

# Synthesis of Asymmetric Tolane Liquid Crystals for Display Application

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## ABSTRACT

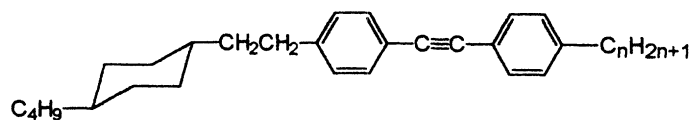
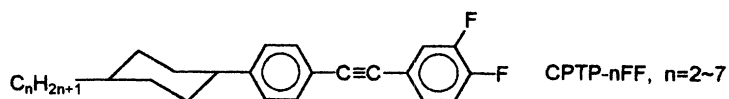
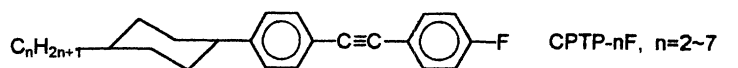
Four series of trans-cyclohexyl-based tolans, i.e., 4-(trans-4-alkylcyclohexyl)-4'-fluorotolans, 4-(trans-4-alkylcyclohexyl)-3',4'-difluorotolans, 4-[2-(trans-4-alkylcyclohexyl)ethyl]-4'-alkyltolans and fluorinated 4-[2-(trans-4-alkylcyclohexyl)ethyl] tolans are prepared and characterized. All the obtained compounds display nematic liquid crystalline phases. The results demonstrate that incorporation of a cyclohexyl ring in the mesogen core structure leads to form a wide temperature range of mesophase. However it also increases the tendency to form a smectic phase. The dielectric anisotropy ( $\Delta \epsilon$ ) and birefringence ( $\Delta n$ ) of some selected compounds were measured by a guest-host method. All of those compounds studied show relatively high dielectric anisotropy and birefringence.

**Keywords:** nematic liquid crystals, fluorinated tolans, trans-cyclohexyl based liquid crystals.

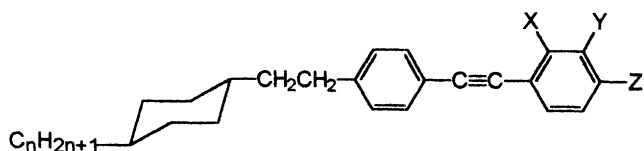
## 1. INTRODUCTION

Nematic liquid crystals (LCs) with high birefringence ( $\Delta n$ ), low viscosity, low threshold voltage ( $V_{th}$ ), and wide nematic range are particularly useful for infrared light valves<sup>1</sup> and polymer dispersed LC displays<sup>2</sup>. High viscosity shortens the response times, and low  $V_{th}$  simplifies the driving electronics. Low  $V_{th}$  is especially important for polymer dispersed LCs where a significant portion of the applied voltage is shielded by the polymer matrix<sup>3</sup>, so that the voltage operating across the LC droplets is far less than the applied voltage. As a result, a relatively high voltage is needed to make the LC device active.

Recently, we synthesized several series of diphenyl-diacetylenic LC compounds which possess a high birefringence<sup>4-7</sup>. However the highly conjugated molecules are often associated with a high melting point and large viscosity. Therefore, their usefulness is quite limited. Fluorinated LC compounds<sup>8-10</sup> are known for their modest dielectric anisotropy and low viscosity. The goal of this study is to present the synthesis and characterization of four series of asymmetric tolane liquid crystals. Their general formulae are as follows:



CEPTP-4n, n=4~6



CEPTP-nF, X=H, Y=H, Z=F, n=4,5

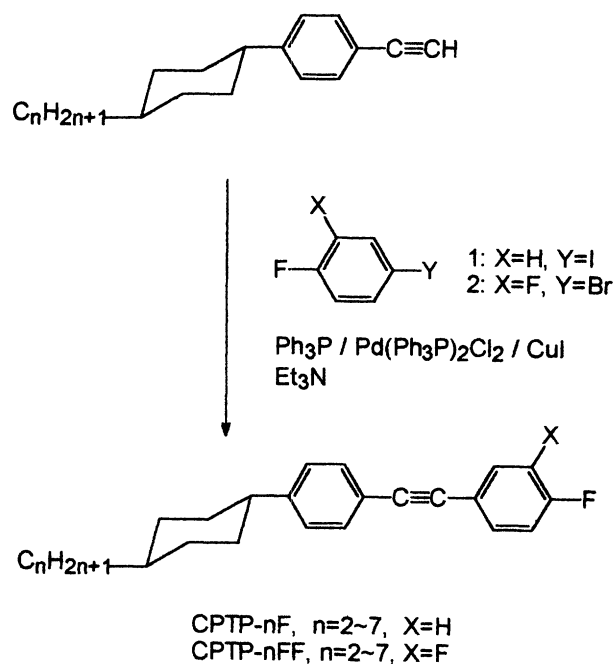
CEPTP-nFF, X=F, Y=H, Z=F, n=4,5

CEPTP-nFFF, X=F, Y=F, Z=F, n=4,5

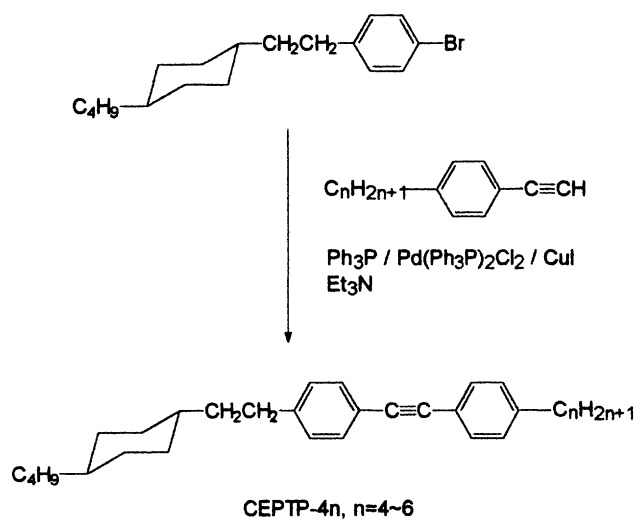
The structure-property relationships for the compounds prepared are discussed.

## 2. EXPERIMENTAL

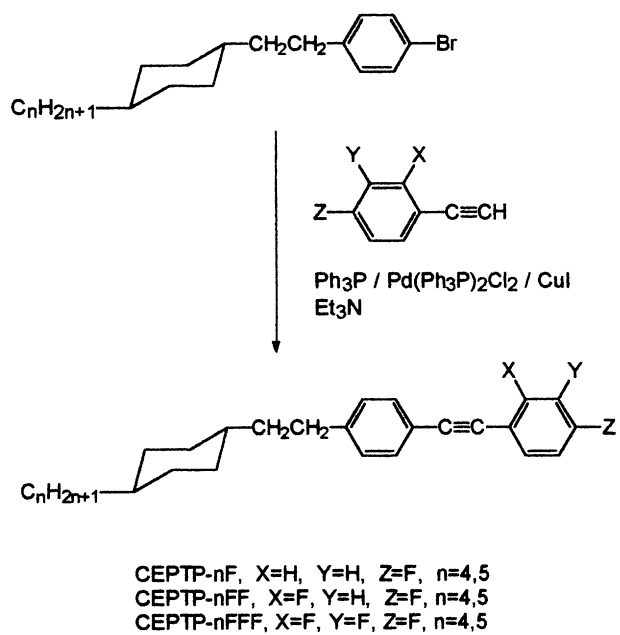
The synthetic route used to prepare the asymmetric tolans is outlined in Schemes 1-3.



Scheme 1: Synthesis of fluorinated 4-(trans-4-alkylcyclohexyl) tolans



Scheme 2 : Synthesis of 4-[2-(trans-4-butylcyclohexyl)ethyl]-4'-alkyltolanes



Scheme 3 : Synthesis of fluorinated 4-[2-(trans-4-alkylcyclohexyl)ethyl]tolanes

4-(trans-4-alkylcyclohexyl)phenylacetylenes and 1-(trans-4-alkylcyclohexyl)-2-(4-bromo-phenyl)ethanes were prepared according to the literature methods<sup>10,11</sup>. 4-(trans-4-alkylcyclohexyl)-4'-fluorotolanes and 4-(trans-4-alkylcyclohexyl)-3', 4'-difluorotolanes were prepared respectively by the coupling of a 4-(trans-4-alkylcyclohexyl)phenylacetylene with 4-fluoroiodobenzene and 3,4-difluorobromobenzene<sup>7,12</sup>. 4-[2-(Trans-4-alkylcyclohexyl)ethyl]-4'-alkyltolanes and fluorinated 4-[2-(trans-4-alkylcyclohexyl)ethyl]tolanes were prepared by the coupling of 1-(trans-4-alkylcyclohexyl)-2-(4-bromophenyl) toluene with 4-alkylphenylacetylene and fluorophenyl acetylene. The products were purified several times by column chromatography and recrystallization until glc proved that their purities were greater than 99 per cent.

### 3. RESULTS AND DISCUSSION

#### 3.1 Phase transitions of CPTP-nF and CPTP-nFF

The phase transitions and corresponding enthalpy changes for compounds CPTP-nF and CPTP-nFF are listed in Table 1. All of the synthesized compounds reveal mesomorphic properties. In the CPTP-nF homologs, both

Table 1 : Phase Transition temperatures and enthalpy changes of compounds CPTP-nF and CPTP-nFF

compound	T/°C ( $\Delta H/\text{kcal mol}^{-1}$ )
CPTP-2F	K 81.7 (3.64) N 162.2 (0.15) I
CPTP-3F	K 97.8 (4.39) N 191.8 (0.21) I
CPTP-4F	K 82.5 (2.36) S 96.2 (0.97) N 183.9 (0.19) I
CPTP-5F	K 85.8 (-) S 91.8 (5.30) N 187.5 (0.21) I
CPTP-6F	K 74.5 (6.34) S 97.6 (1.05) N 180.5 (0.19) I
CPTP-7F	K 63.2 (6.99) S 89.4 (0.75) N 185.7 (0.17) I
CPTP-2FF	K 63.8 (3.42) N 120.3 (0.09) I
CPTP-3FF	K 91.4 (6.23) N 145.7 (0.11) I
CPTP-4FF	K 73.4 (5.32) N 144.1 (0.10) I
CPTP-5FF	K 81.2 (6.58) N 155.0 (0.13) I
CPTP-6FF	K 65.6 (9.47) N 141.5 (0.13) I
CPTP-7FF	K 54.6 (7.19) N 147.5 (0.14) I

K = crystal

N = nematic

S = smectic

I = isotropic

CPTP-2F and CPTP-3F show respectively a nematic phase, while CPTP-4F - CPTP-7F present respectively a nematic and a smectic phases. The tendency to form a smectic phase increases as the alkyl chain length increases. In the CPTP-nFF homologs, all synthesized compounds, however, reveal only a nematic phase. The compounds with difluoro-substitution exhibit a relatively lower melting temperature than the corresponding

compounds with monofluoro-substitution, presumably because the lateral fluoro-substituent increases the intermolecular separation and therefore weakens the molecular attractive forces.

Figures 1 and 2 depict the effect of alkyl chain length on the phase transitions of both series of asymmetric tolane LCs. The odd-even effect is observed for both series of compounds. Those compounds containing even carbon number on the alkyl chains show relatively lower melting points than the others. Generally speaking, among both series of homologs, both CPTP-3F and CPTP-3FF show respectively a highest melting point whereas both CPTP-7F and CPTP-7FF exhibit respectively a lowest melting point. Therefore both CPTP-7F and CPTP-7FF also present respectively a widest temperature range of mesophase.

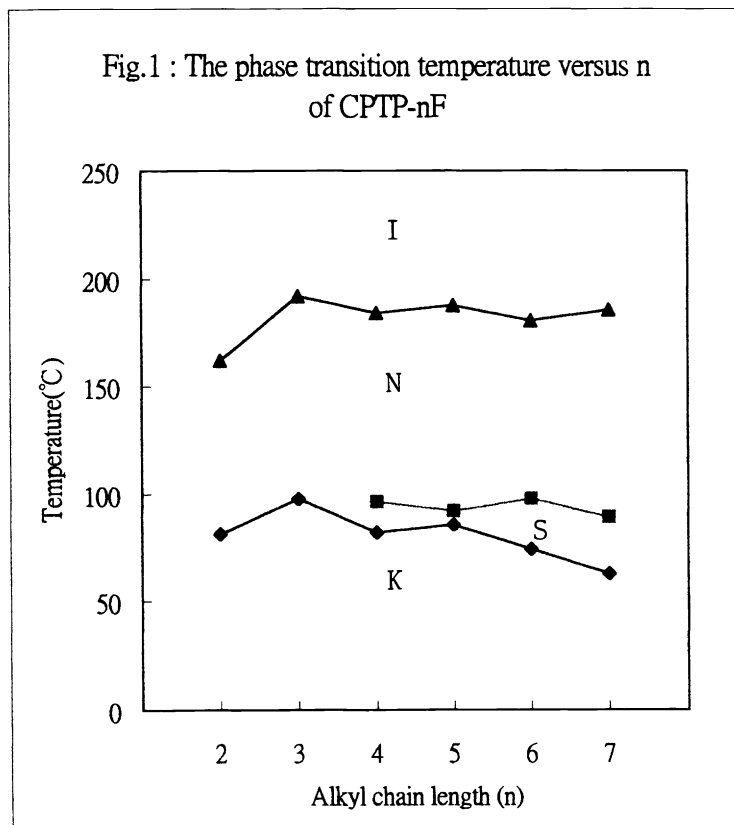
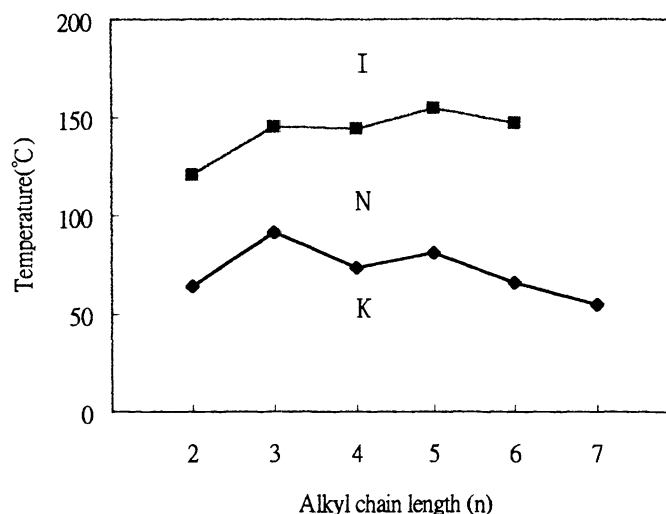


Fig.2 : The phase transition temperature versus n of CPTP-nFF



### 3.2 Phase transitions of CEPTP-4n

The phase transitions and corresponding enthalpy changes of CEPTP-4n are listed in Table 2.

Table 2 : Transition temperatures and enthalpy changes of compounds of 4-[2-(trans-4-alkylcyclohexyl)ethyl]-4'-alkyltolanes

Compound	T/°C ( $\Delta H/\text{kcal mol}^{-1}$ )
CEPTP-44	K 53.4 (5.19) N 125.2 (0.37) I
CEPTP-45	K 47.3 (4.27) N 123.9 (0.35) I
CEPTP-46	K 34.7 (-) S 44.6 (5.64) N 115.5 (0.18) I

All three compounds show very wide temperature range of nematic phase. As the alkyl chain length increases, the melting point of the obtained compound decreases. Compound CEPTP-4,6 show the lowest melting point and widest temperature range of mesophase. However it also form a smectic phase. The results demonstrate that incorporation of a tran-cyclohexylethyl group in the tolane mesogenic core can also increase dramatically the tendency to form a mesophase.

### 3.3 Phase transitions of CEPTP-nF, CEPTP-nFF and CEPTP-nFFF.

Table 3 summarizes the thermal transitions and corresponding enthalpy changes of compounds CEPTP-nF,

CEPTP-nFF and CEPTP-nFFF. Four fluorinated and difluorinated tolanes, CEPTP-4F, CEPTP-5F, CEPTP-4FF and CEPTP-5FF, exhibit respectively a nematic phase. Both difluorinated tolanes reveal relatively lower phase transition temperature than both fluorinated tolanes reveal relatively lower phase transition temperatures than both fluorinated tolanes. This means that the lateral fluoro-substituent increases the intermolecular separation and therefore weakens the molecular attractive forces. Both trifluorinated tolanes show very different mesomorphic behavior in comparison with that of fluorinated and difluorinated tolanes. Compound CEPTP-4FFF exhibits a nematic and smectic phases while CEPTP-5FFF reveals only a monotropic nematic phase. The reason could be due to the odd number carbon chain which is inconsistent with the trifluoro substituents in the molecular packing. Comparing the thermal behavior of this series of fluorinated and difluorinated compounds with that of corresponding CPTP-nF and CPTP-nFF compounds, confirms that incorporating a flexible ethyl group in the mesogenic core decreases not only the phase transition temperatures but also the tendency to form a smectic phase.

### 3.4 Comparison of the mesomorphic behavior of CPTP-nF and CPTP-nFF with that of PTP-nF and PTP-nFF

Table 3 : Transition temperatures and enthalpy changes for the fluorinated 4-[2-(trans-4-alkylcyclohexyl)ethyl]tolanes

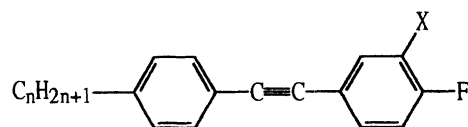
Compound	T/°C ( $\Delta H/\text{kcal mol}^{-1}$ )
CEPTP-4F	K 76.2 (8.08) N 141.0 (0.36) I
CEPTP-5F	K 77.4 (6.08) N 145.3 (0.30) I
CEPTP-4FF	K 60.3 (5.46) N 118.1 (0.23) I
CEPTP-5FF	K 66.6 (6.60) N 133.0 (0.42) I
CEPTP-4FFF	K 89.3 (-) S 98.8 (7.26) N 120.3 (0.29) I
CEPTP-5FFF	K [97.2 (0.16)] N 98.8 (1.26) I

[ ] : means monotropic transition

Table 4 reports the thermal transitions of 4-alkyl-4'-fluorotolanes (PTP-nF) and 4-alkyl-3',4'-difluorotolane (PTP-nFF) which were reported previously<sup>12</sup>. According to the data list in Table 4, both PTP-nF and PTP-nFF homologs exhibit no mesophase. Comparing the thermal behavior of both series of compounds with that of CPTP-nF and CPTP-nFF, confirms that incorporation of a cyclohexyl ring in the tolane mesogenic core increases dramatically the tendency to form a mesophase. Finally, we use a guest-host method to measure the dielectric constants and refractive indices at room temperature ( $T=22^\circ\text{C}$  or  $T_r=0.86$ ). The extrapolated  $\Delta n$  and  $\Delta \epsilon$  values for compounds CPTP-6F are 0.17 and

4.06 respectively, and those for compound CPTP-6FF are 0.15 and 5.82, respectively. Both compounds are useful in formulating eutectic mixtures with enhanced dielectric anisotropy.

Table 4 : Phase transition temperatures and enthalpy changes of compounds PTP-nF and PTP-nFF



Compound	X	T/°C (ΔH/kcal mol <sup>-1</sup> )
PTP-3F	H	K 50.8(5.77) I
PTP-4F	H	K 56.7(4.43) I
PTP-5F	H	K 64.2(6.12) I
PTP-6F	H	K 45.8(5.33) I
PTP-2FF	F	K 28.0(3.97) I
PTP-3FF	F	K 37.8(6.35) I
PTP-4FF	F	K 50.3(6.05) I
PTP-5FF	F	K 49.4(5.29) I
PTP-6FF	F	K 41.7(5.81) I

#### 4. CONCLUSION

Four series of asymmetric tolanes, 4-(trans-4-alkylcyclohexyl)-4'-fluorotolanes, 4-(trans-4-alkylcyclohexyl)-3', 4'-difluorotolanes, 4-[2-(trans-4-alkylcyclohexyl)ethyl]-4'-alkyltolanes and fluorinated 4-[2-(trans-4-alkylcyclohexyl)ethyl]tolanes have been prepared and characterized. All four series of asymmetric tolanes exhibit very wide temperature range of nematic phase. The results demonstrate that incorporation a cyclohexyl ring in the tolane mesogenic core, increases dramatically the tendency to form a mesophase. The synthesized liquid crystal compounds which show moderate Δn value and high Δε value, are useful in formulating eutectic mixtures for display application.

#### 5. ACKNOWLEDGEMENT

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