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Synthesis and mesomorphic properties of novel high birefringence azobenzene liquid crystals with lateral fluorosubstituent

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ABSTRACT

In order to obtain liquid crystals with high birefringence (Δn), four azobenzene compounds based on lateral fluorinated bistolane moieties with trifluoromethyl terminal groups were synthesized with Hagihara– Sonogashira cross-coupling reaction. The molecular structures of the compounds were confirmed by Fourier transform infrared, ¹H-nuclear magnetic resonance. The transition temperatures, optical textures, and optical anisotropies were determined by differential scanning calorimetry, polarizing optical microscopy. The effect of the alkyl substituents on liquid crystal behavior is discussed in detail. The compounds have showed higher birefringence values. KEYWORDS

Azobenzene; birefringence; lateral fluorosubstituent

Introduction

High birefringence (Δn) liquid crystals have attracted much attention in the past few years because they are useful not only in conventional display devices, such as supertwisted nematic liquid crystal displays (STNLCDs), but also in scattering-type polymerdispersed liquid crystal displays (PDLCDs) as reflective liquid crystal displays (LCDs) and in spatial light modulators [1–4]. In addition, these materials are thought to be applicable to laser beam steering, infrared spatial modulators and optical communication [5–6].

Turning to materials, from the single-band model, the Δn of a liquid crystalline compound is determined mainly by π -electron conjugation, order parameter and differential oscillator strength. Molecules that contain highly polarizable groups with high electron density, such as acetylene linking groups or benzene rings, will therefore have large optical anisotropies [7–12]. In addition, liquid-crystalline polymers with the azobenzene in the side chain have attracted much attention because a photo-induced change in birefringence Δn was large when compared with amorphous counterparts [13, 14]. Azobenzene liquid crystals (LCs) have been extensively studied because of their applicability for photoswitching devices [15, 16], optical memory [17], nonlinear optics [18], and holography [19]. By contrast, related small molecular compounds have been less explored.

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In this article, we focus our attention on a series of compounds containing azobenzene core with trifluoromethyl polarizable groups, which were highly conjugated along the molecular long axis to yield materials with high Δn values.

Experimental

Reagents were purchased from commercial sources (Aldrich), and used without further purification. Tetrahydrofuran (THF) and triethylamine (TEA) were distilled and purged with argon before use. Reactions were carried out in an inert atmosphere (dry Ar or N₂). The preparative routes for the azobenzene liquid crystals compounds are shown in Scheme 1. The structures of the final compounds and various synthetic intermediates were characterized by 1H NMR spectroscopy (Bruker DMS-400 spectrometer instrument). All spectra were recorded in CDCl₃ with TMS as internal standard. Fourier transform infrared spectroscopy (FT-IR, Perkin Elmer Spectrum One) was also measured.



Scheme 1. Reagents and conditions (1) Oxone, CH_2CI_2 , H_2O , r. t., 15 h; (2) AcOH, r. t., 15 h; (3) TAE, THF, $PdCI_2(PPh_3)_4$, Cul, 30°C, 8 hr.

The phase transition temperatures of the target compounds were measured by differential scanning calorimetry (DSC, Perkin Elmer Pyris 6). The optical textures were measured using a polarizing optical microscope (POM, Olympus BX51) equipped with a hot stage calibrated to an accuracy of ± 0.1 K (Linkam LK-600PM). The Δn was evaluated using the guest-host method from mixtures containing 10 wt% of each test compound in SLC 1717 (Slichem Liquid Crystal Material Co., Ltd.) and a polarized UV/VIS/NIR spectrophotometer (JASCO V-570) was used to measure the birefringence of the mixtures [20].

Synthesis

General procedure for the synthesis of intermediate m1

4-Trifluoromethyl-aniline (16.1 g, 0.100 mol) dissolved in 200 mL of CH_2Cl_2 and Oxone (123.0 g, 0.200 mol) dissolved in 200 mL of water were added in a round-bottom flask, the reaction mixture then stirred at room temperature for 15 hr under an N₂ atmosphere. After separation of the layers, the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with 1 N HCl, saturated sodium bicarbonate solution, water, brine, and dried with MgSO₄. After filtration, removal of the solvent from the filtrate in vacuo yielded the corresponding labile nitrosoarene, which was submitted to the next condensation step without further purification. To the nitrosoarene dissolved in 200 mL of acetic acid was added 4-bromo-2-fluoro-aniline (19.0 g, 0.100 mol). The resulting mixture was stirred at room temperature for 15 hr. The precipitate was separated by filtration and the collected solid was washed with acetic acid and water and dried in a desiccator over P_2O_5 under reduced pressure for 24 hr.

(4-Bromo-2-fluoro -phenyl)- (4-trifluoromethyl-phenyl)-diazene (m1). Yellow solid, yield: 71.2%, 24.8g.¹H-NMR (400 MHz, CDCl₃) (δ , ppm): 7.34 (s, 1H), 7.42 (d, 1H, J = 8.8 Hz), 7.66 (d, 2H, J = 8.8 Hz), 7.82 (d, 1H, J = 8.4 Hz), 7.88 (d, 2H, J = 8.8 Hz). IR (cm⁻¹): 2109, 1932, 1600, 1492, 1409, 1326, 1174, 1139, 1066, 856,652.

General procedure for the synthesis of the azobenzene liquid crystals

(4-Bromo-2-fluoro -phenyl)- (4-trifluoromethyl-phenyl)-diazene (17.4 g, 0.05 mol) and 1-Ethynyl-4-R-benzene (0.06 mol) dissolved in 500 ml dry Et3N:THF (1:1). Add $Pd(PPh_3)_4$ (1.4 g, 1.2 mmol)) and CuI (0.45 g, 2.4 mmol) The reaction mixture was then stirred at room temperature for 8 hr under an Ar atmosphere. Upon completion, the solvent was removed in vacuo and the crude material purified by chromatography on silica gel (2:1, hexanes: CH2Cl2) to give target compound as a Yellow solid.

[4-(4-Ethyl-phenylethyny)-2-fluoro-phenyl]-(4-trifluoromethyl-phenyl)-diazene (a). yield: 74%, Yellow solid. ¹H-NMR (400 MHz, CDCl₃) (δ , ppm): ¹H-NMR (400 MHz, CDCl₃) (δ , ppm):1.24(t, 3H), 2.60(m, 2H), 7.08 (d, 2H, *J* = 8.8 Hz), 7.34 (s, 1H), 7.40 (d, 2H, *J* = 8.8 Hz), 7.42 (d, 1H, *J* = 8.8 Hz), 7.66 (d, 2H, *J* = 8.8 Hz), 7.82 (d, 1H, *J* = 8.4 Hz), 7.88 (d, 2H, *J* = 8.8 Hz). IR (cm⁻¹): 2109, 1932, 1600, 1492, 1409, 1326, 1174, 1139, 1066, 856,652.

[4-(4-Propyl-phenylethyny)-2-fluoro-phenyl]-(4-trifluoromethyl-phenyl)-diazene (b). yield:73%, Yellow solid. ¹H-NMR (400 MHz, CDCl₃) (δ , ppm): 0.98(t, 3H), 1.66((m, 2H)), 2.56(t, 2H), 7.08 (d, 2H, J = 8.8 Hz), 7.34 (s, 1H), 7.40 (d, 2H, J = 8.8 Hz), 7.42 (d, 1H, J = 8.8 Hz),7.66 (d, 2H, J = 8.8 Hz), 7.82 (d, 1H, J = 8.4 Hz), 7.88 (d, 2H, J = 8.8 Hz). IR (cm⁻¹): 2109, 1932, 1600, 1492, 1409, 1326, 1174, 1139, 1066, 856,652.

[4-(4-butyl-phenylethyny)-2-fluoro-phenyl]- (4-trifluoromethyl-phenyl)-diazene (c).yie-ld:75%, Yellow solid. ¹H-NMR (400 MHz, CDCl₃) (δ , ppm): 0.96(t, 3H), 1.32(m, 2H), 1.64(m, 2H), 2.56(t, 2H), 7.08 (d, 2H, J = 8.8 Hz), 7.34 (s, 1H), 7.40 (d, 2H, J = 8.8 Hz), 7.42 (d, 1H, J = 8.8 Hz), 7.66 (d, 2H, J = 8.8 Hz), 7.82 (d, 1H, J = 8.4 Hz), 7.88 (d, 2H, J = 8.8 Hz). IR (cm⁻¹): 2109, 1932, 1600, 1492, 1409, 1326, 1174, 1139, 1066, 856,652.

[4-(4-amyl-phenylethyny)-2-fluoro-phenyl]- (4-trifluoromethyl-phenyl)-diazene (d).yield:76%, Yellow solid. ¹H-NMR (400 MHz, CDCl₃) (δ , ppm): 0.96(t, 3H), 1.28(m, 2H), 1.33(m, 2H), 1.62(m, 2H), 2.56(t, 2H), 7.08 (d, 2H, *J* = 8.8 Hz), 7.34 (s, 1H), 7.40 (d, 2H, *J* = 8.8 Hz), 7.42 (d, 1H, *J* = 8.8 Hz), 7.66 (d, 2H, *J* = 8.8 Hz), 7.82 (d, 1H, *J* = 8.4 Hz), 7.88 (d, 2H, *J* = 8.8 Hz). IR (cm⁻¹): 2109, 1932, 1600, 1492, 1409, 1326, 1174, 1139, 1066, 856,652.

Results and discussion

Phase transitions

DSC was used to determine the phase transition temperatures during cooling at a scanning rate of 10°C min⁻¹, the DSC curves of these compounds are shown in Fig. 1 and the associated data are listed in Table 1. The phase transition temperatures of the compounds were listed in

Table 1. Phase transition temperatures and Δn of the compounds. Cr = crystal, Sm = smectic phase, I = isotropic.

Compounds	Phase transition temperatures (°C)	Δn
a	Cr 57.6 Sm 89.9 l	0.45
b	Cr 94.7	/
c	Cr 109.1 Sm 144.7 l	0.43
d	Cr 122	/



Figure 1. DSC curves of compounds a-d.

Table 1. It was shown that only the compound **a** and compound **c** are exhibit mesomorphism, that is related to the length of carbon chain in the mols, and present the odd–even effect to carbon atom nos. Moreover, compared with the synthesized compound a, compound c exhibits a higher melting point and a narrower temperature range of mesophase, this is because the alkyl carbon number in compound **a** was less than compound **c**. The Low molecular weight resulted in a lower melting point.

Optical textures

The optical textures of the synthesized compounds \mathbf{a} and \mathbf{c} were investigated primarily by POM. The phases were identified through the comparison of the observed textures with reference textures [21] from POM. Figure 2 shows POM photographs of compounds \mathbf{a} and \mathbf{c} observed in their LC phases in the course of cooling. The observations above indicate that the compounds show enantiotropic phase behavior with the existence of mesophase between the crystal and the isotropic liquid, which are consistent with the DSC results. Compared with compound \mathbf{c} , compound \mathbf{a} tend to form typical smectic textures for the shorter alkyl chain and higher electron density.



Figure 2. Microphotographs of the liquid crystalline phases of compounds a and c.

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Figure 3. UV–vis absorption spectra of compound **c** in CH_2CI_2 .

Optical anisotropy

Having demonstrated the LC properties of the azobenzene derivatives, we focused our attention on their Δn properties. The Δn was evaluated from mixtures containing 10 wt% of each test compound in SLC 1717 using polarizing light interferometry method [20]. The Δn data of the compounds were collected in Table 1. Among compound **a** and **c**, the length of flexible chain is important evaluation factor for Δn . Longer carbon chain decreases π -electron conjugation slightly, the Δn value decreased correspondingly [7].

Photophysical properties

For provides some insight into the electronic structure of the systems, the absorption spectra of the synthesized compound **c** in dilute CH_2Cl_2 solution at room temperature, depicted in Fig. 3. The spectra display a characteristic pattern of two absorption bands at 334 nm and 357 nm. The change of absorption spectra under UV irradiation was tested, the absorption intensity of the absorption band at 357 nm become weaker gradually with the UV irradiation and the absorption band revealed slight blue shifts (~3 nm). One generally approved explanation was that trans-cis photoisomerization of the azobenzene moiety in LC compound by disorganizing the alignment.

Conclusions

We have synthesized and evaluated the properties of a series of azobenzene liquid crystals with lateral fluorosubstituent. The effect of the alkyl substituents on liquid crystal behavior was obtained, and present the odd–even effect to carbon atom nos, compounds with even carbon atom nos showed good liquid-crystalline behavior.

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References

- [1] Yang, D. K., Doane, J. W., Yaniv, Z., & Glasser, J. (1994). Appl. Phys. Lett., 64, 1905-1907.
- [2] Meng, H. H. B., Dalton, L. R., & Wu, S. T. (1994). Mol. Cryst. Liq. Cryst., 259, 303.
- [3] Wu, S. T., Margerum, J. D., Ho, M. S., Fung, M., Hsu, C. S., Chen, S. M., & Sai, K. T. (1995). Mol. Cryst. Liq. Cryst., 261, 79.
- [4] Hsu, C. S., Tsay, K. T., Chang, A. C., Wang, S. R., & Wu, S. T. (1995). Mol. Cryst. Liq. Cryst., 19, 409.
- [5] Mcmanamor, P. F., Watson, E. A., Dorschner, T. A., & Barnes, L. J. (1993). Opt. Eng., 32, 2657.
- [6] WU, S. T. (2001), SID Dig '01, 954.
- [7] Zhang, Z. L., Zhang, L. Y., Guan, X. L., Shen, Z. H., Chen, X. F., Xing, G. Z., Fan, X. H., & Zhou, Q. F. (2010). *Liq. Cryst.*, 37, 69–76.
- [8] Zhao, Y. Z., Wang, D., He, Z. M., Cheng, G., Zhang, L. Y., Yang, H., & Zhang, H. Q. (2015). Chinese Chem. Lett., 26, 785–789.
- [9] Zhang, Y. M., Wang, D., Miao, Z. C., Jin, S. K., & Yang, H. (2012). Liq. Cryst., 39, 1330–1339.
- [10] Miao, Z. C., Wang, D., Zhang, Y. M., Jin, Z. K., Liu, F., Wang, F. F., & Yang, H. (2012). *Liq. Cryst.*, 39, 1291.
- [11] Guan, X. L., Zhang, L. Y., Zhang, Z. L., Shen, Z. H., Chen, X. F., Fan, X. H., & Zhou, Q. F. (2009). *Tetrahedron*, 65, 3728–3732.
- [12] Miao, Z. C., Wang, D., Zhang, Y. M., & Zhao, Y.Z. (2013). Mol. Cryst. liq. Cryst., 577, 44-50.
- [13] Han, D., Tong, X., Zhao, Y., Galstian, T., Zhao, Y. (2010). *Macromolecules*, 43, 3664.
- [14] White, T. J., McConney, M. E., Bunning, T. J. (2010). J. Mater. Chem., 20, 9832.
- [15] Beharry, A. A., Sadovski, O., & Woolley, G. A. (2011). J. Am. Chem. Soc., 133, 19684.
- [16] Sio, L. D., Vasdekis, A. E., Cuennet, J. G., Luca, A. D., Pane, A., & Psaltis, D. (2011). Opt. Express, 19, 23532.
- [17] Lee, K. M., Smith, M. L., Koerner, H., Tabiryan, N., Vaia, R. A., Bunning, T. J., & White, T. J. (2011). *Adv. Funct. Mater.*, 21, 2913.
- [18] riimagi, A., Ogawa, K., Virkki, M., Mamiya, J., Kauranen, M., & Shishido, A. (2012). Adv. Mater., 24, 6387.
- [19] Emoto, A., Uchida, E., & Fukuda, T. (2012). Polymers, 4, 150.
- [20] Miao, Z. C., Zhang, Y. M., Zhao, Y. Z., & Wang, D. (2013). Mol. Cryst. Liq. Cryst., 582, 98-106.
- [21] Demus, D., & Richter, L. (1978). Textures of Liquid Crystals, Verlag Chemie: New York.