Liquid Crystals
Publication details, including instructions for authors and subscription information:
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To cite this Article Mori, Akira , Kubo, Kanji , Takemoto, Manabu and Ujiie, Seiji(2005) 'Non-symmetric calamitic liquid crystal dimers containing troponoid and benzenoid units', Liquid Crystals, 32: 8, 1021 — 1029
To link to this Article: DOI: 10.1080/02678290500183599
URL: http://dx.doi.org/10.1080/02678290500183599

Liquid Crystals, Vol. 32, No. 8, August 2005, 1021–1029

Non-symmetric calamitic liquid crystal dimers containing troponoid and benzenoid units

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(*Received 18 February 2005; accepted 17 March 2005*)

Five types of non-symmetric calamitic dimers were synthesized to investigate the effect of the core structure and length of the spacer on mesomorphic properties. Two non-symmetric dimers containing a troponoid and benzenoid unit showed smectic A and C phases whereas the corresponding benzenoid dimers showed no mesophase. Non-symmetric dimers with a three-ring system showed smectic A and C phases with higher transition temperatures than the two-ring system. We propose packing models for these non-symmetric dimers by considering the direction of the dipole moments of the ring structures and microsegregation between the polar units and the non-polar chains.

1. Introduction

Liquid crystals with two mesogenic units connected via a flexible spacer are called dimers, and their mesomorphic properties and phases are significantly dependent on the length of the spacer [1, 2]. Normally, the mesogenic units of dimers have at least two rings, and typically have a symmetric structure because of synthetic considerations. Non-symmetry is usually introduced into a dimer by connecting two different mesogenic units, by changing the length of the terminal chains or by using different terminal groups [1, 3, 4].

Previously, we have reported the mesomorphic properties of three types of dimer containing two troponoid units, in which the direction of the tropone carbonyl groups is different [5, 6]. When the two tropone carbonyl groups are directed inwards, monotropic smectic C (SmC) phases were observed. The corresponding benzenoid dimers were non-mesomorphic, although the melting points were higher than the troponoid dimers [6]. The dimers, with the carbonyl groups directed outwards, were not mesomorphic. The non-symmetrical dimers, with carbonyl groups facing the same direction, had a smectic A (SmA) phase. When the symmetrical troponoid dimers in which the two carbonyl groups were directed inwards, and which had a SmC phase, were mixed with the non-mesomorphic symmetrical dimer in which the carbonyl groups were directed outwards, a SmA phase was induced with higher transition temperatures than either component [6]. This suggested that they form an aggregate in which their dipole moments are cancelled. Thus, the direction of the dipole moment plays a critical role on the appearance of mesophases. In this paper, we report the mesomorphic properties of non-symmetric dimers (**1**–**5**) consisting of two different mesomorphic units, specifically troponoid and benzenoid cores, connected with a flexible spacer.

2. Synthesis

The synthetic routes used to pepare the dimers are shown scheme 1. Compound **1** was synthesized from the reaction of 2-alkanoyloxy-5-hydroxytropones **6** [6] and 4-alkoxyphenyl ω-bromoalkanoates **7**, which were obtained from 4-alkoxyphenol and ω-bromoalkanoyl chlorides. Compounds **2** and **3** were synthesized from the reaction of **6** with ω-bromoalkyl 4-alkoxybenzoates **8** and ω-bromoalkyl 3,4-dialkoxybenzoates **9**, which were obtained from α,ω-dibromoalkanes with 4-alkoxybenzoic acids and 3,4-dialkoxybenzoic acids, respectively. Compound **4** was synthesized from **8** and 4-hydroxyphenyl alkanoates. Compound **5** was synthesized from the reaction of **6** with 4-(dodecyloxybenzoyloxy)phenyl ω-bromoalkanoates **10**, which were obtained from 4-hydroxyphenyl 4-alkoxybenzoates and ω-bromoalkanoyl chlorides. The structures and purity of the synthetic intermediates (**7**–**10**) were determined by ^{1}H NMR spectra.

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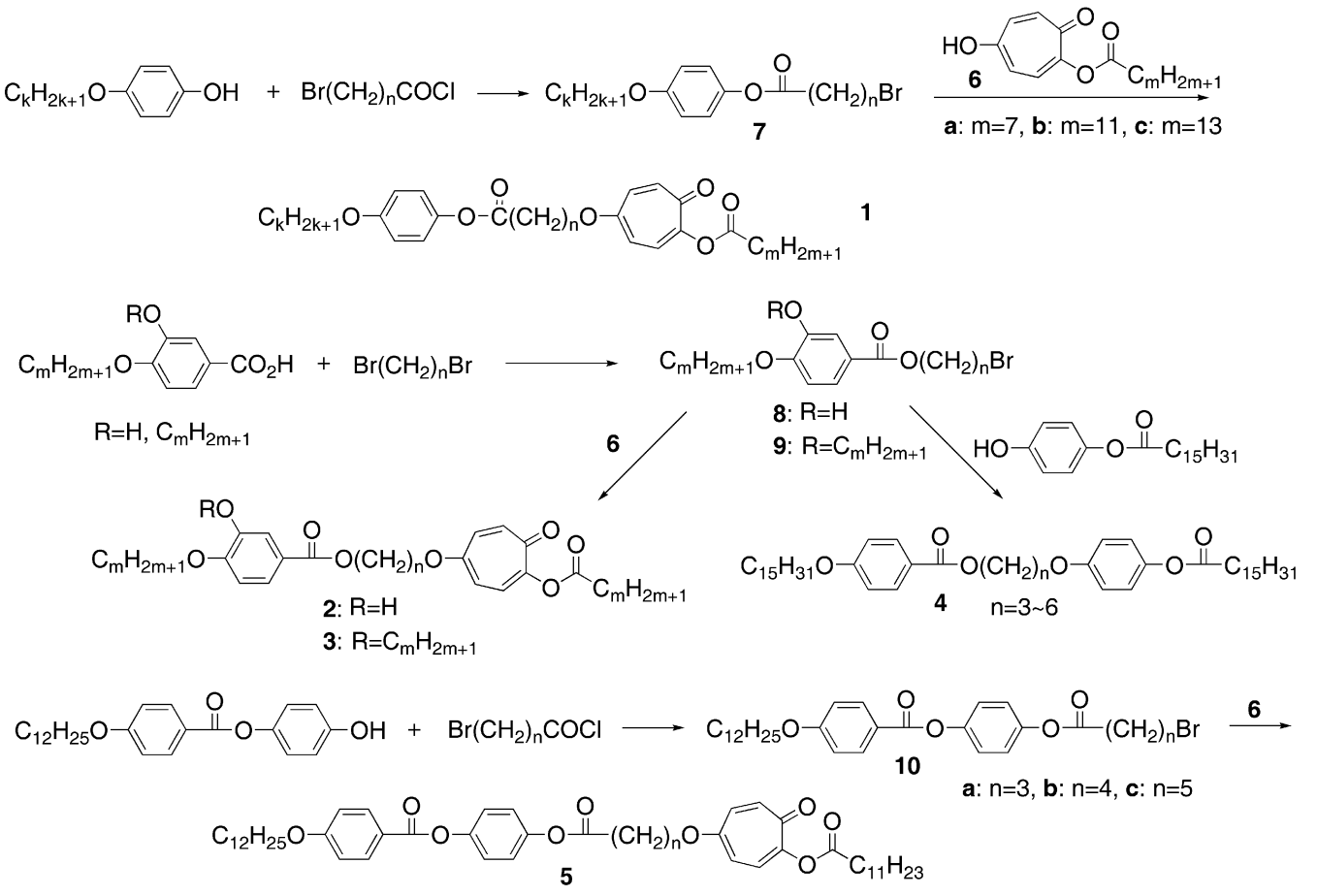
Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2005 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290500183599



Scheme 1.

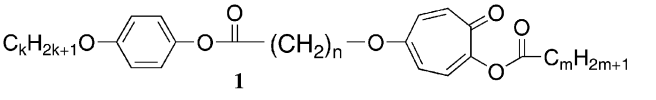
3. Results and discussion

3.1. *Mesomorphic Properties*

The transition temperatures of class **1** are summarized in table 1. Compound **1a** showed two mesophases. The the higher temperature phase showed focal-conic and homeotropic textures, indicating a SmA phase. At lower temperatures the textures changed to broken focal-conic fan and schlieren textures which implied a SmC phase. Compound **1c** also exhibited two mesophases. The phase with focal-fan and homeotropic textures at the higher temperature was assigned as SmA. The phase at the lower temperature also had focal-fan and homeotropic textures. The X-ray diffraction study revealed two reflections in the small angle region at 49.8 and 24.8 Å and a reflection around 21° on the scattering broad peak in the wide angle region. These indicated that the mesophase at the lower temperature was a smectic B (SmB) phase.

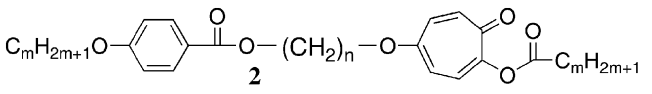
The transition temperatures of class **2** are summarized in table 2. Compound **2b** showed a SmA phase whereas the other homologues had a SmC phase. When

Table 1. Transition temperatures of compounds **1**, by microscopy.



Compound	*k*	*m*	*n*	Transition temp./°C
1a	13	13	3	Cr•87.4•SmC•91.1•SmA•101.2•I
1b	13	13	4	Cr•77.6•(SmA•66.9•) I
1c	13	13	5	Cr•82.7•(SmB•65.5•SmA•82.5•) I
1d	15	15	3	Cr•92.2•SmC•99.4•SmA•101.9•I
1e	15	15	4	Cr•81.8•(SmA•71.0•) I
1f	15	15	5	Cr•86.5•(SmC•85.1•) I
1g	13	15	3	Cr•90.2•SmC•102.0•SmA•103.2•I
1h	13	15	4	Cr•80.8•(SmA•71.0•) I
1i	13	15	5	Cr•88.6•(SmC•85.7•) I
1j	15	13	3	Cr•94.4•(SmC•94.0•) SmA•103.0•I
1k	15	13	4	Cr•81.5•(SmA•69.8•) I
1l	15	13	5	Cr•85.2•(SmC•72.5•) SmA•85.4•I

Table 2. Transition temperatures of compounds **2**, by microscopy.



2

Compound	*m*	*n*	Transition temp./°C
2a	13	4	Cr•70.3•I
2b	13	5	Cr•72.3•(SmA•72.1•) I
2c	13	6	Cr•59.4•(SmC•39.1•) I
2d	15	3	Cr•91.4•(SmC•86.3•) I
2e	15	4	Cr•75.5•I
2f	15	5	Cr•78.6•(SmC•75.8•) I
2g	15	6	Cr•67.1•(SmC•47.7•) I

an alkoxyl group was introduced at the C-3 position of the benzoyl group, no mesophase appeared in class **3**. Furthermore, the corresponding benzenoid **4** showed no mesophases. Class **5** with a three-ring system had a SmA phase at higher temperatures and oily streak and homeotropic textures were observed. At lower temperatures, the homeotropic texture changed to a schlieren texture, which indicated a SmC phase. The transition temperatures are listed in table 3.

It is well known that a very large odd–even effect is observed in the transition temperatures of dimers on varying the length and parity of the spacer [1, 2]. Class **1** with a shorter spacer has the higher transition temperatures and these with an even-membered spacer have higher transition temperatures than those with an odd-membered spacer. (Since the spacer has three atoms except for a methylene group, the number of the spacer is even when *n* is odd and it is odd when *n* is even.) Thus an odd–even effect is observed. This is in accord with the observation that an even-membered spacer is more favourable than an odd-membered spacer in dimers [1, 2]. Furthermore, dimers of class **1** with an even-membered spacer have both SmA and SmC phases or only a SmC phase, whereas those with an odd-membered spacer have only a SmA phase. A similar even–odd effect was observed in other dimers [7], for which even-membered dimers had SmA phases whereas odd dimers showed SmC phases. It was reported that the layer spacings of the smectic phases were about half the molecular length, indicating an intercalated structure.

Table 4. Entropy changes of SmA–I transition of compounds **5**.

Compound	*n*	$\Delta S/R$
5a	3	54.3
5b	4	37.9
5c	5	55.1

Table 4 shows the dependence of the entropy change associated with the SmA–I transitions, and a pronounced odd–even effect can be clearly seen. The value of $\Delta S/R$ for the dimer with the even-membered spacer is almost 1.5 times that of the value for the odd-membered spacer.

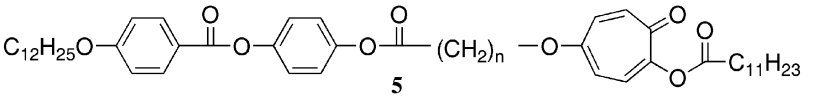
3.2. *Packing models*

3.2.1. **Packing model of compound 1a.** Table 5 summarizes the layer spacings of the smectic phases exhibited by **1a**–**1c**, and these increased when the temperatures were lowered. The SmA phase had a smaller layer spacing than the SmC and SmB phases. Since the layer spacing (45 Å) of the SmA phase of

Table 5. Layer spacing of smectic phases show, by claw **1** compounds.

Compound	*n*	Layer spacing/Å (temp./°C)
1a	3	44.4 (100), 45.1 (90), 45.6 (80)
1b	4	40.1 (65)
1c	5	48.2 (75), 49.3 (63), 49.8 (60)

Table 3. Transition temperatures and enthalpy changes of compounds **5**, by DSC.



5

Compound	*n*	Transition temp./°C (ΔH/kJ mol^{-1})
5a	3	Cr•115 (62.8)•SmC•162[a]•SmA•165(23.8)•I
5b	4	Cr•90 (74.0)•SmC•91[a]•SmA•123 (15.0)•I
5c	5	Cr•103 (58.3)•SmC•139[a]•SmA•146 (23.1)•I

[a]Determined by microscopy.

compound **1a** is shorter than the calculated molecular length (52.3 Å), it forms an interdigitated layer structure. Figure 1 shows three types of packing model for the SmA phase observed in an even-membered spacer. Model A has head-to-tail alignments of the tropone units whereas model B has head-to-tail alignments of the 4-alkoxyphenyl groups. Since the dipole moments of the tropone ring and the benzoyl group face the same direction in model C, this arrangement would be less favoured. Previously, we have observed that monocyclic troponoids show monotropic SmA phases whereas monocyclic benzenoids do not [8]. This indicated that troponoid cores promote microsegregation stabilizing a layer structure even in a monocyclic system. However, the benzenoid cores do not induce microsegregation driving a layer structure in the case of a monocyclic system. From these consideration, model A, in which the benzene rings are mixed with alkyl groups and the tropone rings are arranged in a head-to-tail fashion to cancel their dipole moments, should be more favoured than model B, in which the tropone rings mixed with the alkyl group.

3.2.2. **Packing model of compound 1b.** Compound **1b**, with an odd-membered spacer, has a bent structure and a shorter layer spacing than the compound with the even spacer. Thus the troponoid and benzenoid rings are not arranged in a parallel alignment. Therefore, molecules should be tilted randomly within the layer plane and thus on average are perpendicular with respect to the layer normal, as shown in figure 2. Since the layer spacing (40 Å) is shorter than the calculated molecular length, an interdigitated packing model is proposed.

3.2.3. **Packing model of compound 2b.** The layer spacing of compound **2b**, with an even-membered spacer, was 48.0 Å. Three possible packing models are shown in figure 3. We propose that model C is favoured because the dipole moments of the tropone and benzene rings are cancelled in the head-to-tail arrangement and the aromatic parts are separated from the alkyl chains to induce microsegregation.

3.2.4. **Packing model of compound 5a.** The layer spacing of compound **5a**, with an even-membered spacer, was observed to be 46 Å, which is shorter than the calculated molecular length (54.8 Å). Three possible packing models of the SmA phase of compound **5a** are shown in figure 4. In model A, the phenyl benzoate parts are mixed with the alkyl chains, whereas in model B the tropone rings are mixed with the alkyl chains. Since we have observed that the synthetic intermediate **10** showed nematic and SmA phases, as shown in § 5, model A should be excluded. Similarly, model B should also be excluded. On the other hand, in model C the tropone and phenyl benzoate parts are separated out from the alkyl chains to retain microsegregation. Furthermore, the direction of the dipole moment of

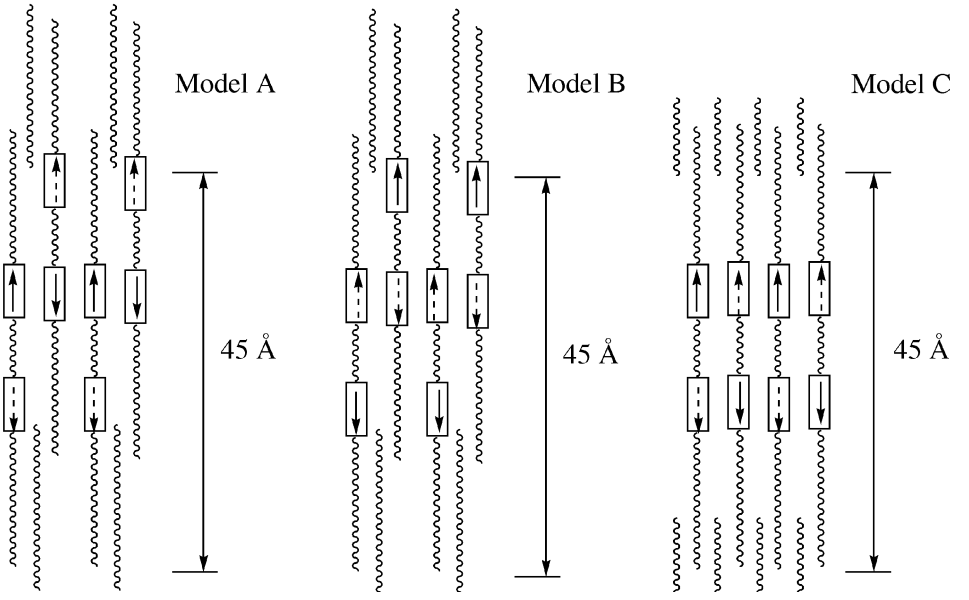


Figure 1. Packing models of the SmA phase of **1a**. The solid arrow shows the direction of the dipole moment of a tropone ring and the dotted one that of a benzoyl group.

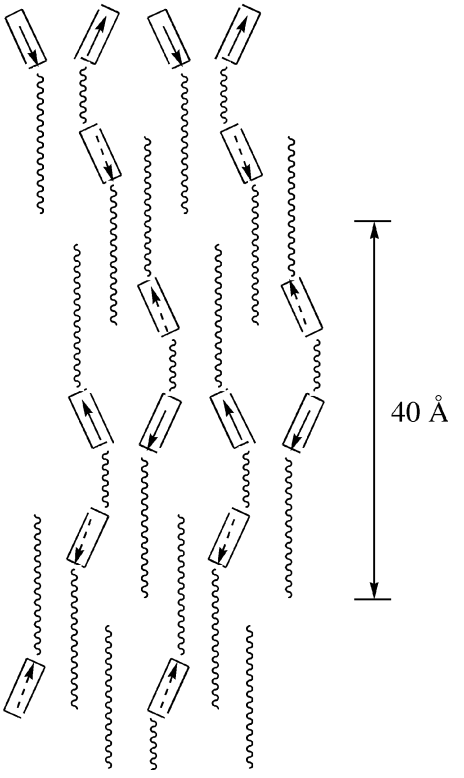


Figure 2. Packing model of the SmA phase of **1b**. The solid arrow shows the direction of the dipole moment of a tropone ring and the dotted one that of a benzoyl group.

the terminal part of the phenyl benzoate group matches the direction of the neighbouring tropone part to stabilize model C.

3.3. *Thermal stability*

When the transition temperatures of compounds **1** and **2** are compared, the former have the higher values. We have proposed that compound **1a** adopts packing A, in which the tropone rings show head-to-tail alignments to cancel their dipole moments, whereas compound **2b** adopts model C in figure 3. Furthermore, since the aromatic parts are separated from the alkyl chains, microsegregation should play a role in stabilizing the mesophases.

Compound **2** has a larger dipole moment than compound **1** because it has a 4-alkoxybenzoyloxy group, containing an electron-donating alkoxyl group and an electron-withdrawing ester group located at the C-1 and C-4 positions [9]. Therefore, model A in figure 3 should be less favourable because the more polar unit has to mix with the non-polar alkyl groups. This might be the reason why compound **2b** adopts pacting model C.

We have already reported the mesomorphic properties of dimers **11** with two troponoid cores, and their transition temperatures are listed in table 6 [6]. They showed a SmA phase with higher transition temperatures than compounds **1**. This is explained by the fact that monocyclic troponoids are mesomorphic whereas the corresponding benzenoids are not.

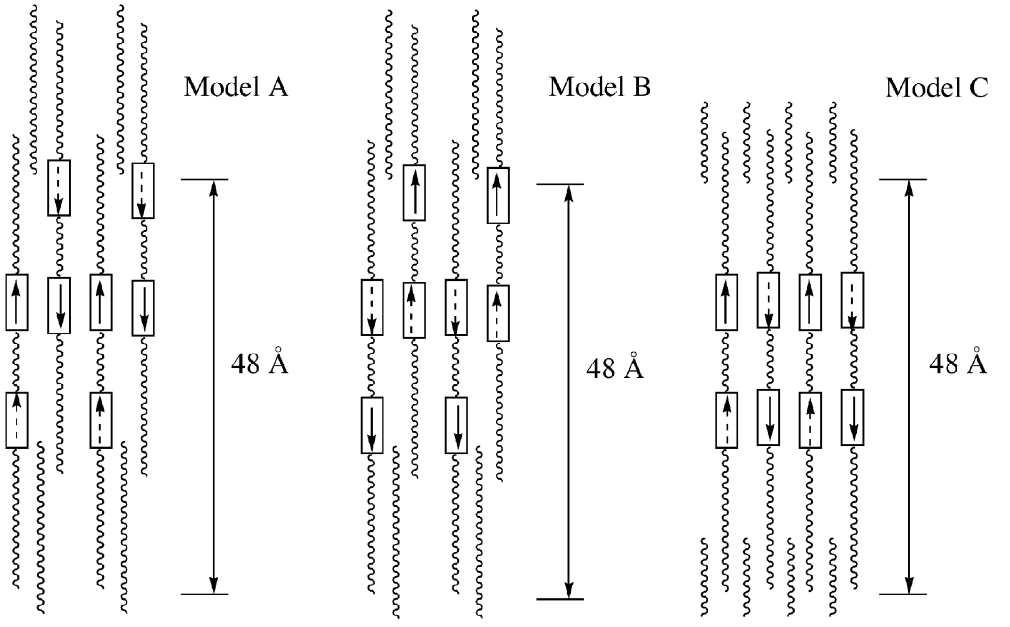


Figure 3. Packing models of the SmA phase of **2b**. The solid arrow shows the direction of the dipole moment of a tropone ring and the dotted one that of a benzoyl group.

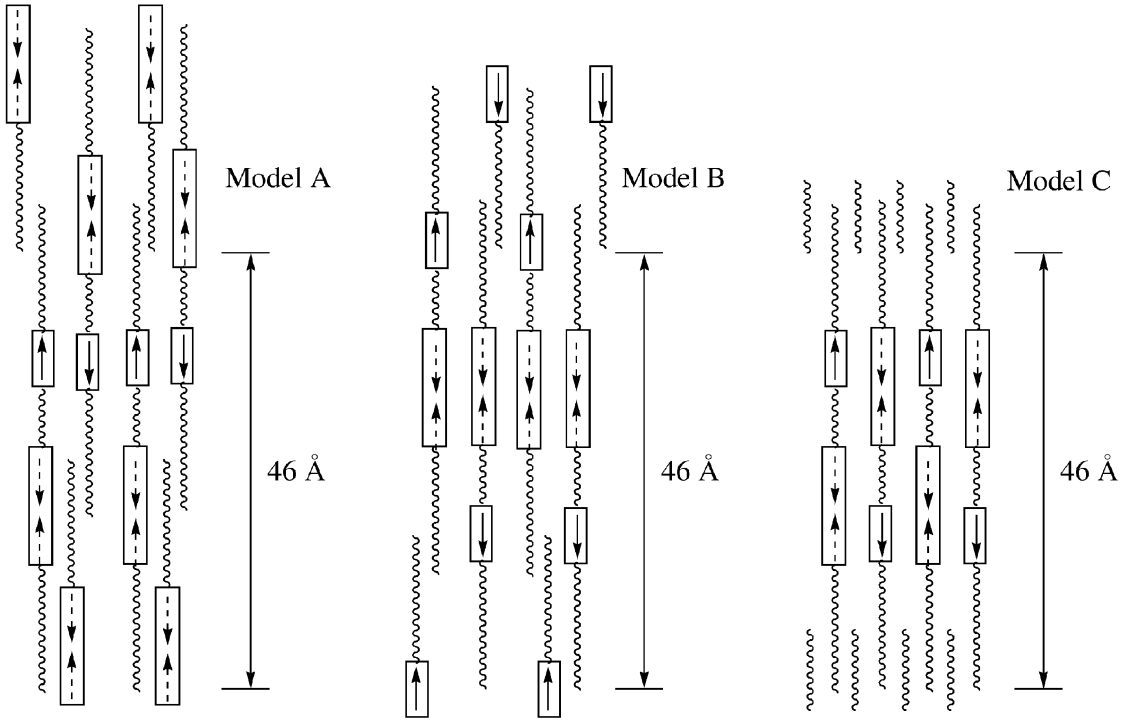
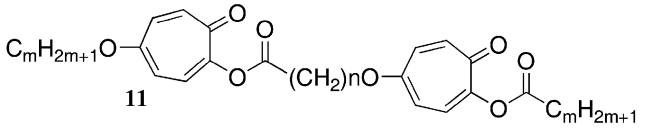


Figure 4. Packing model of the SmA phase of **5a**. The solid arrow shows the direction of the dipole moment of a tropone ring and the dotted ones those of a phenyl benzoyl group.

Table 6. Transition temperatures of compounds **11**, by microscopy.



11

Compound	*m*	*n*	Transition temp./°C
11a	13	3	Cr•133.3•I
11b	13	4	Cr•94.2•(SmA•94•) I
11c	13	5	Cr•118.7•(SmC•96.6•) I
11d	15	3	Cr•131.1•I
11e	15	4	Cr•94.4•(SmA•95.6•) I
11f	15	5	Cr•118.6•(SmC•100.7•) I

4. Conclusion

Five types of non-symmetric dimer were synthesized and their thermal properties characterized. Non-symmetric dimers with a tropone ring were mesomorphic whereas those with two benzene rings were not. We propose packing models for the SmA phase of the non-symmetric dimers by considering the contributions of the dipole moments and also microsegregation between the non-polar alkyl groups and the troponoid or benzenoid units. Compound **1a**, with an even-membered spacer, adopts model A in figure 1, in which the tropone units are in head-to-tail arrangements to cancel their dipole moments. Compound **2b**, with an even-membered spacer, adopts model C in figure 3, which the aromatic cores are separated out from the alkyl chains, and their dipole moments are cancelled by the neighbouring molecules. Compound **5a**, with an even-membered spacer, also adopts model C. On the other hand, the dimer **1b**, with an odd-membered spacer, has a bent structure. It adopts the packing structure shown in figure 2, which is a modification of model A shown by compound **1a** with an even-membered spacer in figure 1.

Normally, the mesomorphic units of dimers contain at least two rings. In the present case, however, the monocyclic troponoid is able to stabilize mesophases in dimers. This is in remarkable contrast to the results for two-ring benzenoids which showed no mesophases without the troponoid unit.

5. Experimental

5.1. *Characterization*

Elemental analyses were performed at the elemental analysis laboratory of Kyushu University. NMR spectra were measured on JEOL GSX 270H, LA 400,

and LA 600 spectrometers in $CDCl_3$; the chemical shifts are expressed in δ units. The mass spectra were measured with a JEOL 01SG-2 spectrometer. The stationary phase for column chromatography was Wakogel C-300 and the eluant was a mixture of ethyl acetate, chloroform, and hexane. Transition temperatures were measured using a differential scanning calorimeter (Seiko DSC 200) and the mesomorphic phase was observed with a polarizing microscope (Olympus BHSP BH-2) equipped with a hot stage (Linkam TH-600RMS). X-ray powder 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.

5.2. *Synthesis of compounds 1*

An HMPA solution (3 cm^3) of 5-hydroxy-2-tetradecyloxytropone (**6c**, 81 mg, 0.23 mmol) and 60% NaH (10 mg, 0.25 mmol) were stirred at room temperature for 1 h. To the resultant mixture was added an HMPA solution (1.5 cm^3) of 4-tridecyloxyphenyl 4-bromobutanoate (102 mg, 0.23 mmol) and the mixture was stirred at 70°C for 3 h. The mixture was poured into 2M HCl solution and extracted with AcOEt. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was chromatographed (hexane:AcOEt=2:1) on a silica-gel column to give **1a** (45 mg, 28%), m.p. 87.4°C. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (6H, t, J=6.6 Hz), 1.26–1.44 (40H, m), 1.76 (4H, m), 2.24 (2H, m), 2.59 (2H, t, J=7.5 Hz), 2.75 (2H, t, J=7.1 Hz), 3.92 (2H, t, J=6.6 Hz), 4.05 (2H, t, J=6.0 Hz), 6.7 (2H, br) [10], 6.87 (2H, d, J=9.2 Hz), 6.98 (2H, d, J=9.2 Hz) and 7.15 (2H, d, J=11.7 Hz). Calcd for $C_{44}H_{68}O_7$, C 74.54, H 9.67; found, C 74.45, H 9.63%. **1b** (30%), m.p. 77.6°C. Calcd for $C_{45}H_{70}O_7$, C 74.75, H 9.76; found, C 74.74, H 9.68%. **1c** (28%), m.p. 82.7°C. Calcd for $C_{46}H_{72}O_7$, C 74.96, H 9.85; found, C 74.82, H 9.84%. **1d** (39%), m.p. 92.2°C. Calcd for $C_{48}H_{76}O_7$, C 75.35, H 10.01; found, C 75.46, H 10.01%. **1e** (49%), m.p. 81.8°C. Calcd for $C_{49}H_{78}O_7$, C 75.54, H 10.09; found, C 75.51, H 10.08%. **1f** (29%), m.p. 86.5°C. Calcd for $C_{50}H_{80}O_7$, C 75.71, H 10.17; found, C 75.70, H 10.16%. **1g** (23%), m.p. 90.2°C. Calcd for $C_{46}H_{72}O_7$, C 74.96, H 9.85; found, C 74.82, H 9.83%. **1h** (26%), m.p. 80.8°C. calcd for $C_{47}H_{74}O_7$, C 75.16, H 9.93; found, C 75.01, H 9.91%. **1i** (29%), m.p. 88.6°C. Calcd for $C_{48}H_{76}O_7$, C 75.35, H 10.01; found. C 75.27, H 9.93%. **1j** (29%), m.p. 94.4°C. Calcd for $C_{46}H_{72}O_7$. C 74.96, H 9.85; found, C 74.89, H 9.89%. **1k** (37%), m.p. 81.5°C. Calcd for $C_{47}H_{74}O_7$, C 75.16, H 9.93; found, C 75.10, H 9.87%. **1l** (22%), m.p. 85.2°C. Calcd for $C_{48}H_{76}O_7$, C 75.35, H 10.01; found, C 75.25, H 9.92%.

5.3. *Synthesis of compounds 2*

An HMPA solution (2 cm^3) of 5-hydroxy-2-tetradecyloxytropone (**6c**, 80 mg, 0.23 mmol) and 60% NaH (10 mg, 0.25 mmol) were stirred at room temperature for 1 h. To the resultant mixture was added an HMPA solution (1.5 cm^3) of 4-bromobutyl 4-tridecyloxybenzoate (103 mg, 0.23 mmol) and the mixture was stirred at 70°C for 4 h. The mixture was poured into 2M HCl solution and extracted with AcOEt. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was chromatographed (hexane:AcOEt=2:1) on a silica-gel column to give **2a** (35 mg, 21%), m.p. 70.3°C. ^{1}H NMR ($CDCl_3$) δ: 0.88 (6H, t, J=7.4 Hz), 1.26–1.46 (42H, m), 1.79 (4H, m), 1.96 (4H, m), 2.59 (2H, t, J=7.6 Hz), 3.99 (4H, m), 4.37 (2H, t, J=5.9 Hz), 6.7 (2H, br) [10], 6.90 (2H, d, J=8.9 Hz), 7.14 (2H, d, J=11.8 Hz) and 7.96 (2H, d, J=8.9 Hz). Calcd for $C_{45}H_{70}O_7$, C 74.75, H 9.76; found, C 74.75, H 9.72%. **2b** (22%), m.p. 72.3°C. Calcd for $C_{46}H_{72}O_7$, C 74.96, H 9.85; found, C 74.93, H 9.78%. **2c** (20%), m.p. 59.4°C. Calcd for $C_{47}H_{74}O_7$, C 75.16, H 9.93; found, C 75.10, H 9.87%. **2d** (32%), m.p. 91.4°C. Calcd for $C_{48}H_{76}O_7$, C 75.35, H 10.01; found, C 75.32, H 10.06%. **2e** (20%), m.p. 75.5°C. Calcd for $C_{49}H_{78}O_7$, C 75.54, H 10.09; found, C 75.50, H 10.03%. **2f** (23%), m.p. 78.6°C. Calcd for $C_{50}H_{80}O_7$, C 75.71, H 10.17; found, C 75.67, H 10.12%. **2g** (20%), m.p. 67.1°C. Calcd for $C_{51}H_{82}O_7$, C 75.89, H 10.24; found, C 75.80, H 10.19%.

5.4. *Synthesis of compounds 3*

An HMPA solution (2 cm^3) of 5-hydroxy-2-octanoyloxytropone (**6a**, 55 mg, 0.21 mmol) and 60% NaH (9 mg, 0.23 mmol) were stirred at room temperature for 1 h. To the resultant mixture was added an HMPA solution (1.5 cm^3) of 4-bromobutyl 3,4-didodecyloxybenzoate (100 mg, 0.16 mmol) and the mixture was stirred at 60°C for 4 h. The mixture was poured into 2M HCl solution and extracted with AcOEt. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was chromatographed (hexane:AcOEt=2:1) on a silica-gel column to give **3a** (13%), m.p. 63.1°C. ^{1}H NMR ($CDCl_3$) δ: 0.88 (6H, t, J=6.8 Hz), 0.89 (3H, t, J=6.9 Hz), 1.26–1.49 (42H, m), 1.63 (2H, m), 1.76 (2H, m), 1.84 (4H, m), 1.96 (4H, m), 2.59 (2H, t, J=7.6 Hz), 3.99 (2H, t, J=5.6 Hz), 4.03 (2H, t, J=6.6 Hz), 4.04 (2H, t, J=6.6 Hz), 4.37 (2H, t,

J=5.8 Hz), 6.7 (2H, br) [10], 6.85 (1H, d, J=8.5 Hz), 7.14 (2H, d, J=11.8 Hz), 7.54 (1H, d, J=2.1 Hz), and 7.61 (1H, dd, J=8.5, 2.1 Hz). Calcd for $C_{50}H_{80}O_8$, C 74.22, H 9.97; found, C 74.19, H 9.94%. **3b** (17%), m.p. 63.2°C. Calcd for $C_{51}H_{82}O_8$, C 74.41, H 10.04; found, C 74.20, H 10.00%. **3c** (41%), m.p. 63.3°C. Calcd for $C_{52}H_{84}O_8$, C 74.60, H 10.11; found, C 74.61, H 10.06%.

5.5. *Synthesis of compounds 4*

A 3-pentanone solution (10 cm^3) of 3-bromopropyl 4-pentadecyloxybenzoate (79 mg, 0.17 mmol), 4-hydroxyphenyl hexadecanoate (60 mg, 0.17 mmol), K_2CO_3 (70 mg, 0.51 mmol) and 18-crown-6 (5 mg, 0.019 mmol) were heated under reflux for 6 h. The mixture was poured into 2M HCl solution and extracted with AcOEt. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was chromatographed (hexane:AcOEt=10:1) on a silica-gel column to give **4a** (50 mg, 40%), m.p. 93.2°C. ^{1}H NMR ($CDCl_3$) δ: 0.88 (6H, t, J=6.9 Hz), 1.26–1.45 (50H, m), 1.77 (4H, m), 2.23 (2H, m), 2.52 (2H, t, J=7.5 Hz), 3.99 (2H, t, J=6.6 Hz), 4.10 (2H, d, J=6.2 Hz), 4.48 (2H, t, J=6.2 Hz), 6.88 (2H, d, J=9.2 Hz), 6.90 (2H, d, J=8.9 Hz), 6.98 (2H, d, J=9.2 Hz), and 7.97 (2H, d, J=8.9 Hz). Calcd for $C_{47}H_{76}O_6$, C 76.58, H 10.39; found, C 76.61, H 10.49%. **4b** (38%), m.p. 77.6°C. Calcd for $C_{48}H_{78}O_6$, C 76.75, H 10.47; found, C 76.77, H 10.49%. **4c** (45%), m.p. 81.2°C. Calcd for $C_{49}H_{80}O_6$, C 76.92, H 10.54; found, C 76.91, H 10.53%. **4d** (45%), m,p. 69.5°C. Calcd for $C_{70}H_{82}O_6$, C 77.07, H 10.61; found, C 77.16, H 10.68%.

5.6. *Synthesis of compounds 10*

A THF solution (10 cm^3) of 4-hydroxyphenyl 4-dodecyloxybenzoate (300 mg, 0.75 mmol) and 60% NaH (34 mg, 0.85 mmol) were stirred at room temperature for 1 h. To the resultant mixture was added 4-bromobutanoyl chloride (0.09 cm^3, 0.78 mmol) and the mixture was stirred at room temperature for 13 h. The mixture was poured into 2M HCl solution and extracted with AcOEt. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was chromatographed ($CHCl_3$) on a silica-gel column to give **10a** (359 mg, 88%), m.p. 78.8°C [Cr•78.8•SmA•80.8•N•87.9•I]. ^{1}H NMR ($CDCl_3$) δ: 0.88 (3H, t, J=6.8 Hz), 1.27–1.48 (18H, m), 1.82 (2H, m), 2.03 (2H, q, J=6.7 Hz), 2.79 (2H, t, J=6.7 Hz), 3.55 (2H, t, J=6.7 Hz), 4.04 (2H, t, J=6.6 Hz), 6.97 (2H, d, J=9.1 Hz), 7.14 (2H, d, J=9.1 Hz), 7.22 (2H, d, J=9.1 Hz), and 8.13 (2H, d, J=9.1 Hz). Calcd for $C_{29}H_{39}O_5Br$, C 63.62, H 7.18; found, C 63.63, H 7.13%. **10b** (96%), m.p. 92.3°C [Cr•92.3•(SmA•86.0•N•87.2•) I]. Calcd for $C_{30}H_{41}O_5Br$, C 64.17, H 7.36; found, C 64.21, H 7.36%. **10c** (92%) m.p. 57.2°C [Cr•57.2•SmA•82.5•N•86.1•I]. Calcd for $C_{31}H_{43}O_5Br$, C 64.69, H 7.53; found, C 65.02, H 7.56%.

5.7. *Synthesis of compounds 5*

An HMPA solution (2 cm^3) of 2-dodecanoyloxy-5-hydroxytropone (**6b**, 55 mg, 0.17 mmol) and 60% NaH (8 mg, 0.2 mmol) were stirred at room temperature for 1 h. To the resultant mixture was added an HMPA solution (1.5 cm^3) of 4-(4-bromobutanoyloxy)phenyl 4-dodecyloxybenzoate (**10a**, 86 mg, 0.16 mmol) and the mixture was stirred at 70°C for 4 h. The mixture was poured into 2M HCl solution and extracted with AcOEt. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was chromatographed (hexane:AcOEt=2:1) on a silica-gel column to give **5a** (15%), m.p. 115°C. ^{1}H NMR ($CDCl_3$) δ: 0.88 (6H, t, J=6.8 Hz), 1.26–1.49 (34H, m), 1.75 (2H, m), 1.82 (2H, m), 2.27 (2H, m), 2.60 (2H, t, J=7.6 Hz), 2.80 (2H, t, J=7.0 Hz), 4.04 (2H, t, J=6.5 Hz), 4.07 (2H, t, J=5.9 Hz), 6.7 (2H, br) [10], 6.97 (2H, d, J=8.9 Hz), 7.14 (2H, d, J=9.2 Hz), 7.16 (2H, d, J=12.3 Hz), 7.22 (2H, d, J=9.2 Hz), and 8.13 (2H, d, J=8.9 Hz). Calcd for $C_{48}H_{66}O_9$, C 73.25, H 8.45; found, C 73.02, H 8.41%. **5b** (10%), m.p. 90°C. Calcd for $C_{49}H_{68}O_9$, C 73.47, H 8.56; found, C 73.51, H 8.54%. **5c** (9%), m.p. 103°C. Calcd for $C_{50}H_{70}O_9$, C 73.68, H 8.66%; found, C 73.64, H 8.61%.

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