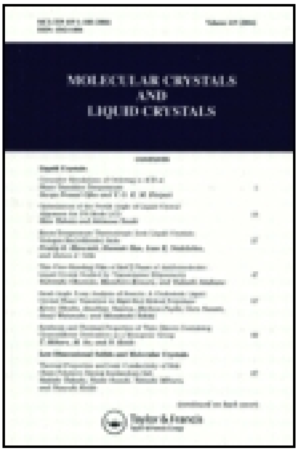

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High Birefringent Liquid Crystals

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HIGH BIREFRINGENT LIQUID CRYSTALS

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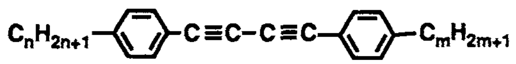
Abstract Several liquid crystal dyes and fluorinated compounds with high birefringence are synthesized and their properties evaluated. These polar compounds are useful dopants for enhancing the dielectric anisotropy of the dialkyl diphenyl-diacetylene host.

1. INTRODUCTION

Liquid crystals (LCs) with high birefringence ($\Delta n>0.3$), low viscosity, low threshold voltage, wide nematic range, and small absorption are particularly attractive for infrared[1] and microwave[2] applications. High Δn can be achieved by increasing the molecular conjugation length. However, the highly conjugated molecules are often associated with a high melting point and large viscosity.

Recently we found that the asymmetric dialkyl diphenyl-diacetylenes (with structure shown below; P stands for phenyl ring, T for triple bond, and n and m for number of carbons in the alkyl chains) exhibit a high birefringence ($\Delta n \sim 0.35$), low viscosity, low melting and high clearing temperatures and small heat fusion enthalpy (ΔH).[3]



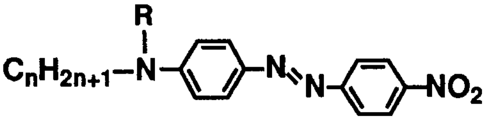
(PTTP-nm)

Low melting point and small ΔH play equally important role in lowering the melting point of the eutectic mixture.[4,5] Thus, PTTP-nm are ideal hosts for forming eutectic mixtures. However, their dielectric anisotropy is too small ($\Delta\varepsilon$~0.8). As a result, the threshold voltage (V_{th}~3.5 V_{rms}) is too high. To improve $\Delta\varepsilon$, several cyano, fluoro and chloro diphenyl-diacetylenes have been developed.[3, 6-8] These polar compounds indeed show enhanced $\Delta\varepsilon$. However, their melting temperatures are too high and ΔH too large so that their solubility in the eutectic mixture is limited.

In this paper, we report on the studies of high birefringent polar LC compounds. The purpose is to use these polar LCs as dopants for enhancing the dielectric anisotropy of the host PTTP-nm mixture. The polar compounds considered include nitroazobenzene LC dyes, fluoro diacetylenes and fluoro tolanes.

2. LC DYES

The nitroazobenzene dyes exhibit a high Δn, modest ΔH, huge dielectric anisotropy ($\Delta\varepsilon$~40) and excellent solubility.[9] Their structure is shown below:



Here R= H or CH_3. Table I shows the phase transition temperatures of the nitroazobenzene dyes we synthesized. From Table I, we see that several dyes exhibit mesogenic phase. In particular, the C-5 dye (with R=H and n=5) shows a melting point of about 85°C and relatively small ΔH. Thus, its solubility to most commercially available LC host mixtures would be very good. In a solubility test, we found that the C-5 dye is soluble to E-7 LC mixture as high as 30%.

For a longer side chain length (larger n), smectic-A phase appears. However, the melting point does not drop too noticeably.

It is surprising to note that simply replacing R by a methyl group, the mesogenic phase no longer exists (c.f. last 3 rows in Table I). Moreover, the melting point increases by about 20 degrees as compares to their corresponding compounds with R=H. The detailed physical mechanisms responsible for the observed phase transition are not yet clear. However, the results listed in Table I imply that hydrogen bonding between molecules plays an important role in increasing the short range interactions at the liquid state. As a result, mesogenic phase appears.

TABLE I Phase transition temperatures (in °C) and heat fusion enthalpy (ΔH in kcal/mol) of the nitroazobenzene dyes. Here K, S_A, N and I stand for crystalline, smectic-A, nematic and isotropic phase, respectively. ( ) means monotropic transition.

R	n	Phase transitions	ΔH
H	4	K 109.1 I	6.55
H	5	K (75.5) N 84.6 I	5.79
H	6	K 85.7 N 86.2 I	7.82
H	7	K (69.7) S_A (79.4) N 86.1 I	7.32
H	8	K (68.2) S_A 81.9 N 85.4 I	8.10
H	9	K 76.0 S_A 85.6 N 86.9 I	9.44
H	10	K 84.3 S_A 89.0 I	9.69
H	11	K 90.7 S_A 93.3 I	10.10
H	12	K 101.1 I	11.39
H	14	K (93.3) S_A 98.8 I	13.30
CH_3	5	K 102.1 I	5.40
CH_3	6	K 119.0 I	8.55
CH_3	7	K 112.4 I	---

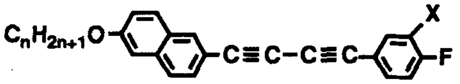
The large Δε of these LC dyes results from their extraordinarily strong dipole moment due to the amino-nitro intramolecular change transfer. Adding 10% of this LC dye to the diphenyl-diacetylenic host reduces the threshold voltage from 3.5 to 1 V_{rms} while only increasing the viscosity by less than 30%. As compared to the commercial anthraquinone dye, the viscosity of the nitroazobenzene dye is about one order of magnitude lower. These LC dyes will also find useful application in the guest-host devices.

3. FLURO COMPOUNDS

Several fluorinated diacetylene and tolane compounds are synthesized. Some exhibit wide nematic range and small heat fusion enthalpy. Thus, they are useful as dopants.

3.1 Fluoro Naphthylene Diacetylenes

The fluoro diacetylenes we studied have structures shown below:



(NTTP-nOF)

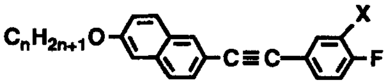
where X=H or F. For X=H, the compound is abbreviated as NTTP-n0F, and for X=F, it is abbreviated as NTTP-n0FF where N stands for the naphthylene ring. Table II shows the phase transition temperatures of the NTTP-n0F and NTTP-n0FF compounds we synthesized.

TABLE II Physical properties of NTTP-n0F and NTTP-n0FF compounds. K, S, N and I represent crystal, smectic, nematic and isotropic phase, respectively. The Δn (at λ=589 nm, 22°C) and Δε (1kHz sine wave frequency) are extrapolated from 10% mixture in ZLI-2359. ΔH is in unit of kcal/mol.

LCs	Phase Transition (°C)	Δn	Δε	ΔH
NTTP-30F	K 132.4 N 176.8 I			6.05
NTTP-40F	K 107.3 N 177.1 I			6.07
NTTP-50F	K 106.8 N 177.9 I			8.82
NTTP-60F	K 113.1 N 173.9 I	0.31	7.70	5.96
NTTP-80F	K 104.8 N 160.0 I			5.86
NTTP-30FF	K 126.1 N 145.8 I			7.58
NTTP-40FF	K 126.0 N 154.6 I			8.19
NTTP-50FF	K 105.1 N 140.3 I			8.01
NTTP-60FF	K 91.4 N 142.9 I	0.28	11.1	5.11
NTTP-80FF	K 88.6 N 133.1 I			6.36

From Table II we find that these highly conjugated LC compounds all exhibit a relatively high melting temperature. The difluoro LCs possess a slightly lower melting point and higher dielectric anisotropy than their corresponding mono-fluoro substitution. The lower melting point is because the difluoro substitutions increase the inter-molecular distance and therefore weakening the molecular attraction forces and the higher dielectric anisotropy results from its larger effective dipole moment. On the other hand, the naphthylene-based LCs do not exhibit a very high Δn. This is because the electron conjugation in these rings is bent from the principal axis. As a result, the differential molecular polarizability is reduced and Δn is not so high as anticipated.

3.2 Fluoro Naphthylene Tolanes



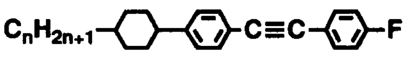
where X=H or F, and their associated compounds are abbreviated as NTP-n0F, and NTP-n0FF, respectively. Table III shows the physical properties of these compounds. Due to the shorter conjugation length, the Δn and $\Delta\varepsilon$ of these compounds are all lower than their corresponding diacetylenes. Also, the nematic range of these naphthylenic tolanes is rather narrow.

TABLE III Same as Table II except for NTP-n0F and NTP-n0FF.

LCs	Phase Transition (°C)	Δn	$\Delta\varepsilon$	ΔH
NTP-30F	K 122.0 N 129.5 I			6.66
NTP-40F	K 110.7 N 134.0 I			6.66
NTP-50F	K 104.9 N 123.0 I			5.05
NTP-60F	K 97.2 N 124.3 I	0.24	5.47	5.50
NTP-80F	K 93.8 N 117.5 I			8.92
NTP-30FF	K 117.9 I			7.21
NTP-40FF	K (69.9) N 92.0 I			6.10
NTP-50FF	K 74.5 N 85.4 I			4.29
NTP-60FF	K 73.1 N 88.2 I	0.21	9.19	4.43
NTP-80FF	K (73.8) N 87.2 I			9.54

3.3 Fluorinated Cyclohexane Tolanes

To widen nematic range while preserving large dielectric anisotropy, fluorinated cyclohexane tolanes are considered. Their structure is shown as following:



(CPTP-nF)

The phase transition temperature, heat fusion enthalpy, birefringence and dielectric anisotropy of CPTP-nF compounds are listed in Table IV.

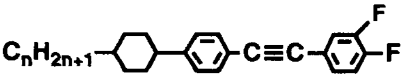
TABLE IV Same as Table II except for CPTP-nF.

LCs	Phase Transition (°C)	Δn	Δε	ΔH
CPTP-2F	K 81.7 N 162.2 I			3.64
CPTP-3F	K 97.8 N 191.8 I			4.39
CPTP-4F	K 82.5 S_G 96.2 N 183.9 I			4.12
CPTP-5F	K 85.8 S_G 91.8 N 187.5 I			5.30
CPTP-6F	K 74.5 S_A 97.6 N 180.5 I	0.17	4.06	6.34
CPTP-7F	K 62.2 S_A 89.4 N 185.7 I			6.99

From Table III, the short-chain homolog CPTP-2F shows a wide nematic range and a very small ΔH. The dielectric anisotropy of these fluoro tolanes is about 4. Moreover, these tolanes are known to have a relatively low viscosity.[10] These compounds are excellent candidates for forming eutectic mixtures for super twist nematic displays where the required Δn ranging from 0.15 to 0.20.

3.4 Difluoro Cyclohexane Tolanes

To further enhance Δε, some difluoro cyclohexane tolanes (with structure shown below) are considered.



(CPTP-nFF)

Results are listed in Table V. Generally speaking, a difluoro tolane shows a lower melting temperature, lower Δn but higher Δε than the corresponding mono-fluoro tolane. From Table V, a longer chain length does not necessarily lead to a lower melting temperature. For example, CPTP-2FF shows both low melting point, wide nematic range and small ΔH. In addition, its viscosity is expected to be the lowest among its homologs. Thus, CPTP-2FF is the most attractive candidate in this series.

A common issue for display application is the chemical-, photo- and thermal-stabilities of LCs. The photostability of a LC depends on its UV absorption. The electronic absorption edge of fluoro tolanes occurs at ~320 nm, similar to cyano-biphenyl.[11] Thus, any UV radiation below this cutoff wavelength has to be filtered in order to protect the LC panel. For direct view displays, the sheet polarizers employed serve as natural UV filters for the LC panel. However, for projection displays, a prism-type polarizer is normally used in order to achieve high brightness. This prism does not block out UV completely. Thus, an additional UV filter is needed.[12]

TABLE V Same as Table II except for CPTP-nFF.

LCs	Phase Transition (°C)	Δn	Δε	ΔH
CPTP-2FF	K 63.8 N 120.3 I			3.42
CPTP-3FF	K 91.4 N 145.7 I			6.23
CPTP-4FF	K 73.4 N 144.1 I			5.32
CPTP-5FF	K 81.2 N 155.0 I			5.30
CPTP-6FF	K 65.6 N 141.5 I	0.15	5.82	6.34
CPTP-7FF	K 54.6 N 147.5 I			7.19

4. CONCLUSION

Several polar compounds, such as nitroazobenzene LC dyes and fluoro diacetylenes and tolanes are synthesized and their properties evaluated. Some compounds exhibit a reasonably large dielectric anisotropy and small heat fusion enthalpy. These polar compounds are useful for mixing with non-polar diphenyl-diacetylenes to enhance the dielectric anisotropy. These high birefringent LC mixtures are particularly attractive for modulating infrared and microwave radiations.

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