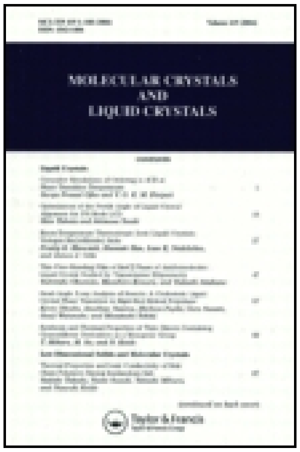

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Room Temperature Difluoro-Tolane and Diphenyl-Diacetylene Liquid Crystals with Negative Dielectric Anisotropy

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ROOM TEMPERATURE DIFLUORO-TOLANE AND DIPHENYL-DIACETYLENE LIQUID CRYSTALS WITH NEGATIVE DIELECTRIC ANISOTROPY

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Abstract Several laterally difluorinated tolane and diphenyl-diacetylene liquid crystals were synthesized and their physical properties evaluated. These compounds exhibit low melting temperature, small heat fusion enthalpy and large negative dielectric anisotropy. Their potential applications are in the high contrast displays using a homeotropic cell and for infrared spatial light modulators.

1. INTRODUCTION

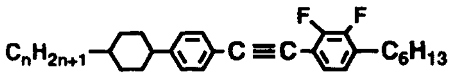
Homeotropic liquid crystal cells[1] are highly desirable for the normally-black display application owing to their excellent contrast ratio. In the voltage-off state, the LC directors are aligned to be nearly perpendicular to substrate surfaces. The incoming linearly polarized light experiences no phase retardation and is blocked by the crossed analyzer. As a result, an excellent dark state can be achieved. This dark state is insensitive to $d\Delta n$ (d=cell gap and Δn=birefringence) of the LC cell which provides a large cell gap tolerance during fabrication. As the applied voltage exceeds the Freedericksz transition threshold, the LC directors are reoriented by the electric field and phase retardation results.

To realize the useful electro-optic effect of a homeotropic cell, the LC employed must exhibit a negative dielectric anisotropy besides the general requirements on wide nematic range and low viscosity. For active matrix displays, an extra requirement on the LC material is high resistivity. High resistivity enables the LC cell to hold the applied voltage without flickering. To satisfy high resistivity and negative dielectric anisotropy at the same time, laterally fluorinated compounds are often considered.

In this paper, we report on the phase transition temperatures and physical properties of some lateral difluoro-tolane and diphenyl-diacetylene liquid crystals. These LCs possess relatively low melting temperature and high clearing temperature, large and negative dielectric anisotropy, and high resistivity. Therefore, they are useful compounds for formulating eutectic mixtures for high contrast liquid crystal display applications.

2. (2,3) DIFLUORO TOLANES

The structures of the laterally difluorinated tolanes we studied are shown below:



We have synthesized several homologues with n=2-7. Similar tolanes with alkoxy side chains have been reported previously.[2] These alkoxy tolanes possess high melting point and large heat fusion enthalpy. Thus, their solubility in a LC mixture is limited even though their high clearing point (T_c) is attractive for enhancing the T_c of the mixture.

2.1 Phase Transition Temperatures

The phase transition temperatures and heat fusion enthalpy (ΔH) of the (2,3) difluorotolanes we synthesized are listed in Table I.

TABLE I Phase transition temperatures (in °C) and heat fusion enthalpy (ΔH in kcal/mol) of the laterally difluoro-tolane LC homologues. Here K, N and I stand for crystalline, nematic and isotropic phase, respectively.

n	Phase transitions					ΔH
2	K	34.6	N	75.9	I	3.52
3	K	38.5	N	94.2	I	2.28
4	K	22.5	N	105.8	I	3.05
5	K	38.3	N	104.6	I	5.22
6	K	36.8	N	68.9	I	2.60
7	K	37.2	N	86.2	I	2.85

These homologues exhibit relatively low melting temperatures and high clearing point. Normally, the asymmetric side chain groups help to reduce melting temperature.[3] However, this phenomenon is not so obvious here. The observed low melting temperature is mainly attributed to the molecular width. The lateral difluoro group widens the molecular separation and weakens the inter-molecular association resulting in low melting temperatures. On the other hand, the high clearing temperature originates from the cyclohexane ring. The small ΔH of these homologues is quite desirable for forming eutectic mixtures. According to the Schroder-Van Laar equation,[4,5] both low melting temperature and small heat fusion enthalpy play equally important roles in reducing the melting temperature of an eutectic mixture. Low melting temperature and high clearing point are critical for practical display applications. Normally, the desirable nematic range of a LC mixture is from -40 to +85°C.

2.2 Dielectric anisotropy:

The dielectric constants of the n=4 homologue were measured by the capacitance method.[6] Results are: $\varepsilon_\perp = 10$ and $\varepsilon_{//} = 4$ at 1 kHz and T=23°C. This large negative dielectric anisotropy originates from the lateral fluoro groups. From mean-field theory, the dielectric constants of a LC compound are determined by the dipole moment and its relative position with respect to the principal molecular axis as: [7]

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

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

$$\Delta\varepsilon = NhF\{(\alpha_\ell - \alpha_t) - (F\mu^2/2kT)(1 - 3\cos^2\theta)\}S \tag{3}$$

where N is the molecular packing density, $h = 3\varepsilon/(2\varepsilon + 1)$ is the cavity field factor, $\varepsilon = (\varepsilon_{//} + 2\varepsilon_\perp)/3$ is the averaged dielectric constant, F is the Onsager reaction field, α_ℓ and α_t 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.

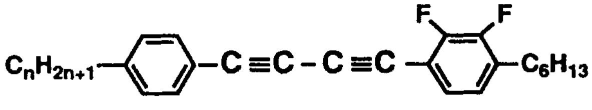
The effective dipole moment of the two fluoro groups is perpendicular to the principal molecular axis. Thus, the dielectric anisotropy $(\varepsilon_{//} - \varepsilon_\perp)$ is large but negative. The threshold voltage of the LC cell was measured to be 2.4 V_{rms}. From the relationship $V_{th} = \pi\,[K_{33}/\Delta\varepsilon]^{1/2}$, the bend elastic constant (K_{33}) of the n=4 homologue is calculated to be 3×10^{-6} dyne.

2.3 Birefringence:

The birefringence of the n=4 homologue was determined to be 0.20 at λ=633 nm by measuring the voltage-dependent phase retardation of a homeotropically-aligned cell.[6] The observed relatively high birefringence is due to linear molecular conjugation of the tolane core. The tolane structure offers reasonably good photostability. Therefore, this series of LC compounds can be employed for high contrast display applications.

3. (2,3) DIFLUORO DIPHENYL-DIACETYLENES

The structure of the (2,3) laterally difluorinated diphenyl-diacetylene liquid crystals we studied is shown below:



The compounds we synthesized have n=3-6. Their phase transition temperatures and heat fusion enthalpy are listed in Table II.

TABLE II Phase transition temperatures (in °C), dielectric anisotropy (Δε at T=25°C and 1 kHz), birefringence (Δn at λ=633 nm) and heat fusion enthalpy (ΔH in kcal/mol) of the laterally difluoro diphenyl-diacetylene LC homologues. Here K, N and I stand for crystalline, nematic and isotropic phase, respectively.

n	Phase transitions	Δε	Δn	ΔH
3	K 37.5 N 71.1 I			4.13
4	K 23.6 N 47.2 I	- 6.4	0.28	4.25
5	K 34.6 N 58.7 I			4.46
6	K 19.6 I			---

Normally, the melting temperature of such a highly conjugated liquid crystal is quite high. However, due to the lateral substitutions, their melting point is reduced to near room temperature.

The physical properties of the n=4 homologue was characterized and results are included in Table II. The high Δn results from long molecular conjugation and the large negative dielectric anisotropy from lateral dipole moment.

The absorption edge of the diphenyl-diacetylene LCs extends to 350 nm.[6] Thus, their photostability in the blue spectral region is a concern and not so desirable for visible display application. However, there are other displays or light modulation in the infrared and microwave regions where photostability of these LCs is not a problem. The high birefringence and negative dielectric anisotropy of these compounds turn out to be attractive for such applications. To improve the lifetime of a LC device, the cell should be sealed peripherally in order to keep moistures and oxygen out. Otherwise, moistures and oxygen tend to interact with LC molecules and cause alignment deterioration. As a result, the contrast ratio of the LC device is degraded gradually.

4. CONCLUSION

The laterally fluorinated tolane and diphenyl-diacetylene liquid crystals exhibit large but negative dielectric anisotropy, high birefringence and low melting temperature. Owing to their low melting temperature and small heat fusion enthalpy, a wide nematic range eutectic mixture consisting entirely of these homologues can be formulated. These LCs would also possess a relatively high resistivity (estimated to be $\sim 10^{12}$ Ω•cm) for active matrix display applications. When these mixtures are used in a homeotropically aligned cell, a contrast ratio higher than 1000:1 can be obtained under the crossed-polarizer configuration.

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