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Akira Mori[a]; Hitoshi Takeshita[a]; Ryoji Mori[b]; Shinji Takematsu[b]; Manabu Takemoto[b]; Seiji Ujiie[c]
[a] Institute of Advanced Material Study, 86 Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan, [b] Graduate School of Engineering Sciences, 39 Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan, [c] Interdisciplinary Faculty of Science and Engineering, Shimane University, Department of Material Science, Matsue 690-8504, Japan,

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Monocyclic rod-type liquid crystals; 2,5-dialkanoyloxytropones and 5-alkanoyloxy-2-alkoxytropones

AKIRA MORI*, HITOSHI TAKESHITA†
Institute of Advanced Material Study, 86 Kyushu University, Kasuga-koen,
Kasuga, Fukuoka 816-8580, Japan

RYOJI MORI, SHINJI TAKEMATSU, MANABU TAKEMOTO
Graduate School of Engineering Sciences, 39 Kyushu University, Kasuga-koen,
Kasuga, Fukuoka 816-8580, Japan

and SEIJI UJIIE
Department of Material Science,
Interdisciplinary Faculty of Science and Engineering, Shimane University,
Matsue 690-8504, Japan

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Two kinds of monocyclic troponoid mesogens, 2,5-dialkanoyloxytropones(**4**) and 5-alkanoyloxy-2-alkoxytropones (**5**), were prepared. The former showed monotropic smectic A phases and the virtual isotropic liquid–smectic A transitions of the latter were determined by extrapolation of results in a binary phase diagram. Comparing the mesogenic properties between the tropones **4** and the 2-alkanoyloxy-5-alkoxytropones (**1**), the alkanoyloxy group at C-5 enhances both the melting points and the transition temperatures of the smectic A phases. From the comparison between **5** and **1**, the alkanoyloxy group at C-2 lowers the melting points.

1. Introduction

The typical structural units of rod-like liquid crystal material possess a fairly rigid core structure, which consists of six-membered ring systems in general [1]. The preparation of new types of liquid crystal materials with rings other than six-membered rings has had less attention. However, it is important to extend the molecular design of liquid crystals to involve other ring systems from not only the theoretical, but also the practical point of view. In 1983, Uemura *et al.* reported the preparation and measurement of the thermal properties of liquid crystal materials containing a tropolone nucleus as a terminal group, because the dipole moment of tropolone (3.5 D) is comparable with that of benzonitrile (3.9 D) [2]. The thermal stabilities of the 5-(4-alkoxyphenyl)-azotropolones were, however, lower than those of the 4-(4-alkoxybenzylidene)aminobenzoic acids [3]. They pointed out that the tropolone ring decreased the stability of the mesophase due to the larger molecular width of the seven-membered ring (6.4 Å) compared with the benzenoid ring (4.8 Å). They also pointed out that tautomerization between the enol and the keto forms was unfavourable for mesophase stability.

Usually, the molecules of liquid crystals have long chains at the termini of the core. When such long chains are introduced into an odd-membered tropolone ring, the shape of the disubstituted troponoids cannot maintain linearity even if the two substituents are introduced at the most remote positions. Thus, the wider molecular breadth and the bent molecular shape of disubstituted troponoids are inferior factors for formation of thermally stable mesogenic states. Before we started to study troponoid liquid crystals, azulene [4] or 1,3-diaza-azulene [5] were used as the core because linearity of the molecules could be kept when the two terminal groups were introduced at the C-2 and C-6 positions.

Previously, we have reported that monocyclic 2-alkanoyloxy-5-alkoxytropones (**1**) show a monotropic smectic A (SmA) phase [6]. We proposed that the mesogenic properties of the compounds **1** would be induced by the migration of an acyl group ([1, 9] sigmatropic rearrangement) between the two oxygen atoms at C-1 and C-2 as indicated by solid state ^{13}C

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*Author for correspondence; e-mail: mori-a@cm.kyushu-u.ac.jp
†Deceased on 1 October, 1998.

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CPMAS (cross polarization magic angle spinning) NMR observations on the mesogenic state of 5-dodecyloxy-2-(4-dodecyloxy)benzoyloxytropone (**2**). In the case of 2,5-dialkoxytropones (**3**), however, no mesomorphic properties were observed. They have higher melting points than the corresponding compounds **1**, although ester groups are more polar than ether groups and induced stronger intermolecular interactions. In this paper, we report the preparation and phase transition temperatures of monocyclic troponoid liquid crystals such as 2,5-dialkanoyloxytropones (**4**) and 5-alkanoyloxy-2-alkoxytropones (**5**) in order to compare their mesogenic properties with those of compounds **1** [7].

2. Experimental

2.1. *General*

Elemental analyses were performed at the elemental analysis laboratory of the Institute of Advanced Material Study, Kyushu University. The melting points were obtained using a Yanagimoto micro melting point apparatus and are uncorrected. The NMR spectra were recorded using JEOL GSX 270H, LA400, and LA600 spectrometers and solutions in $CDCl_3$ at room temperature; the chemical shifts are expressed in δ units. The mass spectra were measured with JEOL 01SG-2 and JMS-700 spectrometers. IR spectra were recorded using a JASCO IR-A102 spectrometer with KBr disks. The stationary phase used in column chromatography was Wakogel C-300. The transition temperatures were measured by differential scanning calorimetry (Seiko DSC 200) 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 Cu-K_α radiation at various temperatures. The measuring temperatures were controlled with a Linkam HFS-91 hot stage.

2.2. *Preparation of the compounds 4*

(a) Anhydrous pyridine (344 mg, 4.3 mmol) was added to a stirred mixture of 5-hydroxytropolone (**6**, 500 mg, 3.6 mmol), anhydrous tetrahydrofuran (18.7 cm^3) and HMPA (hexamethylphosphoric triamide) (1.3 cm^3) maintained at ambient temperature, and the mixture was kept for 30 min at room temperature. Octadecanoyl chloride (1.1 g, 3.6 mmol) was added dropwise to the mixture at − 78°C and the temperature slowly raised to room temperature. After this the reaction mixture was stirred for 4 h. The mixture was poured into a 2M HCl solution and the organic material extracted with ethyl acetate. The organic layer was washed with saturated NaCl solution and dried with $MgSO_4$. The organic layer was evaporated *in vacuo* to leave a residue which was chromatographed in benzene on a silica gel column to give colourless crystals of **7f** (981 mg, 67%; m.p. 101.7°C). Found: C 74.22, H 9.96%. Calc. for $C_{25}H_{40}O_4$: C 74.22, H 9.97%. ^{1}H NMR δ 0.88 (3H, t, $J = 6.7$ Hz) 1.26–1.42 (28H, br m), 1.68–1.79 (2H, m), 2.55 (2H, t, $J = 6.7$ Hz), 7.13 (2H, d, $J = 11.7$ Hz), and 7.29 (2H, d, $J = 11.7$ Hz). ^{13}C NMR δ 14.1, 22.7, 24.8, 29.1, 29.2 (2C), 29.4 (4C), 29.6 (2C), 29.7 (3C), 31.9, 34.2, 122.6, 131.7, 149.5, 170.8, and 172.4. IR 3222, 2918, 2848, 1752, 1626, 1610, 1593, 1567, 1469, 1417, 1268, 1227, 1204, 1151, 1113, 861, 757, and 720 cm^{-1}. MS *m*/*z* (%) 405 ($M^+ + 1$, 3), 404 (M^+, 9), and 267 (100).

Results for **7a**: m.p. 87.1°C. Found: C 68.18, H 7.62%. Calc. for $C_{15}H_{20}O_4$: C 68.16, H 7.63%; **7b**: m.p. 91.2°C. Found: C 69.83, H 8.27%. Calc. for $C_{17}H_{24}O_4$: C 69.84, H 8.27%; **7c**: m.p. 96.1°C. Found: C 70.95, H 8.76%. Calc. for $C_{19}H_{28}O_4$: C 71.22, H 8.81%; **7d**: m.p. 99.4°C. Found: C 72.33, H 9.23%. Calc. for $C_{21}H_{32}O_4$: C 72.38, H 9.26%; **7e**: m.p. 101.7°C. Found: C 73.34, H 9.60%. Calc. for $C_{23}H_{36}O_4$: C 73.37, H 9.64%.

Dodecanoyl chloride (33 mg, 0.15 mmol) was added to a tetrahydrofuran solution (10 cm^3) of 5-octadecanoyloxytropolone (**7f**, 50 mg, 0.12 mmol) and triethylamine (20 mg, 0.18 mmol) and the reaction mixture was stirred at room temperature for 4 h. The mixture was poured into a 2M HCl and the organic matter extracted with ethyl acetate. The organic layer was washed with a saturated NaCl solution and dried over $MgSO_4$. The organic layer was evaporated *in vacuo* to leave a residue which was recrystallized with methanol to give colourless crystals of **4m** (64 mg, 89%). Found: C 75.61, H 10.40%. Calc. for $C_{37}H_{62}O_5$: C 75.72, H 10.64%. ^{1}H NMR δ 0.88 (6H, t, $J = 7.0$ Hz), 1.25–1.4 (44H, br m), 1.7–1.8 (4H, m), 2.55 (2H, t, $J = 7.0$ Hz), 2.61 (2H, t, $J = 7.0$ Hz, 6.88 (2H, br d, $J = 12.1$ Hz), and 7.17 (2H, d, $J = 12.1$ Hz). ^{13}C NMR δ 14.1, 22.7, 24.7, 29.1, 29.2, 29.3 (2C), 29.4 (2C), 29.5 29.6 (4C), 29.7 (7C), 31.9 (4C), 33.9, 34.2, 153.5, 171.0, and 171.7. IR 2954, 2922, 2850, 1760, 1644, 1598, 1470, 1381, 1225, 1161, 1143, 1110, and 931 cm^{-1}; MS *m*/*z* (%) 586 (M^+, 1) and 183 (100).

(b) A pyridine solution (10 cm^3) of 5-hydroxytropolone (**6**, 100 mg, 0.72 mmol) was stirred at room temperature for 30 min in the presence of a catalytic amount of 4-*N*,*N*-dimethylaminopyridine. Octadecanoyl chloride (482 mg, 1.6 mmol) was added to the pyridine solution at 0°C and the mixture was stirred at room temperature for 4 h. The mixture was poured into a saturated aqueous $KHCO_3$ and the whole shaken with ethyl acetate. The organic layer was washed with a saturated NaCl solution and dried over $MgSO_4$. The organic layer was evaporated *in vacuo* to leave a residue which was chromatographed using a mixture of hexane and ethyl acetate (3 : 1) on a silica gel column. The product was recrystallized with methanol to give colourless crystals (**4o**, 214 mg, 44%). Found: C 76.94, H 11.07%.

Calc. for $C_{43}H_{74}O_5$: C 76.96, H 11.12%. ^{1}H NMR δ 0.88 (6H, t, $J = 7.0$ Hz), 1.2–1.5 (56H, br m), 1.7–1.8 (4H, m), 2.55 (2H, t, $J = 7.0$ Hz), 2.61 (2H, t, $J = 7.0$ Hz), 6.88 (2H, br d, $J = 11.7$ Hz), and 7.17 (2H, d, $J = 11.7$ Hz). ^{13}C NMR δ 14.1 (2C), 22.7 (2C), 24.7 (2C), 29.0, 29.1 (2C), 29.2, 29.3 (2C), 29.4 (3C), 29.5, 29.6 (2C), 29.7 (12C), 31.9 (2C), 33.9, 34.2, 153.5, 171.0, and 171.7. IR 2954, 2918, 2850, 1760, 1598, 1469, 1382, 1225, 1139, and 1109 cm^{-1}. MS *m/z* (%) 670 (M$^+$, 0.3) and 267 (100).

Results for **4a**: Found: C 69.62, H 8.33%. Calc. for $C_{21}H_{30}O_5$: C 69.59 H 8.34%; **4b**: Found: C 71.75, H 9.02%. Calc. for $C_{25}H_{38}O_5$: C 71.74, H 9.15%; **4c**: Found: C 72.29, H 9.19%. Calc. for $C_{27}H_{42}O_5$: C 72.61, H 9.48%; **4d**: Found: C 72.88, H 9.15%. Calc. for $C_{27}H_{42}O_5$: C 72.61, H 9.48%; **4e**: Found: C 73.58, H 9.60%. Calc. for $C_{29}H_{46}O_5$: C 73.38, H 9.77%; **4f**: Found: C 73.75, H 9.84%. Calc. for $C_{31}H_{50}O_5$: C 74.06, H 10.03%; **4g**: Found: C 76.28, H 10.70%. Calc. for $C_{39}H_{66}O_5$: C 76.17, H 10.82%; **4h**: Found: C 73.81, H 9.89%. Calc. for $C_{31}H_{50}O_5$: C 74.06, H 10.03%; **4i**: Found: C 74.80, H 10.23%. Calc. for $C_{35}H_{58}O_5$: C 75.22, H 10.41%; **4j**: Found: C 75.51, H 10.39%. Calc. for $C_{37}H_{62}O_5$: C 75.72, H 10.64%; **4k**: Found: C 76.50, H 11.18%. Calc. for $C_{41}H_{70}O_5$: C 76.59, H 10.97%; **4l**: Found: C 74.77, H 10.10%. Calc. for $C_{33}H_{54}O_5$: C 74.67, H 10.25%; **4n**: Found: C 76.00, H 10.59%. Calc. for $C_{39}H_{66}O_5$: C 76.17, H 10.82%.

2.3. *Preparation of 5-pivaloyloxytropolone (8)*

An HMPA solution (50 cm^3) of 5-hydroxytropolone (**6**, 5.50 g, 40 mmol) was stirred in the presence of sodium hydride (60%, 1.92 g, 48 mmol) at 0°C for 1 h under a stream of N_2. Pivaloyl chloride (5.4 cm^3, 44 mmol) was added dropwise to the HMPA solution at room temperature and the reaction mixture was stirred overnight. It was then poured into 2M HCl solution and the organic material was extracted with ethyl acetate. The organic layer was washed with water and a saturated NaCl solution and dried over Na_2SO_4. The solvent was evaporated *in vacuo* and the residue chromatographed using a mixture of hexane and ethyl acetate (3 : 1) on a silica gel column. The product was recrystallized from hexane : ethyl acetate (3 : 1) to give **8** (5.75 g, 65%; pale yellow crystals; m.p. 166.3°C. ^{1}H NMR δ 1.35 (9H, s), 7.09 (2H, dd, $J = 10.6$, 1.5 Hz), and 7.29 (2H, dd, $J = 10.6$, 1.5 Hz). ^{13}C NMR δ 27.0 (3C), 39.0, 122.6, 131.6, 149.8, 170.7, and 177.1. IR 3700–3300, 3142, 2972, 1747, 1621, 1558, 1474, 1425, 1371, 1265, 1214, 1142, 1102, 1027, 905, and 753 cm^{-1}. MS *m/z* (%) 224 (M$^+$ + 2, 5), 223 (M$^+$ + 1, 22), 222 (M$^+$, 22), 138 (77), 110 (84), 85 (73), and 57 (100). Found: C 64.62, H 6.34%. Calc. for $C_{12}H_{14}O_4$: C 64.85, H 6.35%.

2.4. *Preparation of the compounds **10***

An HMPA solution (10 cm^3) of 5-pivaloyloxytropolone (**8**, 222 mg, 1 mmol) was stirred in the presence of sodium hydride (60%, 48 mg, 1.2 mmol) at 0°C for 1 h under a stream of N_2. 1-Iodo-octane (264 mg, 1.1 mmol) was added dropwise to the HMPA solution at room temperature and the reaction mixture was then heated at 80°C for 4 h before it was poured into a 2M HCl solution and the organic matter was extracted with ethyl acetate. The organic layer was washed with water and a saturated NaCl solution and dried over Na_2SO_4. After the solvent was evaporated *in vacuo*, the residue was chromatographed using a mixture of hexane and ethyl acetate (3 : 1) on a silica gel column to give the product **9**, which was heated under reflux in an alkaline aqueous ethanol for 4 h. The reaction mixture was poured into a 2M HCl solution and shaken with ethyl acetate. The organic layer was washed with water and saturated NaCl solution and dried over Na_2SO_4. The solvent was then evaporated *in vacuo* and the product recrystallized from ethyl acetate to give pale yellow crystals of **10a** (189 mg, 76%, m.p. 83.3°C). Found: C 71.89, H 8.80%. Calc. for $C_{15}H_{22}O_3$: C 71.97, H 8.86%. ^{1}H NMR δ 0.88 (3H, t, $J = 6.8$ Hz), 1.28–1.45 (10H, m), 1.82 (2H, m), 4.04 (2H, t, $J = 6.8$ Hz), 6.84 (1H, dd, $J = 12.1$, 2.6 Hz), 7.05 (1H, d, $J = 12.1$ Hz), 7.18 (1H, dd, $J = 13.2$, 2.6 Hz), and 7.31 (1H, d, $J = 13.2$ Hz). ^{13}C NMR δ 14.1, 22.6, 26.0, 29.0, 29.2, 29.3, 31.8, 69.8, 118.0, 120.6, 133.9, 137.0, 157.6, 164.6, and 174.5. IR 3700–3300, 2922, 2850, 1533, 1454, 1420, 1234, 1209, 1115, 849, and 783 cm^{-1}. MS *m/z* (%) 251 (M$^+$ + 1, 8), 250 (M$^+$, 15), 222 (22), 138 (75), 110 (84), and 57 (100).

Results for **10b**: m.p. 90.5°C, 91%. Found: C 73.40, H 9.48%. Calc. for $C_{17}H_{26}O_3$: C 73.35, H 9.41%; **10c**: m.p. 96.6°C, 69%. Found: C 74.80, H 9.96%. Calc. for $C_{19}H_{30}O_3$: C 74.47, H 9.87%; **10d**: m.p. 100.9°C, 50%. Found: C 75.15, H 10.16%. Calc. for $C_{21}H_{34}O_3$: C 75.41, H 10.25%.

2.5. *Preparation of the compounds **5***

2-Octyloxy-5-hydroxytropone (**10a**, 63 mg, 0.25 mmol) was dissolved in a mixture of tetrahydrofuran (10 cm^3) and pyridine (1 cm^3) under a stream of N_2. Decanoyl chloride (61 mg, 0.28 mmol) was added dropwise to the above solution and the reaction mixture stirred at room temperature overnight. The reaction mixture was then poured into a 2M HCl solution and the whole shaken with ethyl acetate. The organic layer was washed with water and saturated NaCl solution, dried over Na_2SO_4, and the solvent evaporated *in vacuo*. The residue was chromatographed as a solution in hexane and ethyl acetate (3 : 1) on a silica gel column and the product was recrystallized from hexane : ethyl acetate (3 : 1) to give colourless crystals of **5a** (18 mg, 17%). ^{1}H NMR δ 0.88 (6H, t, $J = 6.8$ Hz), 1.27–1.48 (26H, m), 1.73 (2H, m), 1.91 (2H, m), 2.53 (2H, t, $J = 6.8$ Hz), 4.03 (2H, t, $J = 6.8$ Hz), 6.63 (1H, d, $J = 11.0$ Hz), 6.76 (1H, dd, $J = 11.0$, 2.6 Hz), 6.97 (1H, dd, $J = 13.2$, 2.6 Hz), and 7.19 (1H, d, $J = 13.2$ Hz). IR 2920, 2852, 1755, 1632, 1577, 1470, 1283, 1240, 1147, 1113, 860, and 719 cm^{-1}. MS *m/z* (%) 433 ($M^+ + 1$, 3), 250 (57), 151 (72), 138 (100), and 57 (52). Found: C 74.60, H 10.04%. Calc. for $C_{27}H_{44}O_4$: C 74.96, H 10.25%.

Results for **5b**: Found: C 76.00, H 10.49%. Calc. for $C_{29}H_{48}O_4$: C 75.61, H 10.50%; **5c**: Found: C 75.92, H 10.61%. Calc. for $C_{31}H_{52}O_4$: C 76.18, H 10.72%; **5d**: Found: C 76.56, H 10.85%. Calc. for $C_{33}H_{56}O_4$: C 76.69, H 10.92%; **5e**: Found: C 76.02, H 10.56%. Calc. for $C_{30}H_{50}O_4$: C 75.90, H 10.62%; **5f**: Found: C 76.33, H 10.67%. Calc. for $C_{32}H_{54}O_4$: C 76.45, H 10.83%; **5g**: Found: C 77.29, H 11.00%. Calc. for $C_{34}H_{58}O_4$: C 76.93, H 11.01%; **5h**: Found: C 76.57, H 10.66%. Calc. for $C_{33}H_{56}O_4$: C 76.69, H 10.92%; **5i**: Found: C 76.91, H 11.02%. Calc. for $C_{35}H_{60}O_4$: C 77.15, H 11.10%; **5j**: Found: C 77.36, H 11.17%. Calc. for $C_{37}H_{64}O_4$: C 77.57, H 11.26%; **5k**: Found: C 77.85, H 11.47%. Calc. for $C_{39}H_{68}O_4$: C 77.95, H 11.41%.

3. Results and discussion

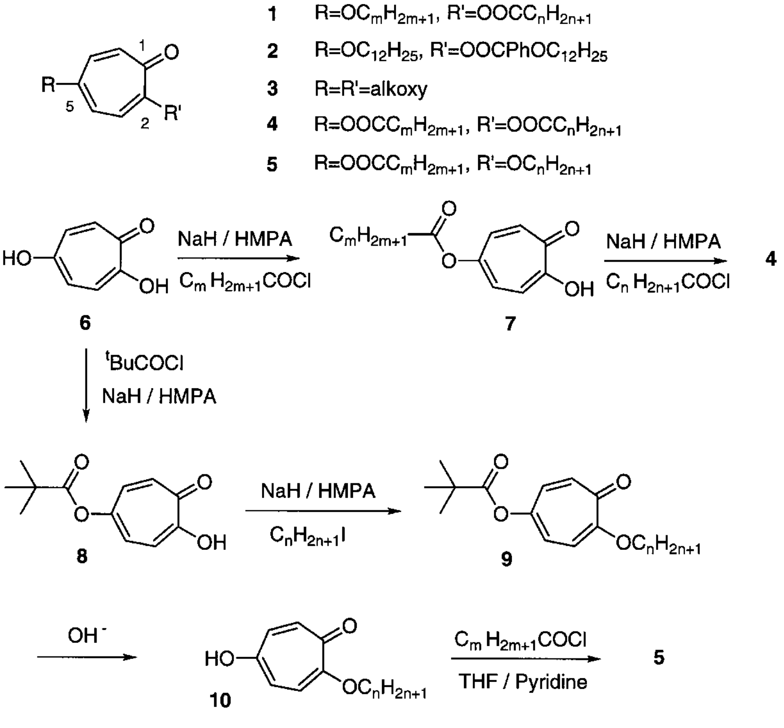
3.1. *Synthesis*

2,5-Dialkanoyloxytropones (**4**) with the same alkyl chain length at C-2 and C-5 were prepared by the reaction of 5-hydroxytropolone (**6**) and two molar equivalents of alkanoyl chloride. On the other hand, 2,5-dialkanoyloxytropones (**4**) with different alkyl chain lengths were prepared in 28–89% yield by the reaction of **6** with a molar equivalent of alkanoyl chloride to give 5-alkanoyloxytropolones (**7**), which were further reacted with the desired alkanoyl chloride. The spectral data for compound **4** are satisfactory for the structure. Some signals of the tropone ring carbons were however missing in the ^{13}C NMR spectra of **4** because of the [1, 9] sigmatropic rearrangement [6]. This is characteristic of compounds having an alkanoyl group at C-2 of the tropone ring.

5-Alkanoyloxy-2-alkoxytropones (**5**) were prepared as follows: when **6** was reacted with pivaloyl chloride in the presence of sodium hydride, 5-pivaloyloxytropolone (**8**) was obtained in 65% yield. Alkylation of **8** with an alkyl iodide gave the 2-alkoxy-5-pivaloyloxytropones (**9**), which on hydrolysis with aqueous potassium hydroxide gave the 2-alkoxy-5-hydroxytropones (**10**) in 50–91% yield. Finally, compound **10** was reacted with various alkanoyl chlorides to give **5** in 16–69% yield.

3.2. *Mesomorphic properties*

Phase transition temperatures were determined by a differential scanning calorimetry (DSC). The mesomorphic phases of the compounds **4** were identified as SmA on the basis of the microscopic texture. Table 1 summarizes the phase transition temperatures. In the case of **4f**, a smectic B (SmB) phase also appeared. Figure 1 shows the optical textures of **4f**. Focal-conic fan textures are observed in the first photograph of



Scheme 1.

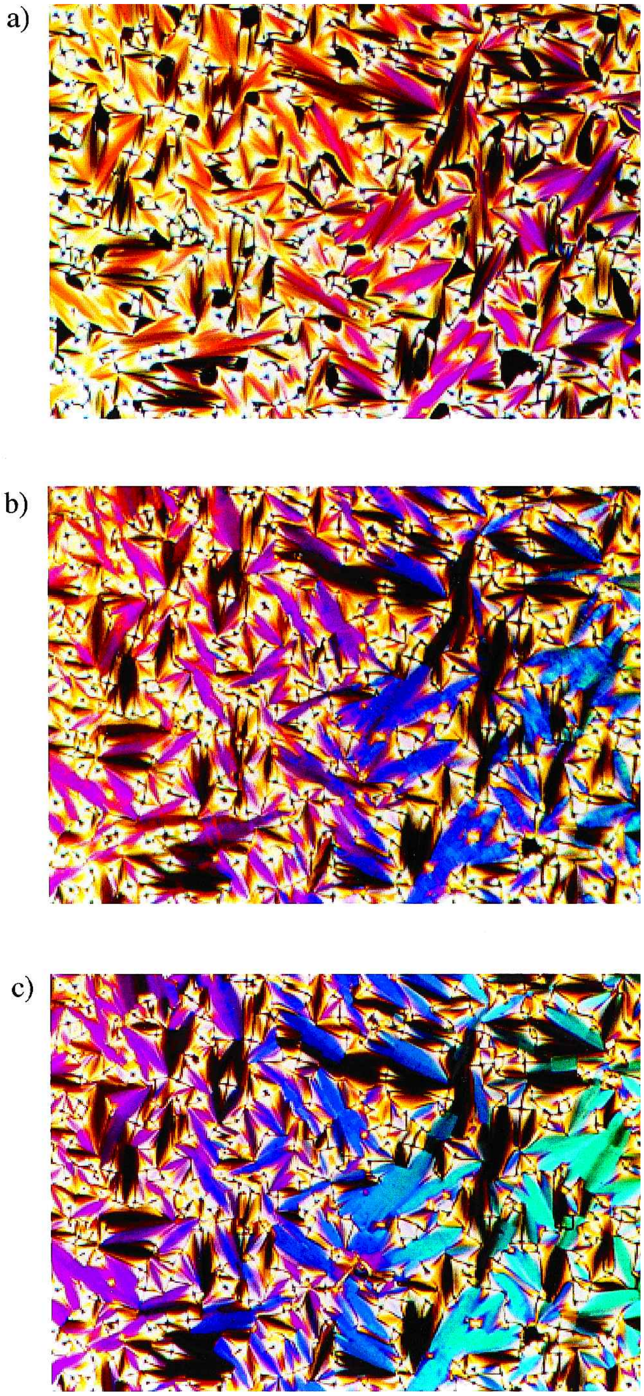
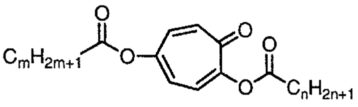


Figure 1. Optical textures of compound **4f** as obtained by cooling from the isotropic liquid: (*a*) at 59.1°C, (*b*) at 55.9°C, (*c*) at 50.7°C.

figure 1. In the second photograph transition bars are observed on the backs of the fans at the transition between SmA and SmB. In the third photograph, the lines disappear to produce the fan texture of the SmB phase.

Table 1. Phase transition temperatures and enthalpy changes for the troponoids **4**. Phases involved in monotropic transitions and their transition temperatures are in ( ).

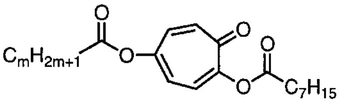


4

Compound	*m*	*n*	Transition temp./°C (ΔH/kJ mol^{-1})
4a	7	5	Cr • 50 • (SmA • 11 •) I
4b	9	7	Cr • 61 (46.5) • (SmA • 43 (8.8) •) I
4c	11	7	Cr • 62 (46.8) • (SmA • 41 (7.8) •) I
4d	13	5	Cr • 59 (33.3) • (SmA • 37 (4.8) •) I
4e	13	7	Cr • 62 (61.2) • (SmA • 52 (13.2) •) I
4f	13	9	Cr • 68 • (SmB • 54 • SmA • 58 •) I
4g	13	17	Cr • 74 • I
4h	15	7	Cr • 59 • (SmA • 55 (10) •) I
4i	15	11	Cr • 71 • I
4j	15	13	Cr • 76 • (SmA • 69 (7.5) •) I
4k	15	17	Cr • 73 • I
4l	17	7	Cr • 61 • I
4m	17	11	Cr • 65 • (SmA • 59 •) I
4n	17	13	Cr • 75 (82.9) • (SmA • 69 (7.5) •) I
4o	17	17	Cr • 90 • I

When the alkyl chain length at C-5 of the compounds **4** is fixed at $C_{13}H_{27}$ and that at C-2 is changed from C_5H_{11} to C_9H_{19}, the phase transition temperatures from the isotropic liquid (I) to the SmA phase changed by more than 20°C from 37°C ($n = 5$) to 58°C ($n = 9$) as shown in table 1. The melting point, however, changed by less than 10°C from 59°C ($n = 5$) to 68°C ($n = 9$). Table 2 summarizes the phase transition temperatures of the compounds **4** when the substituent at C-2 is fixed at C_7H_{15} and the alkyl chain length at C-5 is changed. The melting points are almost the same, whereas the transition temperatures from I to SmA are dependent on the alkyl chain length at C-5. When the mesomorphic properties of compounds **1** and **4** were compared, the ester group at C-5 of **4** raised both the melting point

Table 2. Phase transition temperatures and enthalpy changes for selected troponoids **4**.



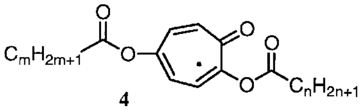
4

Compound	*m*	Transition temp./°C (ΔH/kJ mol^{-1})
4b	9	Cr • 61 (46.5) • (SmA • 43 (8.8) •) I
4c	11	Cr • 62 (46.8) • (SmA • 41 (7.8) •) I
4e	13	Cr • 62 (61.2) • (SmA • 52 (13.2) •) I
4h	15	Cr • 59 • (SmA • 55 (10) •) I
4l	17	Cr • 61 • I

and the transition temperature to the SmA phase as shown in table 3. The ester group at C-5 extends the linearity of the molecule.

By rapidly cooling the compounds **5**, a mesophase was observed momentarily. Then, the virtual I–SmA transition temperatures were determined by extrapolation of results in the binary phase diagram between **5** and 2-dodecanoyloxy-5-(4-tetradecyloxybenzoyloxy)-tropone (**11**) [8] which has an enantiotropic SmA phase. The diagram in figure 2 indicates that compound **5b** intrinsically possesses an I–SmA transition at 45°C. Table 4 summarizes the virtual I–SmA transition temperatures together with the transition temperatures of the monotropic SmA phases of the compounds **1**. The

Table 3. Comparison of transition temperatures between **4** and **1**.



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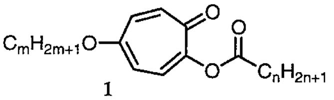
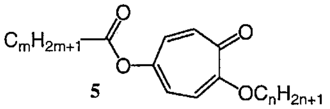


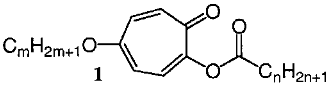
1

Compound	*m*	*n*	Transition temp./°C (ΔH/kJ mol^{-1})	Compound	*m*	*n*	Transition temp./°C
4l	17	7	Cr • 61 • I	**1h**	18	7	Cr • 49 • (SmA • 39 •) I
4m	17	11	Cr • 65 • (SmA • 59 •) I	**1j**	18	11	Cr • 60 • (SmA • 52 •) I
4n	17	13	Cr • 75 (82.9) • (SmA • 69 (7.5) •) I	**1k**	18	13	Cr • 72 • I

Table 4. Transition temperatures for compounds **5** and **1**. The virtual values in [] were determined by extrapolation (see figure 2).

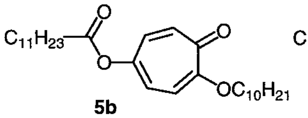


5

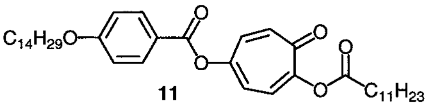


1

Compound	*m*	*n*	Transition temp./°C (ΔH/kJ mol^{-1})	Compound	*m*	*n*	Transition temp./°C
5a	11	8	Cr • 54 • [SmA • 38 •] I	**1a**	12	9	Cr • 48 • (SmA • 46 •) I
5b	11	10	Cr • 59 • [SmA • 45 •] I	**1b**	12	11	Cr • 58 • (SmA • 45 •) I
5c	11	12	Cr • 74 • [SmA • 50 •] I	**1c**	12	13	Cr • 63 • (SmA • 51 •) I
5d	11	14	Cr • 80 • [SmA • 47 •] I	**1d**	15	7	Cr • 41 • (SmA • 39 •) I
5e	14	8	Cr • 57 • [SmA • 36 •] I	**1e**	15	9	Cr • 48 • (SmA • 47 •) I
5f	14	10	Cr • 66 • [SmA • 50 •] I	**1f**	15	11	Cr • 60 • (SmA • 52 •) I
5g	14	12	Cr • 73 • [SmA • 54 •] I	**1g**	15	13	Cr • 67 • I
5h	17	8	Cr • 49 • [SmA • 41 •] I	**1h**	18	7	Cr • 49 • (SmA • 39 •) I
5i	17	10	Cr • 65 • [SmA • 53 •] I	**1i**	18	9	Cr • 53 • (SmA • 46 •) I
5j	17	12	Cr • 75 • [SmA • 54 •] I	**1j**	18	11	Cr • 60 • (SmA • 52 •) I
5k	17	14	Cr • 80 • [SmA • 57 •] I	**1k**	18	13	Cr • 72 • I



5b



11

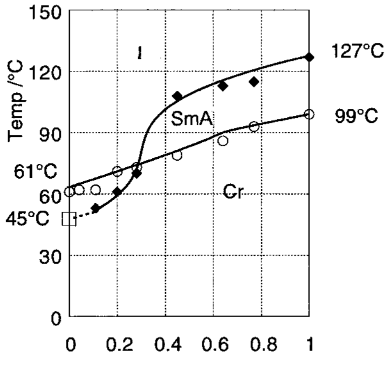


Figure 2. Binary phase diagram for compound **5b** with different mol fractions of compound **11**. ○: Melting point, ◆: I–SmA transition temperature, □: virtual transition temperature.

structural difference between compounds **1** and **5** lies in the position of the substituents on the tropone ring. The transition temperatures from I to SmA phase were similar to each other, but the melting points of the compounds **5** were higher than those of **1**. The ester group at C-2 of **1** made the melting point lower, since the carbonyl group of the compounds **1** is concerned in the sigmatropic rearrangement, so making the intermolecular interaction weaker.

Figure 3 shows the effect of the alkyl chain length on the temperature of the virtual I–SmA transition. Both the I–SmA transition temperatures and the melting points on the left side of the diagram changed more than those on the right side. The chain length C_nH_{2n+1} at C-2 of **5** was more effective than that of C_mH_{2m+1} in affecting both the phase transition temperature and the melting point as observed for the compounds **1**. Compared with the mesogenic properties of compounds **1** and **5**, it is confirmed that the ester group at C-2 of **1** assisted the appearance of the mesophase through the sigmatropic rearrangement. Furthermore, corresponding benzenoids, 4-decyloxyphenyl dodecanoate (**12**) and 1,4-dialkanoyloxybenzenes (**13**), were non-mesogenic (scheme 2) and gave no virtual I–mesophase transitions.

When the mesogenic properties of compounds **4** and **5** were compared, the ester group at C-2 of **4** decreased the melting point and increased the transition temperature to the SmA phase as shown in table 5.

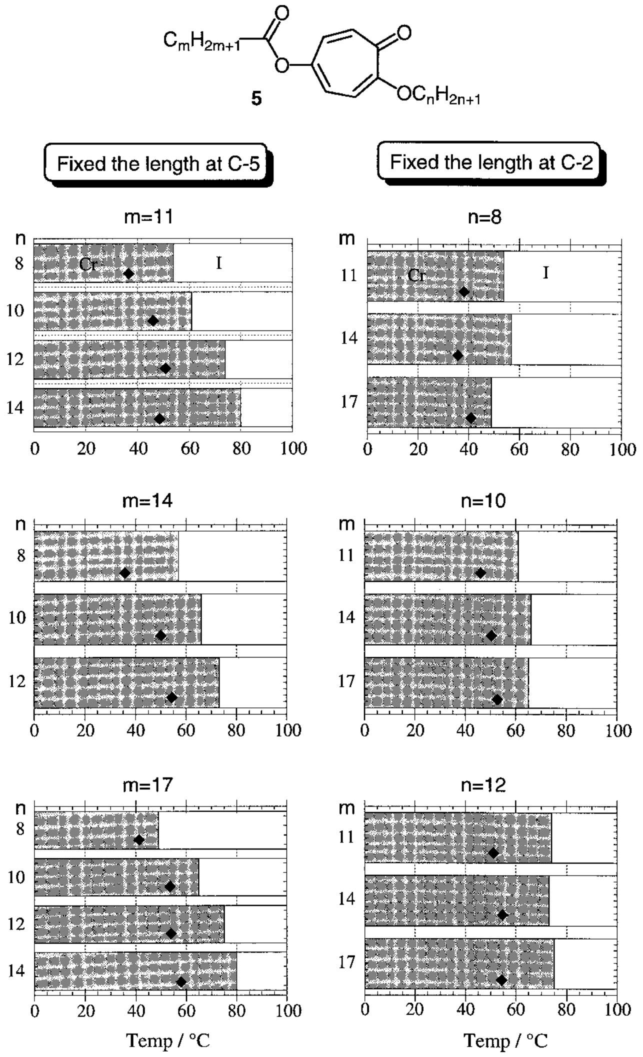
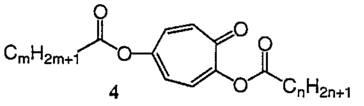


Figure 3. Effect of alkyl chain length on the virtual transition temperatures of compounds **5**. ◆: Virtual I–SmA transition temperatures.

3.3. *X-ray diffraction study*

The X-ray diffraction pattern of compound **4f** was taken at 56°C, when a SmA phase appeared. Figure 4 shows a representative X-ray diffraction pattern obtained from a powder sample of compound **4f**. The layer spacing of **4f** was 34.6 Å, whereas the calculated molecular length from MM2 calculations is 37.4 Å. The layer spacing is almost identical with the calculated molecular length. On the other hand, the layer spacing at 52°C, when a SmB phase was observed, was 36.8 Å. The molecules are perpendicular to the layers, and a uniaxial conoscopic figure was observed as shown in figure 5. A peak of weak intensity appeared around $2\theta = 20°$ together with a diffuse band which corresponds to the distance between neighbouring molecules. The presence of the weak peak shows the

Table 5. Transition temperatures for compounds **4** and **5**.



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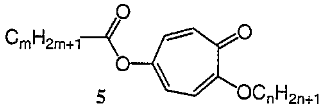
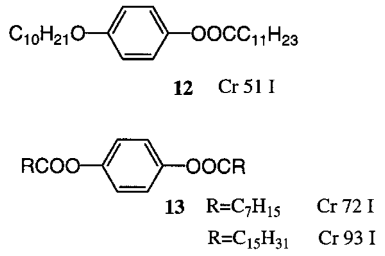


5

	m	*n*	Transition temp./°C (ΔH/kJ mol^{-1})		*m*	*n*	Transition temp./°C
4c	11	7	Cr • 62 (46.8) • (SmA • 41 (7.8) •) I	**5a**	11	8	Cr • 54 • [SmA • 38 •] I
4l	17	7	Cr • 61 • I	**5h**	17	8	Cr • 49 • [SmA • 41 •] I
4m	17	11	Cr • 65 • (SmA • 59 •) I	**5i**	17	10	Cr • 65 • [SmA • 53 •] I
4n	17	13	Cr • 75 (82.9) • (SmA • 69 (7.5) •) I	**5j**	17	12	Cr • 75 • [SmA • 54 •] I



12 Cr 51 I

13 $R=C_7H_{15}$ Cr 72 I
$R=C_{15}H_{31}$ Cr 93 I

Scheme 2.

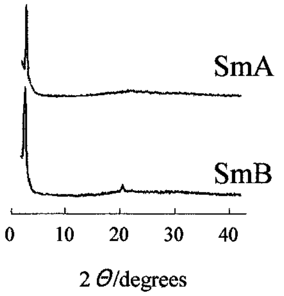


Figure 4. X-ray diffraction pattern of compound **4f**.

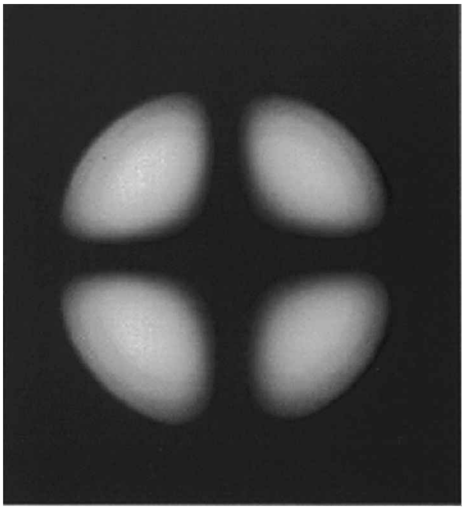


Figure 5. Conoscopic figure observed for compound **4f**.

formation of a hexagonal packing in the SmB phase. The weak peak intensity may be due to poor molecular packing because the molecules are monocyclic.

4. Conclusion

The mesogenic properties of two types of monocyclic troponoid liquid crystal materials have been discussed. 2,5-Dialkanoyloxytropones (**4**) had monotropic SmA phases and 5-alkanoyloxy-2-alkoxytropones (**5**) showed virtual I–SmA transitions. From a comparison of the transition temperatures of compounds **1** and **5**, the ester group at C-2 of the compounds **1** made the melting points lower because both carbonyl groups of **1** are concerned in the [1, 9] sigmatropic rearrangement so making intermolecular interactions weaker. While the ester group of the compounds **5** should lie in the same plane as that of the seven-membered ring so enlarging the core size, it will enhance the intermolecular interactions and make the melting points higher. Compared with the mesogenic properties of compounds **4** and **1**, the corresponding benzenoids were non-mesomorphic. The tropone carbonyl group thus played a decisive role as a lateral polar group in enhancing the thermal stability of the mesomorphic states.

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