

New Tolan-type Liquid Crystals with 1,3-Dithiane Ring

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Two new tolan-type liquid crystalline (LC) materials, 2-[4-(4-pentoxyphenyl)ethynylphenyl]-5-pentyl-1,3-dithiane (A) and 2-[4-(4-pentoxy-2,3,5,6-tetrafluorophenyl)ethynylphenyl]-5-pentyl-1,3-dithiane (B) were synthesized and their mesomorphic behavior was determined. The 1,3-dithiane-type compound A exhibits only nematic phase. The compound B, fluorosubstituted in the LC core, shows the same nematic phase range.

Keywords Liquid crystal, synthesis, 1,3-dithiane

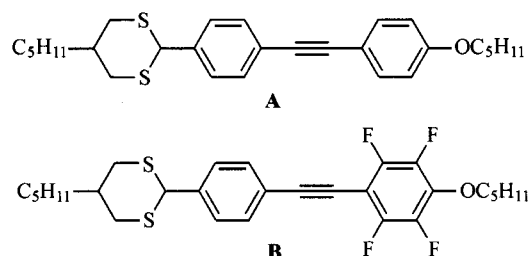
Introduction

For the recent years, tolan-type nematic liquid crystals with cyclohexane, 1,3-dioxane and other heterocyclic rings have been reported as new types of liquid crystalline (LC) materials,¹⁻¹⁴ which possess both low viscosity and high birefringence. Although the effect of the bulky sulfur atoms on the optical properties of LC may be interesting, the tolan-based 2,5-disubstituted 1,3-dithianes have not been reported yet. In previous paper,¹⁴ we reported new tolan-type liquid crystals containing a 1,3-dioxane ring. These compounds exhibit only a broad nematic phase, and should be suitable for TN-model liquid crystal display (LCD). In this paper, the synthesis and the mesomorphic behavior of di-sulfur containing analogues are reported and their structures are shown in Scheme 1.

Experimental

The structures of all intermediates and final mesogens were determined by spectroscopic methods. IR

Scheme 1



spectra were recorded on a PE-983G spectrometer using a KBr disc. ¹H NMR spectra (with TMS as the internal standard) and ¹⁹F NMR spectra (with trifluoroacetic acid (TFA) as the external standard) in CDCl₃ as the solvent were recorded on a Varian EM360L NMR (60 MHz) or Bruker 300 NMR (300 MHz) instrument. For ¹⁹F NMR spectra, the high field was positive. MS spectra were measured with a Finnigan 4021 spectrometer. The phase transition temperatures of all compounds were measured by optical microscopy using a polarizing optical microscope (POM, Olympus PM-6) equipped with a hot stage (Mettler FP-80) and a control unit (FP-82), and by differential scanning calorimetry (DSC, Shimadzu DSC-50 calorimeter with a data system) at heating and cooling rates of 5°C/min. The transition temperatures shown in this paper are the peak values of the transitions on DSC traces. Phase identification was made by comparing the observed textures with those reported in the literatures.^{15,16}

Two novel liquid crystalline compounds were prepared according to the procedures as shown in Scheme 2. 2-Pentyl-1,3-propanedithiol (4) was prepared ac-

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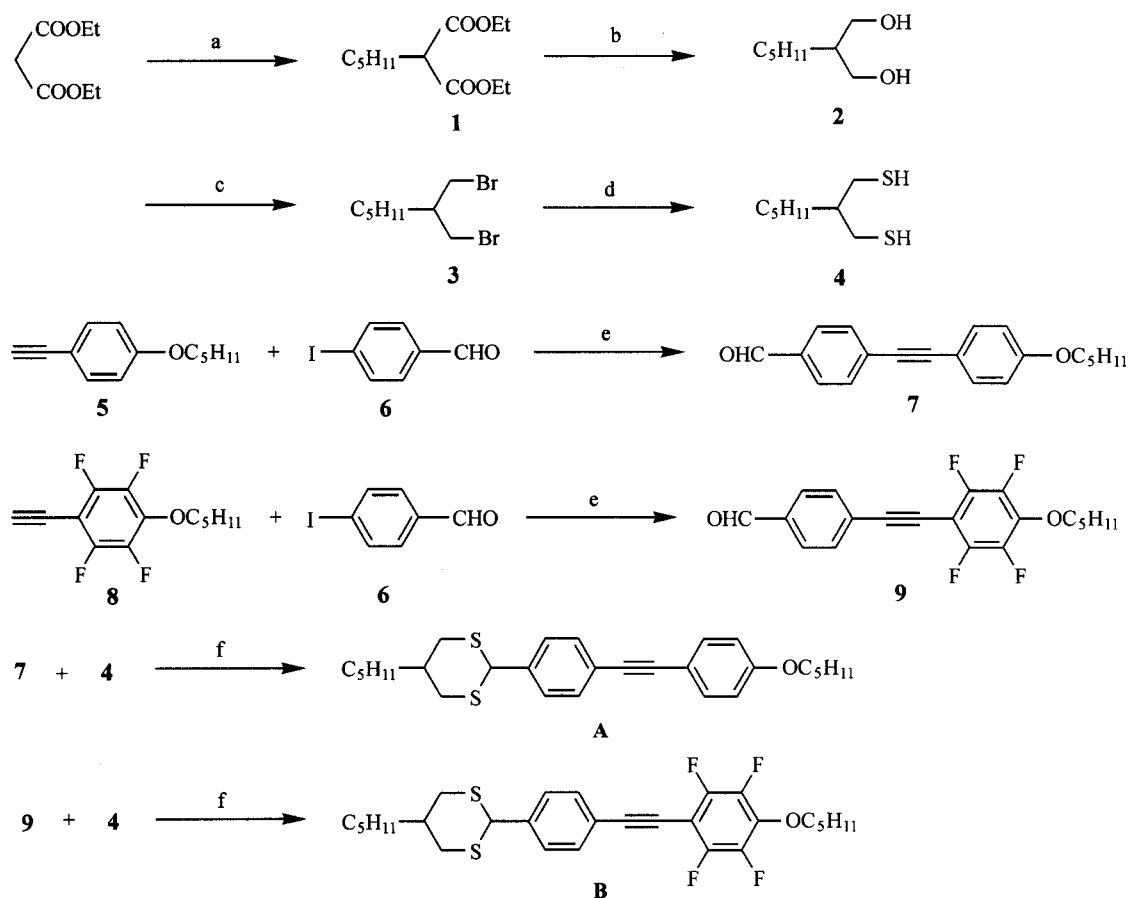
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ording to a published procedure,¹⁷ and the substituted phenylacetylenes (**5** and **8**) were obtained by the same method reported in previous works.^{11,18} The disubstituted tolanes (**7** and **9**) were prepared from *p*-iodobenzaldehyde and **5** or **8** by Pd-catalyzed coupling reaction. Then

the condensation of compound **7** or **9** with compound **4** gave the target compound **A** or **B** respectively. The two compounds were purified by recrystallisation from *iso*-propanol.

Scheme 2 Synthetic path way of the target compounds



Reagents and conditions: (a), EtONa, EtOH, *n*-C₅H₁₁Br; (b), LiAlH₄, Et₂O; (c), HBr, H₂SO₄; (d), thiourea, triethylene glycol, 75°C, 18 h then tetraethylenepentamine, 75°C, 2 h; (e), Pd(PPh₃)₂Cl₂, CuI, Et₃N; (f), TsOH, toluene, reflux.

4-(4'-Pentoxyphenyl)ethynylbenzaldehyde (**7**)

A mixture of 4-iodobenzaldehyde (**6**, 2.12 g, 10 mmol), 4-pentoxyphenylacetylene (**5**, 2 g, 10.6 mmol), bis(triphenylphosphine)palladium dichloride (0.5 g), copper(I) iodide (0.5 g) and 20 mL of anhydrous triethylamine was stirred at 60°C for 24 h, then the formed precipitate was filtered and washed with ethyl ether. The filtrates were washed with water and dried over anhydrous

sodium sulfate. The solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel using petroleum ether (b. P. 60–90°C)-dichloromethane (*V/V* = 9:1) as the eluent to give a white crystal of compound **7** (2.7 g, yield 92%). ¹H NMR (CDCl₃/TMS, 90 MHz) δ: 0.90–1.87 (m, 9H, aliphatic hydrogen), 3.99 (t, *J* = 6 Hz, 2H), 6.87–6.97 (m, 2H), 7.47–7.94 (m, 6H), 10.07 (s, 1H). MS *m/z* (%): 292 (M⁺, 63.99), 222 (100.00)

4-(4'-Pentoxy-2',3',5',6'-tetrafluorophenyl) ethynylbenzaldehyde (**9**)

The compound **9** was synthesized with the same procedure for the compound **7**, yield 81%. ^1H NMR (CDCl_3/TMS , 90 MHz) δ : 0.88—1.87 (m, 9H, aliphatic hydrogen), 4.26 (t, $J = 6$ Hz, 2H), 7.64—7.91 (m, 4H), 10.07 (s, 1H); ^{19}F NMR (CDCl_3/TFA , 56.4 MHz) δ : 60.3—60.5 (m, 2F), 80.0—80.9 (m, 2F); MS m/z (%): 364 (M^+ , 19.76), 294 (100.0).

2-[4'-(4''-Pentoxyphenyl) ethynylphenyl]-5-pentyl-1,3-dithiane (**A**)

A mixture of compound **7** (0.4 g, 1.37 mmol), 2-pentyl-1,3-propanedithiol (**4**) (2.63 g, 1.64 mmol), dry toluene (50 mL) and *p*-toluenesulphonic acid (25 mg) was heated under reflux using a Dean and Stark trap to remove the formed water. On cooling to room temperature, the mixture was poured into an aqueous sodium hydrogen carbonate solution (5%, 50 mL) and the separated organic layer was washed subsequently with an aqueous sodium hydrogen carbonate solution (5%, 2×50 mL), water (2×50 mL) and anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue was purified by crystallization from *n*-hexane to remove the *cis*-isomer. Then solid was purified by recrystallisation from *iso*-propanol to give **A** as white crystals 218 mg, yield 38%. The data for this compounds were shown as follows: ^1H NMR (CDCl_3/TMS , 300 MHz) δ : 0.88—1.84 (m, 20H, aliphatic hydrogen), 2.15—2.18 (m, 1H, 5-H), 3.54 (t, $J = 11.5$ Hz, 2H, H_a), 3.98 (t, $J = 6.5$ Hz, 2H, OCH_2), 4.25 (dd, $J = 11.5$, 4.6 Hz, 2H, H_e), 5.41 (s, 1H, 2-H), 6.84—6.90 (m, 2H), 7.44—7.53 (m, 6H); IR (KBr) ν : 2922, 1597, 1563, 1467, 1407, 1250, 1174, 1054, 1021, 833 cm^{-1} ; MS m/z (%): 420 (M^+ , 100.00), 222 (27.96); Anal. calcd for $\text{C}_{28}\text{H}_{36}\text{O}_3$: C 79.96, H 8.63; found C 80.23, H 8.78.

2-[4'-(4''-Pentoxy-2'',3'',5'',6''-tetrafluorophenyl) ethynylphenyl]-5-pentyl-1,3-dithiane (**B**)

The compound **B** was synthesized with the same procedure for compound **A**, yield: 33%. ^1H NMR (CDCl_3/TMS , 300 MHz) δ : 0.88—1.80 (m, 20H,

aliphatic hydrogen), 2.15—2.19 (m, 1H, 5-H), 3.54 (t, $J = 11.5$ Hz, 2H, H_a), 4.27 (t, $J = 6.5$ Hz, 2H, OCH_2), 4.25 (dd, $J = 11.5$, 4.6 Hz, 2H, H_e), 5.42 (s, 1H, 2-H), 7.54 (AABB, 4H); ^{19}F NMR (CDCl_3/TFA , 56.4 MHz) δ : 60.0—60.6 (m, 2F), 79.6—78.0 (m, 2F); MS (m/z , %): 492 (M^+ , 84.02), 294 (100.0); Anal. calcd for $\text{C}_{28}\text{H}_{32}\text{F}_4\text{O}_3$: C 68.28, H 6.55, F 15.43; found C 68.29, H 6.49, F 15.49.

Results and discussion

The phase transition temperatures of the target compounds were determined by DSC at heating and cooling rates of $5^\circ\text{C}/\text{min}$. The mesomorphic textures were observed on the polarizing optical microscope for determining the type of mesophases. The transition temperatures shown in the Table 1 are the data of transition peaks on each DSC traces.

Table 1 Transition temperatures of the compounds ($^\circ\text{C}$)

Compounds	T (Cr \rightarrow N)	T (N \rightarrow I)
A	120.2	196.5
B	105.9	181.6
C	100.2	205.5
D	65.2	167.8

The compounds **A** and **B** both exhibit only a wide nematic phase, and their phase ranges show almost no difference, about 76°C . It can be explained by the special effect of the bulky 1,3-dithiane rings. Because the 1,3-dithiane ring is more bulky than the tetrafluorophenyl unit in the LC core, the fluoro-substitution in the phenyl ring does not increase the width of the molecule additionally and shows no effect on the phase range. But the introduction of fluorine atom decreases the interaction force between the molecules, and results directly in the drops of the melting and clearing points.

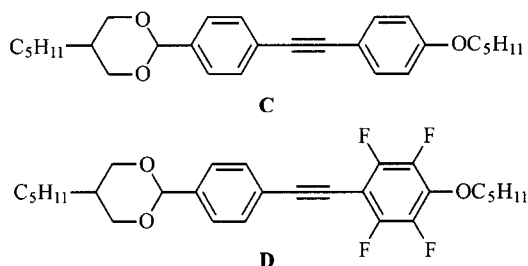
In our previous work,¹⁴ Some tolan-type liquid crystals with a 1,3-dioxane ring were synthesized. Two compounds (**C** and **D**) with the similar structure were selected for comparison as shown in Scheme 3.

Compared with the corresponding 1,3-dioxane derivatives, the 1,3-dithiane derivatives exhibit higher melting points than those of the formers. It is plausibly attributed to that the sulfur atom has larger dispersion

force than that of the oxygen atom,¹⁹ so there is a stronger interaction force among the molecules of 1,3-dithiane derivatives. And obviously, in the melting process, it needs more energy to destroy the order arrangement. The 1,3-dithiane derivatives also exhibit a shorter phase range for the bulky 1,3-dithiane ring.

In conclusion, the principal feature of the mesomorphic behaviors of 1,3-dithiane-type liquid crystals is to exhibit only a nematic phase, and to possess higher melting points and shorter phase ranges than the corresponding 1,3-dioxane-type compounds.

Scheme 3



References

- 1 Takatsu, H.; Sasaki, M.; Sato, H.; Tanaka, Y. *JP 60155142*, **1985** [*Chem. Abstr.* **1985**, 104, 100055] (in Japanese).
- 2 Goto, Y.; Ogawa, T. *Eur. Pat. Appl. EP 276067*, **1988** [*Chem. Abstr.* **1988**, 109, 241515].
- 3 Goto, Y.; Kitano, K. *Eur. Pat. Appl. EP 377516*, **1990** [*Chem. Abstr.* **1990**, 114, 52990].
- 4 Sasaki, M.; Takatsu, H.; Takeuchi, K. *JP 04082853*, **1992** [*Chem. Abstr.* **1992**, 117, 202046] (in Japanese).
- 5 Buchecker, R.; Schadt, M. *Eur. Pat. Appl. EP 598354*, **1994** [*Chem. Abstr.* **1994**, 121, 312199].
- 6 Naito, T.; Sakamaki, Y.; Yamamoto, K.; Niino, K. *JP 09118651*, **1997** [*Chem. Abstr.* **1997**, 127, 58195].
- 7 Naito, T.; Yamamoto, K.; Niina, K. *JP 10195025* **1998** [*Chem. Abstr.* **1998**, 129, 168195] (in Japanese).
- 8 Tachibana, T. *JP 11012198*, **1999** [*Chem. Abstr.* **1999**, 130, 131885] (in Japanese).
- 9 Lou, X.; Yang, Z. *Yejing Yu Xianshi* **1999**, 14(2), 90 (in Chinese).
- 10 Chen, X.; Li, H.; Chen, Z.; Lou, J.; Wen, J. *Liq. Cryst.* **1999**, 26, 1743.
- 11 Chen, X.; Wen, J. *Liq. Cryst.* **1999**, 26, 1563.
- 12 Naito, T. *JP 2000212105*, **2000** [*Chem. Abstr.* **2000**, 133, 127680] (in Japanese).
- 13 Shibata, T.; Kimura, M.; Irisawa, M.; Kozaki, Y. *JP 2000026340*, **2000** [*Chem. Abstr.* **2000**, 132, 100570] (in Japanese).
- 14 Li, H.; Wen, J. *Liq. Cryst.* in press.
- 15 Demus, D.; Richter, L. *Textures of Liquid Crystals*, Verlag Chemie, Weinheim, New York, **1978**.
- 16 Gray, G. W.; Goodby, J. W. *Smectic Liquid Crystals; Textures and Structures*, Heyden & Son Inc., Philadelphia, **1984**.
- 17 Haramoto, Y.; Nanasawa, M. *Liq. Cryst.* **1996**, 21, 341.
- 18 Wen, J.; Chen, H. Shen, Y. *Liq. Cryst.* **1999**, 26, 1833.
- 19 Haramoto, Y.; Nanasawa, M. *Liq. Cryst.* **1997**, 23, 263.

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