T_c (°C)	ΔH
PTTP-20CF ₃	151.7	--	7.83
PTTP-30CF ₃	142.7	--	4.50
PTTP-40CF ₃	141.1	--	6.07
PTTP-60CF ₃	121.6	--	8.13

Table 4 Phase transition temperatures and heat fusion enthalpy of the fluoro alkoxy and alkenyloxy diphenyldiacetylene and tolane LC homologs; T_m =melting temperature, T_c =clearing temperature, () = monotropic, and two dashes indicate no LC phase. The nematic range for 0d₁₀ PTTP-110F is from 94.5 to 82.3°C and from 52.3 to 47.3°C for PTP-60F.

LCs	T_m (°C)	T_c (°C)	ΔH (kcal/mol)
PTTP-20F	127.0	--	8.11
0d ₂ PTTP-30F	88.7	102.4	5.95
PTTP-40F	106.7	133.5	11.27
PTTP-60F	98.4	122.8	7.68
0d ₅ PTTP-60F	96.8	123.8	4.46
1d ₄ PTTP-60F	72.8	81.2	6.22
2d ₃ PTTP-60F	88.5	103.6	6.55
0d ₁₀ PTTP-110F	96.3	(82.3)	9.54
PTP-20F	81.2	--	5.46
PTP-30F	83.6	--	6.48
PTP-40F	73.5	--	6.07
PTP-50F	57.7	--	6.51
PTP-60F	59.1	(52.3)	7.21
0d ₅ PTP-60F	48.2	--	4.70
1d ₄ PTP-60F	24.0	--	3.36
2d ₃ PTP-60F	53.1	--	5.20

into an enantiotropic phase because the mixture decreases the melting point more significantly than the clearing point. The nematic to isotropic temperature T_{NI} of the mixture is linearly proportional to the $(T_{NI})_i$ of the individual component i as

$$T_{NI} = X_1(T_{NI})_1 + X_2(T_{NI})_2, \quad (5)$$

where $X_{1,2}$ is the molar fraction of the individual component. In the example we demonstrate in Table 5, the T_{NI} of PTP-60F is 52.3°C. By comparing the T_{NI} of the mixtures with Eq. (5), we extrapolate that PTP-20F has a virtual $T_{NI} \sim 61.5^\circ\text{C}$. As the molar fraction of PTP-20F increases to 60%, the mixture is further away from its eutectic point (35%), the melting point is too high, and a monotropic phase takes place. As the concentration of PTP-20F exceeds $\sim 80\%$, the mesogenic phase of the mixture is suppressed completely. We also performed the binary mixtures of two monotropic mesogens. Most mixtures show an enantiotropic phase. This evidence proves that although some fluoro PTTP and tolane homologs

Table 5 Binary mixtures of PTP-20F and PTP-60F; *K*, *N*, and *I* represent crystal, nematic, and isotropic phase, respectively. The phase transition temperatures are measured using a Mettler heating plate (at 3°C/min) under polarizing microscope. Note that PTP-20F shows no mesogenic phase and PTP-60F shows a monotropic phase. However, their binary mixtures may exhibit either an enantiotropic, monotropic, or nonmesogenic phase, depending on the concentration of PTP-60F. The calculated eutectic mixture is the one with 35% PTP-20F and 65% PTP-60F.

PTP-20F (%)	PTP-60F (%)	Transition Temperature (°C)
0	100	K $\xrightarrow{59.1}$ N $\xrightarrow{52.3}$ I 47.3
20	80	K $\xrightarrow{42.3}$ N $\xrightarrow{55}$ I 37 53
35	65	K $\xrightarrow{45.0}$ N $\xrightarrow{56.8}$ I
40	60	K $\xrightarrow{38}$ N $\xrightarrow{56}$ I 34 54
50	50	K $\xrightarrow{41}$ N $\xrightarrow{56.5}$ I 32 55
60	40	K $\xrightarrow{60}$ N $\xrightarrow{56}$ I 36
80	20	K $\xrightarrow{71.1}$ I 64
100	0	K $\xrightarrow{81.2}$ I 64.0

show no mesogenic phase, they are still quite useful for formulating the mixtures to enhance the dielectric anisotropy. The selection criteria are their low melting point and small heat fusion enthalpy.

4 Conclusion

The fluoro diphenyldiacetylene and tolane LC homologs exhibit a high birefringence, high resistivity, low threshold voltage, and low viscosity. Their phase behaviors are difficult to predict. Some fluoro compounds show reasonably low melting temperatures and small heat fusion enthalpies. Generally speaking, however, their melting temperatures are too high and nematic range too narrow. They have to be mixed with different types of LC compounds to satisfy the wide nematic range requirement for practical application.

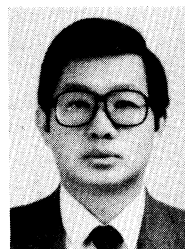
Acknowledgment

The authors are indebted to Elena Sherman of Hughes for formulating the binary mixtures and checking the purity of the LC compounds.

References

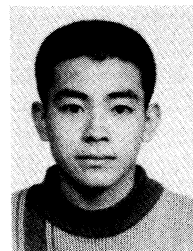
- K. Takeuchi, Y. Funazo, M. Matsudaira, S. Kishimoto, and K. Kanatani, "A 750-TV-line-resolution projector using 1.5-megapixel a-Si TFT LC modules," *Society for Information Display: Digest of Technical Papers* **22**, 415–422 (1991).
- U. Efron, J. Grinberg, P. O. Braatz, M. J. Little, P. E. Reif, and R. N. Schwartz, "The silicon liquid crystal light valve," *J. Appl. Phys.* **57**, 1356–1361 (1985).
- J. W. Doane, N. A. Vaz, B. G. Wu, and S. Zumer, "Field controlled light scattering from nematic microdroplets," *Appl. Phys. Lett.* **48**, 269–271 (1986).
- J. Kelly and D. Seekola, "Dielectric losses in a polymer-dispersed liquid crystal film," *Proc. SPIE* **1257**, 17–28 (1990).
- S. T. Wu, J. D. Margerum, H. B. Meng, L. R. Dalton, C. S. Hsu, and S. H. Lung, "Room temperature diphenyldiacetylene liquid crystals," *Appl. Phys. Lett.* **61**, 630–632 (1992).
- E. C. H. Hsu and J. F. Johnson, "Phase diagrams of binary nematic mesophase system," *Mol. Cryst. Liq. Cryst.* **20**, 177–190 (1973).
- B. Grant, N. J. Clecak, and R. J. Cox, "Novel liquid crystalline materials," *Mol. Cryst. Liq. Cryst.* **51**, 209–214 (1979).
- M. Schadt, M. Petrzilka, P. E. Gerber, and A. Villiger, "Polar alkenyls: physical properties and correlations with molecular structure of new nematic liquid crystals," *Mol. Cryst. Liq. Cryst.* **122**, 241–260 (1985).
- M. Schadt, R. Buchecker, and K. Muller, "Material properties, structural relations with molecular ensembles and electro-optical performance of new bicyclohexane liquid crystals in field-effect liquid crystal displays," *Liq. Cryst.* **5**, 293–312 (1989).
- S. T. Wu, C. S. Hsu, Y. N. Chen, and S. R. Wang, "Fluorinated diphenyldiacetylene and tolane liquid crystals with low threshold voltage," *Appl. Phys. Lett.* **61**, 2275 (1992).
- V. Reiffenrath, U. Finkenzeller, E. Poetsch, B. Rieger, and D. Coates, "Synthesis and properties of liquid crystalline materials with high optical anisotropy," *Proc. SPIE* **1257**, 84–94 (1990).
- Y. Goto, T. Ogawa, S. Sawada, and S. Sugimori, "Fluorinated liquid crystals for active matrix displays," *Mol. Cryst. Liq. Cryst.* **209**, 1–8 (1991).
- A. I. Pavluchenko, N. I. Smirnova, and V. F. Petrov, "Synthesis and properties of liquid crystals with fluorinated terminal substituents," *Mol. Cryst. Liq. Cryst.* **209**, 225–235 (1991).
- M. Schadt, R. Buchecker, and A. Villiger, "Synergisms, structural-material relations and display performance of novel fluorinated alkenyl liquid crystals," *Liq. Cryst.* **7**, 519–536 (1990).
- L. N. Ferguson, *The Modern Structural Theory of Organic Chemistry*, Prentice-Hall, Englewood Cliffs, New Jersey (1964).
- M. A. Osipov and E. M. Terentjev, "Rotational diffusion and rheological properties of liquid crystals," *Z. Naturforsch. Teil A* **44**, 785–792 (1989).
- S. T. Wu and C. S. Wu, "Experimental confirmation of the Osipov-Terentjev theory on the viscosity of nematic liquid crystals," *Phys. Rev. A* **42**, 2219–2227 (1990).
- S. T. Wu, "A semi-empirical model for liquid crystal refractive index dispersions," *J. Appl. Phys.* **69**, 2080–2087 (1991).
- W. Maier and G. Meier, "A simple theory of the dielectric characteristics of homogeneous oriented crystalline-liquid crystal phases of the nematic type," *Z. Naturforsch. Teil A* **16**, 262–267 (1961).
- T. K. Bose, B. Campbell, S. Yagihara, and J. Thoen, "Dielectric-relaxation study of alkylcyanobiphenyl liquid crystals using time-domain spectroscopy," *Phys. Rev. A* **36**, 5767–5773 (1987).
- S. T. Wu, D. Coates, and E. Bartmann, "Physical properties of chlorinated liquid crystals," *Liq. Cryst.* **10**, 635–646 (1991).
- A. M. Lackner, J. D. Margerum, L. J. Miller, and W. H. Smith, Jr., "Photostability tilted-perpendicular alignment of LC for light values," *Proc. Society for Information Display* **31**, 321–326 (1990).

Shin-Tson Wu: Biography and photograph of author appear with the paper "Refractive index dispersions of liquid crystals" in this issue.



applied Chemistry at National Chiao Tung University. His research interests include synthesis and applications of liquid crystals and liquid-crystalline polymers.

Chain-Shu Hsu received his BS degree in chemistry from the National Taiwan Normal University in 1975 and the MS degree in applied chemistry from the National Tsing Hua University in 1977. He was a research chemist at the Taiwan Fertilizer Company from 1980 to 1983. Subsequently, he studied macromolecular science at Case Western Reserve University and received a PhD in 1987. He is currently a professor in the Department of Applied Chemistry at National Chiao Tung University. His research interests include synthesis and applications of liquid crystals and liquid-crystalline polymers.



Yee-Nan Chen received his BS degree in chemistry from Tam Kang University, Taipei, in 1990. He was a graduate student at Chiao Tung University, where he worked on various synthetic aspects of liquid crystals and liquid-crystalline polymers and received a MS degree in 1992. He is currently on his military service.

LIQUID CRYSTALS FOR DISPLAY APPLICATION



Show-Ru Wang received her BS degree in chemistry from Tam Kang University, Taiwan, in 1990. Subsequently she was a graduate student at Chiao Tung University, where she worked on the preparation of liquid crystals and polymer-dispersed liquid crystals. She received a MS degree in 1992 and is currently a teaching assistant at the University.



Shu-Hua Lung received her BS degree in chemistry from the Fu Jen Catholic University, Taiwan, in 1991. Subsequently she was a graduate student at Chiao Tung University and performed her research on the synthesis of liquid crystals. She is currently completing her MS thesis.