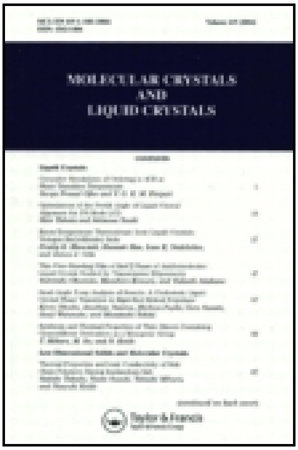

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis and Physical Properties of Asymmetric Diphenyldiacetylenic Liquid Crystals

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Version of record first published: 24 Sep 2006.

To cite this article: H.-H. B. Meng , L. R. Dalton & S.-T. Wu (1994): Synthesis and Physical Properties of Asymmetric Diphenyldiacetylenic Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 250:1, 303-314

To link to this article: http://dx.doi.org/10.1080/10587259408028215

Mol. Cryst. Liq. Cryst., 1994, Vol. 250, pp. 303–314
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Printed in the United States of America

Synthesis and Physical Properties of Asymmetric Diphenyldiacetylenic Liquid Crystals

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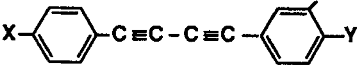
(Received August 3, 1993; in final form August 25, 1993)

Fifty-six asymmetric diphenyl-diacetylene liquid crystal homologs including dialkyl, alkyl-alkoxy, cyano-alkyl, chloro-alkyl, fluoro-alkyl, difluoro-alkyl, lateral chloro-substituted fluoro-alkyl (or alkoxy), lateral fluoro-substituted asymmetric dialkyl, and vinyl-alkyl are synthesized and their physical properties evaluated. Among these asymmetric diphenyl-diacetylene liquid crystals, many dialkyl homologs exhibit low melting point, wide nematic range, and low heat of fusion. They are ideal host candidates for formulating eutectic mixtures. The polar groups make important contributions to the phase transition temperature, dielectric anisotropy, refractive indices and viscosity. Detailed effects depend on the position of the substitution. These new liquid-crystals compounds and mixtures are particularly useful for electro-optic modulation of infrared radiation.

Keywords: Diphenyl-diacetylenes, eutectic mixtures, electro-optic modulation, physical properties

I. INTRODUCTION

Diphenyl-diacetylene liquid crystals[1–7] provide a useful electro-optic medium for modulating infrared radiation[8] (where photostability is not a problem) and for high-speed light shutters due to their high birefringence (Δn) and relatively low viscosity. The general structure which we studied is shown below and abbreviated as PTTP for simplicity; here P stands for a phenyl ring and T stands for a triple bond.



In the above structure, X is a *n*-alkyl group ($R_n = C_nH_{2n+1}$), Z can be a hydrogen, chloro (Cl), or fluoro (F) group; Y can be either a nonpolar group such as a *n*-alkyl

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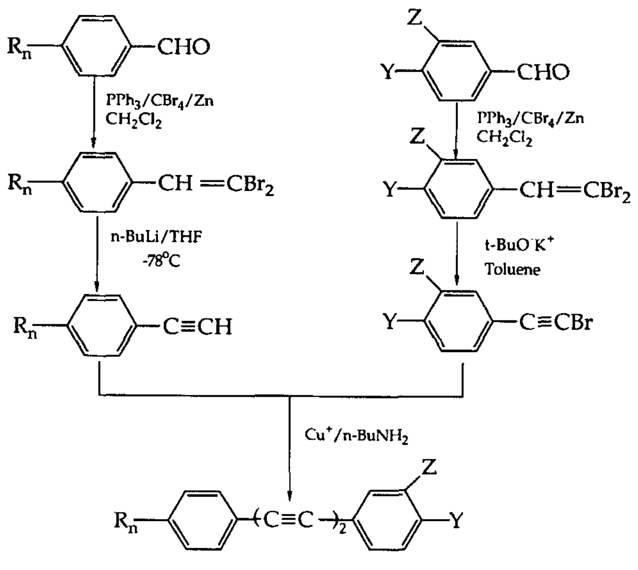
group ($C_mH_{2m+1}, n \neq m$ for the asymmetric dialkyl PTTPs), *n*-alkoxy (OR_m) group, a vinyl group, or a polar group such as cyano (CN), chloro, or fluoro. The high birefringence of PTTP compounds results from their long π-electron conjugation,[8] whereas low viscosity is the consequence of linear molecular shape and low activation energy.[8,9] We have synthesized and evaluated physical properties of fifty-six new asymmetric PTTP liquid crystals.

Section II presents two frequently employed synthetic routes for these asymmetric diphenyl-diacetylene derivatives. Examples of some detailed procedures are given in Section III. Effects of different substituents on the mesomorphic behavior and associated physical properties are discussed in Section IV.

II. SYNTHESIS

Two different routes, as outlined in Schemes 1 and 2, were used for synthesizing the aforementioned asymmetrical diphenyl-diacetylenic liquid crystals. Scheme 1 was employed for all asymmetric diphenyldiacetylenes except for the 4-*n*-alkyl-3′-fluoro-4′-methyl-diphenyldiacetylenes and 4-*n*-alkyl-4′-vinyl-diphenyldiacetylenes. For these two special homologs, Scheme 2 was used. The Cadiot–Chodkiewicz coupling of



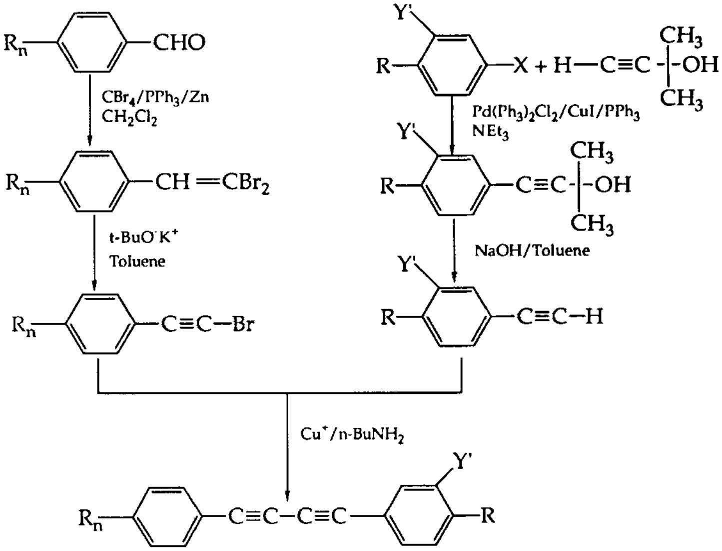
(1) $R_n = n\text{—}C_nH_{2n+1}\text{—}$ $n = 3,4,5,6$ or 8, $n \neq m$

$Y = R_m = m\text{—}C_mH_{2m+1}\text{—}$ $m = 2,3,4,5,6$, $Z = H$

(1) $R_n = n\text{—}C_nH_{2n+1}\text{—}$ $n = 3,4,5,6$ or 8,

$Y = F$, Cl or CN, $Z = H$, F or Cl

SCHEME 1 Synthesis of all asymmetric diphenyldiacetylenic compounds except for 4-n-alkyl-3′-fluoro-4′-methyl-diphenyldiacetylenes and 4-n-alkyl-4′-vinyl-diphenyldiacetylenes.



(1) $R_n = n{-}C_nH_{2n+1}{-}$ $n = 3\text{–}6$

$Y' = F, R = CH_3, X = I$

(1) $R_n = n{-}C_nH_{2n+1}{-}$ $n = 3\text{–}6$

$R = CH_2 = CH{-}$, $Y' = H, X = Br$

SCHEME 2 Synthesis of 4-*n*-alkyl-3'-fluoro-4'-methyl diphenyldiacetylenes and 4-*n*-alkyl-4'-vinyl diphenyldiacetylenes.

terminal acetylenes with 1-bromoacetylenes[10] is the standard procedure for the present syntheses.

In Scheme 1, the general scheme for the preparation of 4-*n*-alkyl-phenylacetylenes (except for 4-vinyl-phenylacetylene and 3-fluoro-4-methyl-phenylacetylene) and 1-bromoacetylenes is based on the Corey and Fuchs[11] procedure via the Wittig reaction with the appropriate para-substituted benzaldehyde as the starting materials to produce the intermediate β,β'-dibromostyryl derivative. Then one appropriate β,β'-dibromostyryl derivative was treated with *n*-butyllithium at −78°C and converted into the 4-*n*-alkyl-phenylacetylene. The other derivative was reacted with potassium t-butoxide in refluxing toluene and converted into the bromoacetylide. The synthesis of 4-cyanophenyl-1-bromoacetylene has been reported by Grant[1]. The resulting asymmetrical diphenyldiacetylenes were obtained by the Cadiot–Chodkiewicz coupling of 4-*n*-alkylphenylacetylenes with 1-bromoacetylenes.

In Scheme 2, 4-vinyl-phenylacetylene and 3-fluoro-4-methyl-phenylacetylene were prepared by a two-step procedure[12–15]. First, an aromatic halide (2-fluoro-4-iodotoluene or 4-bromostyrene) was coupled (employing Pd(0)/Cu(I) catalyst) with 2-methyl-3-butyn-2-ol as a monoprotected acetylene to form a protected aryl acetylide (carbinol derivative). Second, the resulting carbinol derivative is deprotected by sodium hydroxide or potassium hydroxide to form an aryl acetylene. Finally, the same

Cadiot–Chodkiewicz coupling of terminal acetylenes with 1-bromoacetylenes is apllied to synthesis of these asymmetrical diphenyldiacetylenes.

III. EXPERIMENTAL

A. Materials

Dichloromethane, toluene, and triethylamine were purchased from Aldrich and dried by distillation from phosphorus pentoxide or sodium and stored over 3Å molecular sieves under nitrogen. All other materials such as 4-*n*-alkylbenzaldehydes, bis(triphenylphosphine)palladium(II)chloride, 2-methyl-3-butyn-2-ol, 2-fluoro-4-iodotoluene, 4-bromostyrene, and the other reagents were purchased from Aldrich or Kodak and used as received without further purification.

B. Instrumental

Structures of the final compounds and various synthetic intermediates were characterized by a variety of instrumental methods and by elemental analysis. For examples, ^1H NMR spectra were obtained utilizing a Bruker AC 250-MHz spectrometer. All spectra were recorded in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. Elemental analysis was performed by Atlantic Microlab., Inc. Microscopy data were obtained with polarized light utilizing a Mettler FP52 hot stage at a heating/cooling rate of 3°C per minute. Thermal analysis was accomplished employing a Perkin–Elmer DCS-7 system with a heating/cooling rate of 5°C per minute.

General procedure for the synthesis of asymmetric diphenyldiacetylenes (except for 4-*n*-alkyl-3′-fluoro-4′-methyl diphenyldiacetylenes and 4-*n*-alkyl-4′-vinyl diphenyldiacetylenes)

All these compounds were synthesized according to the routes shown in Scheme 1. The following synthesis of 4-*n*-propyl-4′-*n*-hexyldiphenyldiacetylene is described as an

TABLE 1

^1H NMR Chemical Shifts for Some Asymmetric Diphenyldiacetylenes

PTTP	250 MHz ^1H NMR ($CDCl_3$, δ, ppm)
15	0.88 (t, 3H, CH_3—), 1.25 $\sim$ 1.36 [m, 4H, —$(CH_2)_2$—], 1.61 (m, 2H, —CH_2—), 2.36 (s, 3H, CH_3—), 2.61 (t, 2H, —CH_2— Ph—), 7.12 $\sim$ 7.45 (m, 8 aromatic protons).
24	0.92 (t, 3H, CH_3—), 1.23 (t, 3H, CH_3—), 1.35 (m, 2H, —CH_2—), 1.58 (m, 2H, —CH_2), 2.60 $\sim$ 2.70 (m, 4H, —CH_2— & —CH_2—), 7.12 $\sim$ 7.46 (m, 8 aromatic protons).
6FCl	0.89 (t, 3H, CH_3—), 1.30 [m, 6H, —$(CH_2)_3$—], 1.59 (m, 2H), 2.60 (t, 2H), 7.07 $\sim$ 7.59 (m, aromatic protons)
8FF	0.88 (t, 3H, CH_3—), 1.30 [m, 10H, —$(CH_2)_5$—, 1.59 (m, 2H, —CH_2—), 2.59 (t, 2H, —CH_2—Ph—), 7.06 $\sim$ 7.45 (m, 7 aromatic protons).
1F5	0.88 (t, 3H, CH_3—), 1.29 [m, 4H, —$(CH_2)_2$—], 1.58 (m, 2H, —CH_2—), 2.27 (d, 3H, CH_3—), 2.60 (t, 2H, —CH_2—), 7.11 $\sim$ 7.44 (m, 7H, aromatic protons).
2d3	0.93 (t, 3H, CH_3—), 1.63 (m, 2H, —CH_3—), 2.59 (t, 2H, —CH_2—), 5.31; 5.78 (d; d, CH_2=), 6.69 (d; d, =CH—), 7.13 $\sim$ 7.49 (m, 8 aromatic protons).

TABLE 2

Elemental Analysis Data for Some Asymmetric Diphenyldiacetylenes

	Found (calculated)		
PTTP	C%	H%	Cl%
15	92.23 (92.26)	7.73 (7.74)	
24	92.25 (92.26)	7.74 (7.74)	
6FCl	78.08 (77.98)	6.00 (5.95)	10.36 (10.46)
8FF	82.10 (82.26)	7.03 (6.9)	
2d3	93.20 (93.29)	6.75 (6.71)	
1F5	86.83 (86.81)	7.02 (6.95)	

example. Tables 1 and 2 summarize ^1H NMR chemical shifts and elemental analysis data for some prepared asymmetric diphenyldiacetylenes, respectively.

4-*n*-Propyl-β,β'-dibromostyrene and 4-*n*-hexyl-β,β'-dibromostyrene

Triphenylphosphine (26.2 g, 0.1 mole) was added in portions to a suspension of CBr_4 (33.1 g, 0.1 mole), Zn powder (6.5 g, 0.1 mole) in 340 ml of dry dichloromethane. The suspension was stirred at room temperature for about 48 hours until a pink color developed. The appropriate 4-*n*-alkylbenzaldehyde (0.05 mole) was then added to this pink suspension and the reaction was stirred for another two hours. A deep brown color appeared as the reaction proceeded. The solution was filtered and the filtrate was evaporated to dryness under reduced pressure. The residue was extracted, several times, with pentane. The solvent of the combined extracts was removed under reduced pressure and then it gave the crude β,β'-dibromostyrene which was purified by column chromatography (silica gel, *n*-hexane as eluent) to yield the product as the pale yellow oil residue (85 ~ 90% yield).

4-*n*-Propylphenyl-1-bromoacetylene

The purified 4-*n*-propyl-β,β'-dibromostyrene (6.11 g, 0,02 mole) and potassium t-butoxide (2.24 g, 0.02 mole) were dissolved in 75 ml of dry toluene and then heated at reflux for four hours. The reaction was cooled to room temperature and filtered. The filtrate was evaporated to dryness and purified by column chromatography (silica gel, *n*-hexane as eluent) to give the bromoacetylide (80% yield). ^1H NMR: $\delta = 0.91$ (t, 3H, CH_3—), 1.61 (m, 2H, —CH_2—), 2.57 (t, 2H, —CH_2—), 7.10 ~ 7.50 (m, 4 aromatic protons).

4-*n*-Hexylphenylacetylene

The purified 4-*n*-hexyl-β,β-dibromostyrene (17.31 g, 0.05 mole) in 50 ml of dry tetrahydrofuran at −78°C under nitrogen atmosphere was treated with 49 ml of 2.5 M *n*-butyllithium and stirred at −78°C for one hour, followed by one hour at room temperature. The reaction was quenched with water, and the ethereal layer was separated. After reextraction of the aqueous layer with ether, the combined extracts were washed with water three times, dried over $MgSO_4$ and evaporated to dryness. The pale yellow oil residue was purified by column chromatography (silica gel, n-hexane as eluent) to yield a colorless liquid of 4-*n*-hexylphenylacetylene (89% yield).

4-*n*-Propyl-4′-*n*-hexyldiphenyldiacetylene

A catalytic amount of cuprous chloride (4 mg) dissolved in a large excess of *n*-butylamine (5 ml) was added to a stirred methanolic solution (15 ml) containing 4-n-hexylphenylacetylene (5 mmole), then hydroxylamine hydrochloride (250 mg) was added in order to reduce any cupric ion formed. The 4-*n*-propylphenyl-1-bromoacetylene (5 mmole) in 15 ml of methanol was added dropwise to this vigorously stirred mixture at 0°C under nitrogen. After about two hours, the product was obtained by filtration and purified by column chromatography (silica gel, *n*-hexane as eluent) to yield the asymmetric 4-*n*-propyl-4′-hexyldiphenyldiacetylene. ^{1}H NMR: $\delta = 0.80 \sim 1.00$ (m, 6H, $2CH_3$—), $1.19 \sim 1.40$ [m, 6H, —$(CH_2)_3$—], $1.50 \sim 1.74$ (m, 4H, 2—CH_2—), $2.49 \sim 2.69$ (m, 4H, 3—CH_2—Ph—), $7.05 \sim 7.55$ (m, 8 aromatic protons). Calculated for $C_{25}H_{28}$: C 91.41, H 8.59; Observed: C 91.40, H 8.60.

Synthesis of 4-*n*-alkyl-3′-fluoro-4′-methyldiphenyldiacetylenes and 4-*n*-alkyl-4-vinyldiphenyldiacetylenes

All these compounds were synthesized by the routes outlined in Scheme 2. An example of the synthesis of 4-*n*-butyl-3′-fluoro-4′-methyldiphenyldiacetylene is given below.

3-Fluoro-4-methylphenlyacetylene

2.7 g of the 2-methyl-3-butyn-2-ol was added dropwise to a stirred mixture of cuprous iodide (70 mg), bis(triphenylphosphine) palladium chloride (70 mg), triphenylphosphine (140 mg) and 2-fluoro-4-iodotoluene (7 g) in 50 ml of dry triethylamine under nitrogen. The reaction mixture was heated to reflux for eight hours and then cooled to room temperature. The saturated aqueous ammonium chloride and dichloromethane were added and the reaction was stirred for another half hour. The aqueous layer was removed and the organic layer washed with dilute HCl and H_2O twice then dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the resulting residue was purified by column chromatography on silica gel to give the alkynol product. The alkynol (0.02 mole) and sodium hydroxide (0.042 mole) were dissolved in 100 ml of dry toluene and heated to reflux for 4 hours until the protecting group was completely removed. After cooling to room temperature, filtration and evaporation of the filtrate gave the crude acetylene which was purified by column chromatography (silica gel, *n*-hexane/dichloromethane = 5:1). ^{1}H NMR: $\delta = 2.25$ (d, 3H, CH_3—), 3.00 (s, 1H, —C≡C—*H*), $7.05 \sim 7.16$ (m, 3 aromatic protons).

4-*n*-Pentyl-3′-fluoro-4′-methyldiphenyldiacetylene

To a stirred methanolic solution (30 ml) of the 3-fluoro-4-methylphenylacetylene (10 mmole) containing a large excess of *n*-butylamine (10 ml) was added a catalytic quantity of cuprous chloride (7 mg), followed by hydroxyammonium chloride (500 mg) to reduce any cupric ion formed. The 4-*n*-pentylphenyl-1-bromoacetylene (10 mmole) dissolved in 30 ml of methanol was then added dropwise and the mixture was stirred at 0°C under nitrogen. After about two hours, the product was obtained by filtration and purified by column chromatography (silica gel, *n*-hexane/dichloromethane = 5:1) to give the white solid products. ^{1}H NMR: $\delta = 0.92(t, 3H, CH_3—)$, 1.25 ~ 1.45 [m, 4H, —$(CH_2)_2$—], 1.52 ~ 1.65 (m, 2H, —CH_2—), 2.25 (d, 3H, CH_3—), 2.58 ~ 2.69 (t, 2H, —CH_2—Ph—), 7.13 ~ 7.45 (m, 7 aromatic protons). Calculated for $C_{22}H_{21}F$: C 86.81, H 6.95; Observed: C 86.83, H 7.00.

IV. RESULTS AND DISCUSSION

We have synthesized fifty-six new asymmetric diphenyldiacetylene compounds. Their representative analytical data are in good agreement with the structures shown. The thermal behavior of these asymmetric dialkyl PTTPs including phase transition temperatures and molar heat of fusion are listed in Table 3. Five symmetric PTTPs which have been reported previously[1] are included for comparison.

All the 4-*n*-alkyl-4′-*n*-alkyl-diphenyldiacetylenes display an enantiotropic nematic phase. Figure 1 presents the DSC heating and cooling thermograms of 4-*n*-ethyl-

TABLE 3

The Phase Transition Temperatures (in °C) and Corresponding Enthalpy Changes (ΔH, in kcal/mol) of the Asymmetric Dialkyl and Alkyl-Alkoxy PTTP Liquid Crystals. Five Symmetric PTTPs Taken from Reference 1 are Included for Comparison.

PTTP	T_{mp}	T_c	ΔH
13	102.5	112.4	3.65
14	75.8	99.2	3.90
15	81.0	104.7	3.06
16	77.5	87.5	5.59
18	78.8	82.5	5.45
22	98.0	(88.0)	4.90
23	79.2	113.5	5.51
24	43.6	97.7	2.47
25	44.7	101.7	4.26
26	50.7	84.2	4.16
28	41.7	77.9	4.39
33	107.5	131.9	6.00
34	83.7	115.0	3.53
35	62.0	115.3	3.41
36	41.5	97.5	2.91
38	44.6	87.5	4.23
44	75.1	101.0	3.40
45	63.5	104.2	3.17
46	24.9	79.7	4.84
48	25.1	78.9	4.15
55	86.0	111.3	4.60
56	60.0	97.8	3.49
58	40.7	88.5	3.20
66	58.6	85.3	–
68	34.1	77.5	2.54
202	104.4	162.5	5.33
302	88.0	187.7	4.42
402	98.4	142.1	5.82
502	68.5	123.7	6.62
602	84.7	108.3	6.02

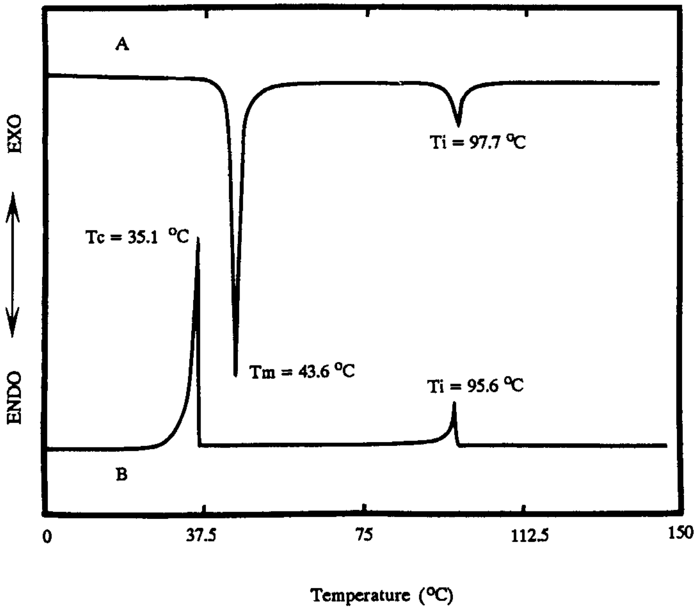


FIGURE 1 DSC thermograms (5°C/min) of PTTP-24: (A) heating scan; (B) cooling scan.

4′-*n*-butyl-diphenyldiacetylene (PTTP-24). From Table 3, we also find that the asymmetric dialkyl PTTPs generally show a lower melting temperature (T_{mp}) and wider nematic range than the symmetric ones with the same total chain length. The melting temperature of PTTP-46 is 24.9°C and PTTP-48 is 25.1°C. Due to supercooling, they remain liquid at room temperature ($\sim$ 22°C) for a few hours. On the other hand, three asymmetric dialkyl PTTP-24, – 36, and – 68 show a modest melting temperature, wide nematic range, and extremely small molar heat of fusion enthalpy ($\Delta H < 3$ kcal/mole). From the Shroder–van Laar equation[16,17] low melting temperature and small ΔH of the individual components play equally important roles in determining the melting point of the eutectic mixture. Thus, the asymmetric dialkyl PTTPs are excellent host candidates for forming eutectic mixtures with a wide nematic range. For demonstration purpose, we formulated a binary eutectic mixture containing 52 wt% of PTTP-24 and 48 wt% of PTTP-36. The melting point of this mixture drops to 10°C while the clearing point stays at 97.7°C. To further lower the melting point, multiple component eutectics consisting of entirely PTTP homologs can be formulated.

From Table 3, the 4-alkyl-4′-alkoxy diphenyldiacetylenes also display an enantiotropic nematic phase. But the alkoxy end group increases both melting and clearing points. All these symmetric and asymmetric PTTP liquid crystals exhibit high birefringence and relatively low viscosity. However, the dielectric constants and the anisotropy ($\Delta\varepsilon$) of these nonpolar liquid crystals are small ($\Delta\varepsilon \sim 1$).[18] The small $\Delta\varepsilon$ results from the high degree of molecular symmetry.

To enhance $\Delta\varepsilon$, three types of polar (F, Cl and CN) PTTPs were synthesized. The dipole moment[19] of CN, Cl and F group is known to be 4.05, 1.55 and 1.43 Debyes, respectively. Thus, the dielectric anisotropy of these PTTP compounds will follow the same order. In addition to dielectric anisotropy these three polar groups also make different contributions to birefringence. The conjugated, two atom linear CN group contributes four π-electrons to the core resulting in a significant enhancement in birefringence. On the other hand, the fluoro group is an electron withdrawing group so that its electronic transitions experience a blue shift[8]. As a result. the fluorinated compounds exhibit a much lower birefringence than the corresponding cyano ones. However, the fluoro compounds possess a much lower viscosity and higher resistivity than the cyano homologs.[20] These two properties are highly desirable for display application. The physical properties of the chloro compounds lie between the CN and F groups.

The phase transition temperatures and corresponding enthalpy changes of the polar PTTPs are listed in Table 4. Unfortunately, most of the axial polar groups cause the melting temperature and molar heat of fusion to increase substantially. The three PTTP-nCl ($n = 2, 4$, and 6), four PTTP-nFCl ($n = 5, 6$ and 8) and PTTP-nOFCl ($n = 6$) show no mesogenic phase at all. The two cyano PTTP homologs (PTTP-6CN, − 8 CN) show quite high melting points, very narrow (~ 2°C) monotropic range, and large heat of fusion enthalpy. Although these cyano compounds exhibit a unusually high birefringence (~ 0.46 at $\lambda = 589$ nm) and large dielectric anisotropy (~ 17), their solubility to a LC host is poor due to the large ΔH value. On the other hand, all the PTTP-nF homologs exhibit an enantiotropic nematic phase except PTTP-2F which shows a monotropic phase transition (its nematic range is from 89.5 to 68.0°C). The well-known odd-even effects[21] are observed for both crystal-to-nematic and nematic-to-isotropic transitions. The dielectric anisotropy of PTTP-4F was measured to be 5 at 1 kHz and at room temperature by the guest-host mixture method.[22]

TABLE 4

The Phase Transition Temperatures (°C) and Corresponding Enthalpy Changes (in kcal/mol) of the Asymmetric Polar Diphenyldiacetylenes. Four PTTP-nF ($n = 3$–6), Taken from Reference 22, are Included for Comparison.

PTTP	T_{mp}	T_c	ΔH
2Cl	143.7		8.76
4Cl	126.7		8.85
6Cl	112.9		6.87
5FCl	82.6		7.21
6FCl	75.4		7.43
6OFCl	111.7		8.42
8FCl	66.7		6.59
2F	92.6	(68.0)	5.95
3F	94.4	102.2	4.85
4F	85.4	87.7	6.00
5F	85.7	89.3	6.23
6F	76.0	80.1	7.43
8F	67.1	73.2	6.30
6FF	65.3	(48.5)	5.95
8FF	69.3	(43.6)	6.75
6CN	145.3	(144.0)	8.06
8CN	139.7	(135.8)	10.12

To further enhance $\Delta\varepsilon$, 4-*n*-alkyl-3′,4′-difluoro-diphenyldiacetylenes (PTTP-*n*FF) were prepared. From Maier–Meier theory,[23] the difluoro compounds should possess a ~ 80% higher $\Delta\varepsilon$ than the corresponding monofluoro ones. In addition, the lateral fluoro substitution widens the inter-molecular separation which, in turn, weakens the molecular associations. As a result, the melting point is reduced. Two disadvantages, decreased birefringence and increased viscosity, of the difluro compounds are observed. The decreased Δn originates from a lower molecular packing density, whereas the increased rotational viscosity results from the increased moment of inertia owing to the lateral fluoro substitution. Both of the two homologs (PTTP-6FF and the − 8FF) exhibit a monotropic phase, as indicated in Table 5. Their nematic range is observed from 40.2 to 31.6°C and from 43.6 to 38.7°C, respectively, through a polarizing microscope. In many binary mixtures containing monotropic LC substances, the melting point may drop significantly and the enantiotropic transition takes place. Table 5 also shows the binary mixtures using two PTTP-6FF and − 8FF homologs at different ratios. Both monotropic and enantiotropic phase transitions may exist depending on the resultant melting point of the binary mixtures.

Another lateral fluoro substitution we studied is represented by the 4-*n*-alkyl-3′-fluoro-4′-methyl-diphenyldiacetylenes (designated as PTTP-1F*n*, $n = 3$–6). Their thermal transition temperatures and corresponding enthalpy changes are listed in Table 6. Relative to the corresponding dialkyl PTTPs, the lateral fluoro group

TABLE 5

Phase Transition Temperatures of Binary Mixtures Consisting of PTTP-6FF and PTTP-8FF at Various Ratios.

PTTP-6FF (%)	PTTP-8FF (%)	Transiton Temperature (°C)
0	100	$\mathrm{K} \xrightarrow{64.7} \mathrm{I}$ $\mathrm{K} \xleftarrow[38.7]{} \mathrm{N} \xleftarrow[43.6]{} \mathrm{I}$
20	80	$\mathrm{K} \xrightarrow{61.5} \mathrm{I}$ $\mathrm{K} \xleftarrow[39.6]{} \mathrm{N} \xleftarrow[42.0]{} \mathrm{I}$
40	60	$\mathrm{K} \xrightarrow{52} \mathrm{I}$ $\mathrm{K} \xleftarrow[29.6]{} \mathrm{N} \xleftarrow[39]{} \mathrm{I}$
50	50	$\mathrm{K} \underset{22}{\overset{30.0}{\rightleftharpoons}} \mathrm{N} \underset{41.8}{\overset{44}{\rightleftharpoons}} \mathrm{I}$
60	40	$\mathrm{K} \underset{24}{\overset{30.2}{\rightleftharpoons}} \mathrm{N} \underset{42}{\overset{44}{\rightleftharpoons}} \mathrm{I}$
80	20	$\mathrm{K} \xrightarrow{35.0} \mathrm{N} \xrightarrow{44} \mathrm{I}$
100	0	$\mathrm{K} \xrightarrow{65.2} \mathrm{I}$ $\mathrm{K} \xleftarrow[31.6]{} \mathrm{N} \xleftarrow[40.2]{} \mathrm{I}$

TABLE 6

The Phase Transition Temperatures (in °C) and Corresponding Enthalpy Changes (ΔH, in kcal/mol) of the PTTP-1Fn and PTTP-2*dn*($n = 3$–6).

PTTP—	T_{mp}	T_c	ΔH
1F3	86.3		6.40
1F4	62.1		5.56
1F5	63.5	70.3	7.53
1F6	40.0		5.67
2d3	87.0	147.5	2.45
2d4	72.2	131.5	2.86
2d5	67.6	133.9	4.19
2d6	68.1	120.3	4.77

decreases the melting point, suppresses the nematic phase and enhances the enthalpy of heat fusion. Among the PTTP-1F*n* homologs synthesized, only PTTP-1F5 shows a narrow nematic phase, from 63.5 to 70.3°C. The melting point suppression can be realized because the lateral fluorine atom reduces the molecular symmetry thus leading to a less efficient molecular packing in the solid phase. It is well-known that lateral substituents broaden a molecule and reduce intermolecular attractions resulting in a lower nematic phase stability.[24]

Also included in Table 6 are four 4-*n*-alkyl-4′-vinyl-diphenyldiacetylene (PTTP-2*dn*, $n = 3$–6) homologs. From Table 6, we find that the vinyl group not only increases the melting point but also broadens the nematic range, as compared to the corresponding dialkyl PTTPs (PTTP-2*n*; $n = 3$–6). The double bond of the vinyl group effectively extends the electronic conjugation length of the molecule. Thus, the terminal vinyl substituent leads to a higher Δn.

IV. CONCLUSION

The synthesis procedures of various derivatives of asymmetric dialkyl and polar PTTP compounds are presented. All the asymmetric dialkyl PTTP liquid crystals show a lower melting temperature and wider nematic range than the symmetric ones with the same total chain length. The alkyl-alkoxy PTTPs still show a wide nematic range except for the increased melting points. For the polar PTTPs, 4-*n*-alkyl-4′-chloro, 4-*n*-alkyl-3′-chloro-4′-fluoro and 4-*n*-hexoyl-3′-chloro-4′-fluoro homologs show no mesogenic phase at all. The 4-*n*-alkyl-4′-fluoro PTTPs display an enantiotropic nematic phase, although narrow. Both 4-*n*-alkyl-3′,4′-difluoro PTTPs and 4-*n*-alkyl-4′-cyano PTTPs ($n = 6$ and 8) exhibit a monotropic phase transition. With the exception of the one with *n*-pentyl end group, the 4-*n*-alkyl-3′-fluoro-4′-methyl PTTPs show no mesomorphic behavior. The lateral fluoro group decreases melting temperature and suppresses the thermal stability of nematic phase dramatically. The cyano group increases melting temperature and enthalpy changes greatly. All the prepared 4-*n*-alkyl-4′-vinyl-PTTPs display an enantiotropic nematic phase. The vinyl end group contributes to the increased melting point and the wider nematic range.

Acknowledgment

The authors would like to thank Prof. C. C. Hsu of National Chiao Tung University for many useful discussions and E. Sherman of Hughes Research Labs. for purity checks. H.B.M. also thanks the U.S. Department of Education grant for Graduate Assistance in Areas of National Need for financial and educational support at USC. This research was supported by the Air Force Office of Scientific Research under contracts F49620-91-0054 and F49620-91-0270 and by the National Science Foundation under contract DMR-9107806.

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