Synthesis and Mesomorphic Properties of Tropon-4-yl 4-*n*-Alkoxybenzoates: Roles of a Tropone Ring as a Polar Terminal Group

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Abstract: New troponoid liquid crystals with a tropone terminal group were prepared. Tropon-4-yl 4-*n*-alkoxybenzoates (**1T**) had a monotropic smectic A phase. However the corresponding benzenoid derivatives (**1B**), tropolon-5-yl 4-*n*-alkoxybenzoates (**2T**), 2-methoxytropone-5-yl 4-*n*-alkoxybenzoates (**3T**), and tropon-2-yl 4-*n*-alkoxybenzoates (**4T**) were not mesomorphic. X-ray diffraction studies revealed that **1T** formed the interdigitated bilayers in the smectic A phase.

Key words: tropone, tropolone, liquid crystal, smectic A phase, bilayer structure

1 Introduction

The typical structural units of rod-like liquid crystals possess a fairly rigid core, which generally consists of six-membered ring systems. The preparation of new types of liquid crystals materials with rings other than six-membered rings had received less attention. However, it is important to extend the molecular design of liquid crystals to involve other ring systems from not only theoretical, but also the practical, points of views. Liquid crystals having a polar group such as a cyano group give rise to some interesting behaviors and some of them have successfully proved to be useful electrooptical devices employing the twisted nematic mode (1,2). Tropone and tropolone, seven-membered ring compounds with a carbonyl group, which have the large

dipole moments (4.1 and 3.5 D, respectively), which are comparable with that (4.18 D) of benzonitrile (3,4). Hence, tropone and tropolone will be suitable as a terminal group for high stability of liquid crystals. Although previously some liquid crystals with tropolone and 2-methoxytropone as a terminal group have been prepared, they were not mesomorphic (5). However the compounds with a tropone ring as a terminal group have not been reported. In this paper, we will report the syntheses and mesomorphic properties of new liquid crystals (**1-4T**) with tropone as a terminal group.

2 Experimental

2.1 Analysis

Elemental analyses were performed at the elemental

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analysis laboratory of Kyushu University. The melting points were obtained using a Yanagimoto micro-melting-point apparatus and are uncorrected. The NMR spectra were recorded using JEOL Lambda 400 and 600 spectrometer and solutions in CDCl_3 at room temperature; the chemical shifts are expressed in δ units. The mass spectra were measured with JEOL JMS-700 spectrometers. The transition temperatures were measured by differential scanning calorimetry (Seiko DSC 6200) and the mesomorphic phases were observed by polarizing optical microscopy (Olympus BHSP BH-2 equipped with a Linkam TH-600MS hot stage). X-ray diffraction measurements were carried out with a Rigaku Rint 2100 system using Ni-filtered $\text{Cu-K}\alpha$ radiation at various temperatures. The measuring temperatures were controlled with a Linkam HFS-91 hot stage.

2·2 Synthesis

2·2·1 Preparation of **1T**, **2T**, and **4T**

Alkoxybenzoyl chloride (0.6 mmol) was added to a pyridine (0.5 cm^3) solution of the corresponding tropolones (4-hydroxytropone (**6**), 5-hydroxytropolone, and tropolone: 0.5 mmol) and 4,4-dimethylaminopyridine (DMAP: 12.2mg, 0.1 mmol). The reaction mixture was stirred at room temperature for 3 h. The mixture was poured into a saturated KHSO_4 solution and extracted with chloroform. The organic layer was washed with a saturated NaCl solution and dried over Na_2SO_4 . The organic layer was evaporated in vacuo to leave a residue which was chromatographed in a hexane-ethyl acetate or a hexane-chloroform mixture on a silica-gel column (Wako gel C-300) to give pale yellow crystals. The crystals were recrystallized with hexane-ethyl acetate (1 : 1 v/v) to give pale yellow crystals.

1T8 (85%); MS(FAB) m/z 355 ($\text{M}+\text{H}^+$). Anal. Found: C, 74.30; H, 7.43%. Calcd for $\text{C}_{22}\text{H}_{26}\text{O}_4$: C, 74.55; H, 7.39%. ^1H NMR (CDCl_3): δ 0.89 (3H, t, $J = 6.6$ Hz), 1.25-1.39 (8H, m), 1.47 (2H, quit, $J = 6.6$ Hz), 1.82 (2H, quit, $J = 6.6$ Hz), 4.05 (2H, t, $J = 6.6$ Hz), 6.86 (1H, d, $J = 9.5$ Hz), 6.97 (2H, d, $J = 8.8$ Hz), 7.00-7.10 (3H, m), 7.13 (1H, dd, $J = 12.1, 9.5$ Hz), 8.08 (2H, d, $J = 8.8$ Hz). ^{13}C NMR (CDCl_3): δ 14.1, 22.7, 26.0, 29.1, 29.2, 29.3, 31.8, 68.5, 114.5 (2C), 120.2, 125.0, 132.5 (2C), 134.6, 134.7, 140.6, 141.0, 155.2, 164.1, 164.5, 186.9.

1T12 (89%); MS(FAB) m/z 411 ($\text{M}+\text{H}^+$). Anal. Found: C, 75.89; H, 8.35%. Calcd for $\text{C}_{26}\text{H}_{34}\text{O}_4$: C, 76.06; H, 8.35%. ^1H NMR (CDCl_3): δ 0.88 (3H, t, $J = 6.6$ Hz),

1.27-1.36 (16H, m), 1.47 (2H, quit, $J = 6.6$ Hz), 1.82 (2H, quit, $J = 6.6$ Hz), 4.05 (2H, t, $J = 6.6$ Hz), 6.86 (1H, d, $J = 9.5$ Hz), 6.97 (2H, d, $J = 8.8$ Hz), 7.01-7.09 (3H, m), 7.13 (1H, dd, $J = 12.1, 9.5$ Hz), 8.08 (2H, d, $J = 8.8$ Hz). ^{13}C NMR (CDCl_3): δ 14.1, 22.6, 25.9, 29.0, 29.3, 29.5 (2C), 29.7, 29.6 (2C), 31.9, 68.4, 114.5 (2C), 120.2, 125.1, 132.4 (2C), 134.6, 134.7, 140.5, 141.0, 155.2, 164.1, 164.4, 186.9.

1T16 (82%); MS(FAB) m/z 467 ($\text{M}+\text{H}^+$). Anal. Found: C, 76.92; H, 9.07%. Calcd for $\text{C}_{30}\text{H}_{42}\text{O}_4$: C, 77.21; H, 9.07%. ^1H NMR (CDCl_3): δ 0.88 (3H, t, $J = 6.6$ Hz), 1.26-1.38 (24H, m), 1.47 (2H, quit, $J = 6.6$ Hz), 1.82 (2H, quit, $J = 6.6$ Hz), 4.05 (2H, t, $J = 6.6$ Hz), 6.86 (1H, d, $J = 9.5$ Hz), 6.97 (2H, d, $J = 8.8$ Hz), 7.01-7.09 (3H, m), 7.13 (1H, dd, $J = 12.1, 9.5$ Hz), 8.08 (2H, d, $J = 8.8$ Hz). ^{13}C NMR (CDCl_3): δ 14.1, 29.1, 29.3, 29.4, 29.55, 29.59 (2C), 29.65 (2C), 29.68 (2C), 29.69 (3C), 31.9, 68.5, 114.5 (2C), 120.2, 125.1, 132.5 (2C), 134.6, 134.7, 140.6, 141.0, 155.2, 164.0, 164.4, 186.9.

2T8 (47%); MS(FAB) m/z 371 ($\text{M}+\text{H}^+$). Anal. Found: C, 71.29; H, 7.08%. Calcd for $\text{C}_{22}\text{H}_{26}\text{O}_5$: C, 71.33; H, 7.07%. ^1H NMR (CDCl_3): δ 0.90 (3H, t, $J = 6.6$ Hz), 1.25-1.38 (8H, m), 1.48 (2H, quit, $J = 6.6$ Hz), 1.83 (2H, quit, $J = 6.6$ Hz), 4.05 (2H, t, $J = 6.6$ Hz), 6.98 (1H, d, $J = 8.8$ Hz), 7.27 (2H, d, $J = 12.0$ Hz), 7.34 (1H, d, $J = 12.0$ Hz), 8.10 (2H, d, $J = 8.8$ Hz). ^{13}C NMR (CDCl_3): δ 14.1, 22.7, 26.0, 29.1, 29.2, 29.3, 31.8, 68.4, 114.5, 120.4, 122.6, 132.0, 132.4, 154.1, 164.0, 165.0, 170.8.

2T12 (52%); MS(FAB) m/z 427 ($\text{M}+\text{H}^+$). Anal. Found: C, 72.93; H, 8.02%. Calcd for $\text{C}_{26}\text{H}_{34}\text{O}_5$: C, 73.21; H, 8.03%. ^1H NMR (CDCl_3): δ 0.88 (3H, t, $J = 6.6$ Hz), 1.27-1.38 (16H, m), 1.48 (2H, quit, $J = 6.6$ Hz), 1.83 (2H, quit, $J = 6.6$ Hz), 4.05 (2H, t, $J = 6.6$ Hz), 6.98 (1H, d, $J = 8.8$ Hz), 7.27 (2H, d, $J = 12.0$ Hz), 7.34 (1H, d, $J = 12.0$ Hz), 8.10 (2H, d, $J = 8.8$ Hz).

2T16 (54%); MS(FAB) m/z 483 ($\text{M}+\text{H}^+$). Anal. Found: C, 74.44; H, 8.76%. Calcd for $\text{C}_{30}\text{H}_{42}\text{O}_5$: C, 74.65; H, 8.77%. ^1H NMR (CDCl_3): δ 0.88 (3H, t, $J = 6.6$ Hz), 1.26-1.37 (24H, m), 1.48 (2H, quit, $J = 6.6$ Hz), 1.83 (2H, quit, $J = 6.6$ Hz), 4.05 (2H, t, $J = 6.6$ Hz), 6.98 (1H, d, $J = 8.8$ Hz), 7.27 (2H, d, $J = 12.0$ Hz), 7.34 (1H, d, $J = 12.0$ Hz), 8.09 (2H, d, $J = 8.8$ Hz).

4T8 (88%); MS(FAB) m/z 355 ($\text{M}+\text{H}^+$). Anal. Found: C, 74.25; H, 7.34%. Calcd for $\text{C}_{22}\text{H}_{26}\text{O}_4$: C, 74.55; H, 7.39%. ^1H NMR (CDCl_3): δ 0.89 (3H, t, $J = 6.6$ Hz), 1.27-1.38 (8H, m), 1.47 (2H, quit, $J = 6.6$ Hz), 1.82 (2H, quit, $J = 6.6$ Hz), 4.03 (2H, t, $J = 6.6$ Hz), 6.96

(2H, d, $J = 8.8$ Hz), 7.06-7.43 (5H, m), 8.12 (2H, d, $J = 8.8$ Hz).

4T12 (89%); MS(FAB) m/z 411 ($M+H^+$). Anal. Found: C, 76.03; H, 8.32%. Calcd for $C_{26}H_{34}O_4$: C, 76.06; H, 8.35%. 1H NMR ($CDCl_3$): δ 0.88 (3H, t, $J = 6.6$ Hz), 1.28-1.38 (16H, m), 1.47 (2H, quit, $J = 6.6$ Hz), 1.82 (2H, quit, $J = 6.6$ Hz), 4.03 (2H, t, $J = 6.6$ Hz), 6.96 (2H, d, $J = 8.8$ Hz), 7.06-7.43 (5H, m), 8.12 (2H, d, $J = 8.8$ Hz).

4T16 (90%); MS(FAB) m/z 467 ($M+H^+$). Anal. Found: C, 77.34; H, 9.03%. Calcd for $C_{30}H_{42}O_4$: C, 77.21; H, 9.07%. 1H NMR ($CDCl_3$): δ 0.88 (3H, t, $J = 6.6$ Hz), 1.26-1.37 (24H, m), 1.47 (2H, quit, $J = 6.6$ Hz), 1.82 (2H, quit, $J = 6.6$ Hz), 4.03 (2H, t, $J = 6.6$ Hz), 6.96 (2H, d, $J = 8.8$ Hz), 7.06-7.43 (5H, m), 8.12 (2H, d, $J = 8.8$ Hz).

2·2·2 Preparation of 3T

A THF solution (10 cm^3) of tropolon-5-yl 4-*n*-alkoxybenzoates (**2T**, 0.2 mmol) was treated with an ethereal solution (10 cm^3) of CH_2N_2 . After 12 hr, the mixture was evaporated in vacuo to leave a residue, which was chromatographed in a hexane-ethyl acetate or a hexane-chloroform mixture on a silica-gel column to give crystals. The crystals were recrystallized with hexane-ethyl acetate (1:1 v/v) to give pale yellow crystals.

3T8 (90%); MS(FAB) m/z 385 ($M+H^+$). Anal. Found: C, 71.70; H, 7.28%. Calcd for $C_{23}H_{28}O_5$: C, 71.85; H,

7.34%. 1H NMR ($CDCl_3$): δ 0.89 (3H, t, $J = 6.6$ Hz), 1.25-1.38 (8H, m), 1.48 (2H, quit, $J = 6.6$ Hz), 1.82 (2H, quit, $J = 6.6$ Hz), 3.97 (3H, s), 4.05 (2H, t, $J = 6.6$ Hz), 6.70 (1H, d, $J = 11.0$ Hz), 6.94 (1H, dd, $J = 11.0$, 2.7 Hz), 6.98 (2H, d, $J = 8.8$ Hz), 7.16 (1H, dd, $J = 13.0$, 2.7 Hz), 7.26 (1H, d, $J = 13.0$ Hz), 8.10 (2H, d, $J = 8.8$ Hz). ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 26.0, 29.1, 29.2, 29.3, 31.8, 56.4, 68.4, 110.4, 114.5 (2C), 120.5, 123.6, 132.4 (2C), 134.0, 136.4, 149.5, 164.0, 164.2, 164.9, 179.6.

3T12 (95%); MS(FAB) m/z 441 ($M+H^+$). Anal. Found: C, 73.81; H, 8.14%. Calcd for $C_{27}H_{36}O_5$: C, 73.61; H, 8.24%. 1H NMR ($CDCl_3$): δ 0.88 (3H, t, $J = 6.6$ Hz), 1.27-1.37 (16H, m), 1.48 (2H, quit, $J = 6.6$ Hz), 1.82 (2H, quit, $J = 6.6$ Hz), 3.97 (3H, s), 4.05 (2H, t, $J = 6.6$ Hz), 6.70 (1H, d, $J = 11.0$ Hz), 6.94 (1H, dd, $J = 11.0$, 2.7 Hz), 6.98 (2H, d, $J = 8.8$ Hz), 7.16 (1H, dd, $J = 13.0$, 2.7 Hz), 7.26 (1H, d, $J = 13.0$ Hz), 8.10 (2H, d, $J = 8.8$ Hz).

3T16 (92%); MS(FAB) m/z 497 ($M+H^+$). Anal. Found: C, 74.79; H, 8.91%. Calcd for $C_{31}H_{44}O_5$: C, 74.96; H, 8.93%. 1H NMR ($CDCl_3$): δ 0.88 (3H, t, $J = 6.6$ Hz), 1.26-1.36 (24H, m), 1.48 (2H, quit, $J = 6.6$ Hz), 1.82 (2H, quit, $J = 6.6$ Hz), 3.97 (3H, s), 4.05 (2H, t, $J = 6.6$ Hz), 6.70 (1H, d, $J = 11.0$ Hz), 6.94 (1H, dd, $J = 11.0$, 2.7 Hz), 6.98 (2H, d, $J = 8.8$ Hz), 7.16 (1H, dd, $J = 13.0$, 2.7 Hz), 7.26 (1H, d, $J = 13.0$ Hz), 8.10 (2H, d, $J = 8.8$ Hz).

Scheme

3 Results and Discussion

3.1 Synthesis of Troponoid Compounds

Tropon-4-yl 4-alkoxybenzoates (**1T**) and 5-(4-alkoxybenzoyloxy)tropolones (**2T**), 2-(4-alkoxybenzoyloxy)tropolones (**4T**) were prepared by the esterification of 4-hydroxytropone, 5-hydroxytropolone, and tropolone with 4-alkoxybenzoyl chloride. Methylation of **2T** with diazomethane afforded 5-(4-alkoxybenzoyloxy)-2-metoxytropolones (**3T**). The structure and purity of the compounds (**1-4**) were ascertained by NMR spectroscopy, FAB MS and elemental analysis.

3.2 Mesomorphic Properties

The transition temperatures and thermal behaviors of the compounds (**1-4**) were determined using a differential scanning calorimeter and a polarizing microscope equipped with a hot stage as well as an X-ray diffraction study.

Optical micrograph and conoscopic figure of **1T12** are shown in **Figs. 1** and **2**. The smectic A phase was determined by observation of the bâtonnets, focal-conic fan, and homeotropic textures under a polarizing microscope. When a Bertrand lens was used in the observation of homeotropic texture of **1T12**, a dark cross could be seen in the conoscopic figure. This means that **1T** align perpendicularly to the layers.

The thermal behaviors of the troponoids (**1-4T**) and the corresponding benzenoids (**1-4B**) (**7**) are summarized in **Table 1**. The tropone derivatives (**1T**) have a

Fig. 1 Texture of the Smectic A Phase of **1T12** at 38°C Obtained on Cooling from the Isotropic Liquid.

Fig. 2 Conoscopic Figure of **1T12** at 38°C Obtained on Cooling from the Isotropic Liquid.

Table 1 Transition Temperatures (°C) of **1-4**.

	n	Transition Temperatures		n	Transition Temperatures
1T8	8	Cr · 37.0 · (SmA · 2.6 ·) I	1B8 ⁷	8	Cr · 59.7 · I
1T12	12	Cr · 63.4 · (SmA · 39.8 ·) I	1B12	12	Cr · 79.3 · I
1T16	16	Cr · 71.4 · (SmA · 63.0 ·) I	1B16	16	Cr · 72.8 · I
2T8	8	Cr · 124.9 · I	2B8 ⁷	8	Cr · 111 · I
2T12	12	Cr · 115.2 · I	2B12 ⁷	12	Cr · 113 · I
2T16	16	Cr · 114.8 · I	2B16 ⁷	16	Cr · 114.8 · I
3T8	8	Cr · 90.6 · I	3B8 ⁷	8	Cr · 82 · (N · 76 ·) I
3T12	12	Cr · 110.6 · I	3B12 ⁷	12	Cr · 91 · (N · 75 ·) I
3T16	16	Cr · 110.7 · I	3B16 ⁷	16	Cr · 84 · SmA · 101 · I
4T8	8	Cr · 73.3 · I	4B8 ⁷	8	Cr · 75.6 · N · 88.0 · I
4T12	12	Cr · 84.4 · I	4B12 ⁷	12	Cr · 72.7 · SmA · 90.0 · I
4T16	16	Cr · 93.0 · I	4B16 ⁷	16	Cr · 83.2 · SmA · 96.3 · I

Cr: Crystals, SmA: Smectic A Phase, N: Nematic Phase, I: Isotropic Liquid.

Fig. 3 Packing Model of **1T12** in the Smectic A Phase and Molecular Structure of **1T12** Generated by Sybyl Calculation.

monotropic smectic A phase, while the corresponding benzenoids (**1B**) and troponoid derivatives (**2T-4T**) were not mesomorphic. However the clearing and melting points of the troponone derivatives (**1T**) were lower than those of 4-cyanophenyl 4-alkanoxybenzoate (**4B**). This is due to the wider molecular width of the seven-membered ring compared with the benzene ring.

3.3 X-Ray Diffraction Analysis

Furthermore, we measured the X-ray diffraction pattern of the mesophases. The smectic layer spacing (d) of **1T12** were observed to be 35.5 Å (36°C). The molecular length (l) of **1T12** is 27.4 Å (calculated by the Sybyl method of *Spartan* '04 (8)). The d/l ratio of the smectic A phase of **1T12** are 1.3. This result suggests that **1T12** formed the interdigitated bilayers (9,10) in the smectic A phase as shown in **Fig. 3**. The d/l value of **1T** was similar to those (1.4 and 1.3) of 4-cyanophenyl 4-alkoxybenzoate (7) and 2-(4-alkoxybenzoyl)-5-cyanotropone (9).

4 Conclusion

The tropon-4-yl 4-alkoxybenzoates (**1T**) had a monotropic smectic A phase. They formed the interdigitated bilayers. The 4-hydroxytropone could be used as a terminal group of a mesogenic unit.

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