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Synthesis of terminally substituted stilbene-tolane liquid crystals

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Methods for synthesizing substituted alkyl and fluoro stilbene-tolane (PTPDP) liquid crystal materials are presented. These compounds show a slightly higher birefringence than the analogous bistolanes, but higher melting points and heats of fusion. Potential applications of these compounds for optical communications and displays are discussed.

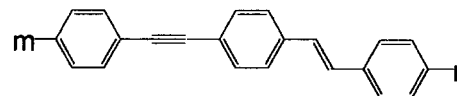
1. Introduction

High birefringence (Δn) liquid crystals have shown promise in a wide variety of applications including polymer-dispersed liquid crystal (PDLC) [1], cholesteric liquid crystal display (Ch-LCD) employing Bragg reflection [2], and optical communications using optical phased arrays (OPA) [3]. In PDLC and Ch-LCD, high Δn improves display brightness and contrast ratio. In OPA, high birefringence reduces cell gap, which results in a faster response time. It has been illustrated that high birefringence LCs can be designed by increasing the molecular conjugation length [4]. Despite their promise, major challenges still remain in lowering the melting temperatures of these compounds.

Polar and non-polar bistolanes (abbreviated as PTPP- mn where P represents a phenyl ring, T a carbon-carbon triple bond, m an alkyl group C_mH_{2m+1} and n can be an alkyl or polar group such as F and CN) have been prepared and their physical properties evaluated [5–18]. Among these compounds, the cyano bistolane exhibits a wide nematic range and birefringence as high as 0.54. However, as might be expected from their symmetric core structure and linear molecular shape, melting temperatures were routinely in excess of 200°C. Substitution of lateral groups on the centre phenyl ring of these species resulted in successful reduction of melting and clearing temperatures [9].

In this paper we report the synthesis and properties of stilbene-tolane compounds (abbreviated as PTPDP,

where D is a double bond) in an attempt to lower melting points from the reported bistolanes. The molecular structure of PTPDP is shown below:



The incorporation of the vinylene (double bond) into the structures should decrease symmetry and thus lower melting points.

2. Experimental

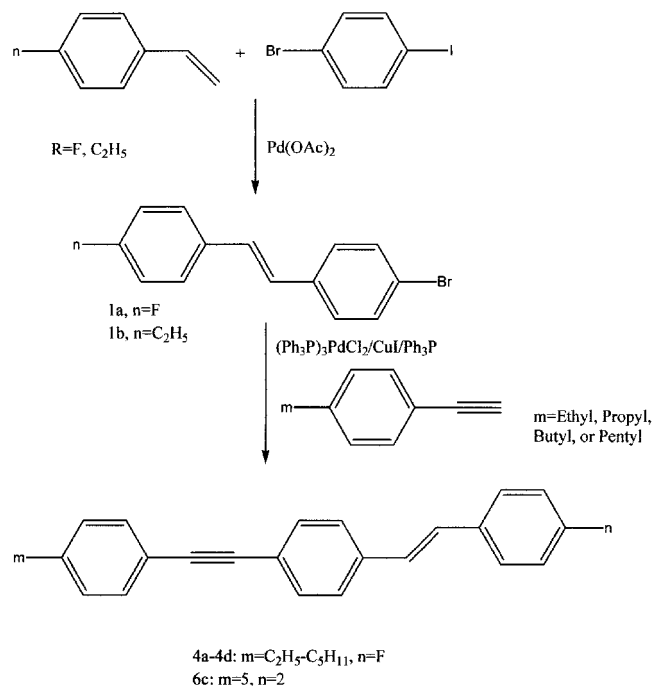
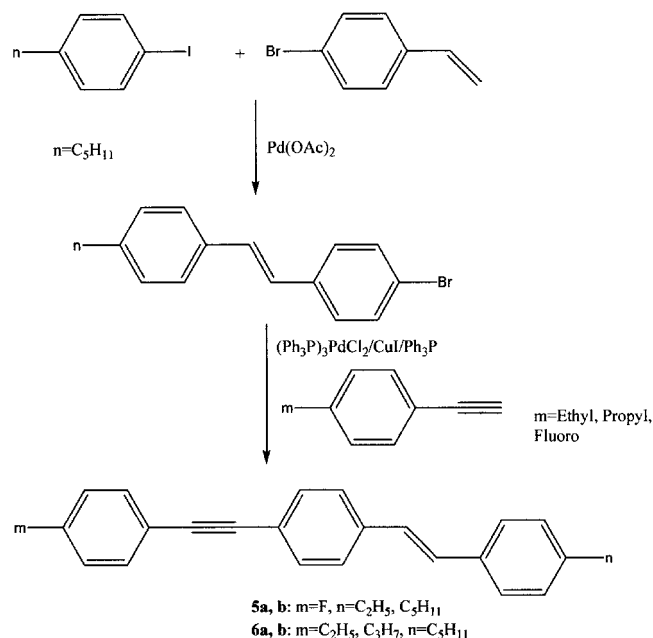
2.1. Characterization and data

All reactions were carried out under N_2 unless otherwise noted. All reagents were of the highest commercial grade available and used without further purification. Substituted ethynylbenzenes were prepared as described in the literature [10] except for the fluoro and pentyl derivatives which were purchased from Aldrich. All NMR spectra were taken on a Bruker AC-250, 250 MHz spectrometer using eight scans, with chemical shifts reported downfield relative to tetramethyl silane. Data was analysed using NUTS software. Differential scanning calorimetry was performed on a Mettler DSC 30 with a heating rate of 10°C min⁻¹.

2.2. Synthesis of PTPDP compounds

Schemes 1 and 2 illustrate the procedures used to synthesize the PTPDP compounds.

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Scheme 1. Synthesis of compounds **4a–4d**, **6c**.Scheme 2. Synthesis of compounds **5a, b** and **6a, b**.

2.2.1. Synthesis of (*E*)-4-bromo-4'-fluorostilbene (**1a**), (*E*)-4-bromo-4'-ethylstilbene (**1b**) and (*E*)-4-bromo-4'-pentylstilbene (**1c**)

Compounds **1a**, **1b** and **1c** were prepared using palladium acetate catalysed coupling [11] according to schemes 1 and 2. The synthesis of **1a** is described below.

A mixture of 5.66 g (20 mmol) of 4-bromoiodobenzene, 2.68 g (22 mmol) of fluorostyrene, 0.045 g (0.2 mmol)

of palladium acetate, 3.1 ml (22 mmol) of triethylamine and 4 ml of acetonitrile was placed in a septa-capped vial under nitrogen and was heated at 100°C for 24 h. After cooling, the solid mass was quenched with 100 ml of 10% HCl and the insoluble solid was collected by vacuum filtration. The collected solid was recrystallized from absolute ethanol yielding 3.38 g of white solid (61%). ¹H NMR, $\delta = 87.0$ (m, 4H), 7.4 (m, 6H).

2.2.2. Synthesis of PTPDP compounds (**4a–d**, **5a, b** and **6a–c**)

PTPDP compounds were prepared by the coupling of 4-*n*-alkylphenylacetylenes or 4-fluoroethynylbenzene with compounds **1a**, **1b** or **1c**. The preparation of PTPDP-5F is described below.

A mixture of 0.172 g (1 mmol) of ethynylpentylbenzene and 0.277 g (1 mmol) of **1c** was dissolved in 10 ml of triethylamine. To this solution was added 0.026 g of triphenyl phosphine (0.1 mmol, 10%), 0.002 g cuprous iodide (0.01 mmol, 1%) and 0.007 g of dichlorobis(triphenyl)phosphine palladium (0.01 mmol, 1%). This mixture was heated under reflux for 5 h and the resulting mixture concentrated by rotary evaporation. The residue was dissolved in dichloromethane and washed three times with 10% HCl. The organic layer was dried over anhydrous MgSO₄ and again concentrated by rotary evaporation. The resulting solid was recrystallized from chloroform to give 0.191 g of light yellow crystalline solid (52%). ¹H NMR, $\delta = 0.873$ (t, 3H, $J = 6.6$ Hz), 1.29 (m, 4H), 1.55 (m, 2H), 2.59 (t, 2H, $J = 7.5$ Hz), 7.06 (m, 6H), 7.46 (m, 8H).

3. Results and discussion

3.1. Effect of double bond

Phase transitions and corresponding enthalpy changes for PTPDP compounds and two bistolanes are listed in the table. All PTPDP compounds showed melting points greater than 195°C and clearing temperatures in excess of 240°C. The melting temperatures compare unfavourably with those of the corresponding bistolanes, which exhibit melting temperatures in the 140°C range and clearing temperatures near 200°C. Nevertheless, the enthalpy value for the PTPDP compounds remain not too large, which helps boost the solubility while forming eutectic mixtures.

- (i) For PTPDP-*mn* where $m = \text{C}_2\text{--C}_5$ and $n = \text{fluoro}$, **4a–4d**, melting temperatures increase slightly from C₂–C₄ with a marked increase for C₅. Clearing temperatures decrease from C₂–C₄ with an increase for C₅.
- (ii) For compounds where $m = \text{fluoro}$ and $n = \text{alkyl}$, **5a, b**, melting and clearing temperatures decrease with increasing chain length (see figure 1).

Table. Phase transition temperatures (in °C) and fusion enthalpy (ΔH , in kcal mol⁻¹) of the PTPDP-*mm* homologues. The bistolanes PTPTP-25 and -35 are included here for comparison. Δn is extrapolated from 10% mixture in E63 host at $\lambda = 633$ nm and $T = 22^\circ\text{C}$.

	Compound	<i>m</i>	<i>n</i>	Phase transitions	ΔH	Δn
4a	PTPDP-2F	2	F	Cr 224.0 N 261.2 I	6.40	
4b	PTPDP-3F	3	F	Cr 225.5 N 256.0 I	4.89	
4c	PTPDP-4F	4	F	Cr 225.0 N 243.9 I	4.32	
4d	PTPDP-5F	5	F	Cr 230.2 N 252.4 I	5.21	
5a	PTPDP-F2	F	2	Cr 229.2 N 263.2 I	6.39	
5b	PTPDP-F5	F	5	Cr 227.7 N 248.9 I	4.36	
6a	PTPDP-25	2	5	Cr 203.5 N 250.4 I	4.34	
6b	PTPDP-35	3	5	Cr 205.5 N 252.5 I	4.30	
6c	PTPDP-52	5	2	Cr 195.1 N 240.7 I	3.92	0.41
7a	PTPDP-25	2	5	Cr 138.6 N 202.2 I	3.87	0.40
7b	PTPDP-35	3	5	Cr 145.2 N 192.5 I	3.38	

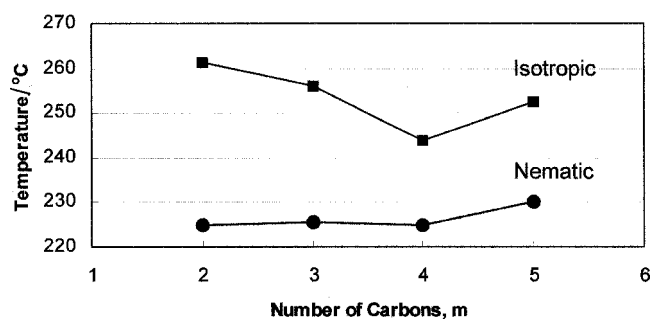


Figure 1. Phase transition temperatures of PTPDP-*mm* homologues with $n = \text{F}$.

- (iii) For compounds in which $n = \text{alkyl}$ and $m = \text{alkyl}$, **6a–c**, significantly higher melting temperatures than for the bistolane analogs **7a, b** are seen.

3.2. Absorption spectra

The double bond is expected to elongate the molecular conjugation. To evaluate the absorption spectra, we doped 1% of PTPDP-25 into a UV transparent ZLI-2359 LC mixture and measured the optical density in the 185–400 nm range using a Perkin-Elmer Lambda 9 spectrophotometer. A 6 μm homogeneous cell with quartz substrates was used for absorption measurements. Results are shown in figure 2. Also included for comparison is the absorption spectra of PTPTP-25. From figure 2, the absorption edge of PTPDP-25 extends to 380 nm, which is nearly 30 nm longer than that of PTPTP-25.

3.3. Physical properties

Due to the high melting points of these PTPDP liquid crystals, measurement of their physical properties in the nematic phase is difficult. Thus, we doped 10% of PTPDP-52 into a commercial E63 mixture and extracted its birefringence value. The extrapolated Δn is 0.41 at

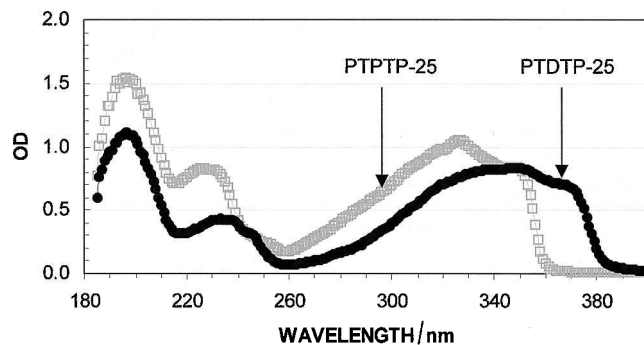


Figure 2. Measured optical density (OD) of PTPTP-25 and PTPDP-25. In experiments, 1% of each compound was dissolved in ZLI-2359. Cell gap $d = 6 \mu\text{m}$, homogeneous alignment, $T = 22^\circ\text{C}$.

$T = 22^\circ\text{C}$ and $\lambda = 633$ nm. This value is comparable to that of the bistolane PTPTP-52.

From the birefringence dispersion model, Δn is affected by several factors, such as electronic transition wavelengths, differential oscillator strength, molecular packing density, and temperature. The double bond makes positive and negative contributions to the observed birefringence. On the positive side, it elongates the conjugation. On the negative side, the kink somewhat decreases the differential oscillator strength. As a result, the birefringence of PTPDP-52 is only slightly higher than that of PTPTP-52.

4. Conclusion

A series of PTPDP compounds, terminally substituted liquid crystals, were synthesized and characterized in an attempt to decrease phase transition temperatures relative to the previously known bistolane analogues. Insertion of the double bond in place of one of the triple bonds of the bistolane, though decreasing symmetry, actually increased the phase transition temperatures. This phenomenon can be attributed to increased conjugation efficiency of the double bond relative to the triple bond [12]. This conjugation efficiency causes increased rigidity, and thus higher phase transitions. Another example of this is the difference in melting temperature of *t*-stilbene and diphenyl acetylene. In the fluoro series, the position of the fluorine relative to the double or triple bonds showed little effect, while the alkyl-alkyl species showed decreased phase transition temperatures relative to the fluoro series.

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