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# Dimeric liquid crystals with 5-(4-alkoxybenzoyloxy)tropone or 4-(4-alkoxybenzoyloxy)phenyl cores: evaluation of the tilt angles of the cores, spacers, and side chains

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Two types of symmetric dimers with 5-(4-alkoxybenzoyloxy)tropone cores or with 4-(4-alkoxybenzoyloxy)phenyl cores were synthesized to evaluate the effect of the core structure and the length of the spacer on the mesomorphic properties. The former had smectic C phases whereas the latter had smectic C and F phases. Both types of dimer showed a remarkable odd–even effect on varying the spacer on the mesomorphic properties. Comparison of the thermal stability between them demonstrated that benzenoid twins are more stable than troponoid ones. The layer spacings of the smectic C phases were measured to determine the tilt angles of the core part, the spacer, and the side chains on changing the length of the spacer and the side chains. Troponoid dimers had a larger tilt angle of the core part of the smectic C phase than benzenoid twins, which lowered the thermal stability of the troponoid. Entropy changes of the smectic C phase to the isotropic liquid showed a contrast between troponoids and benzenoids. The former had smaller values and odd–even effects than the latter, which indicated that the former troponoids had a limited number of conformers in mesophases.

## 1. Introduction

Many reports on the thermal properties of liquid crystalline dimers have appeared in the literature [1,2]. The dimers are usually composed of two identical groups, joined by a flexible spacer, and their thermal properties differ from conventional monomeric liquid crystals. When mesomorphic groups are polar and have a large dipole moment, the molecules sometimes form a head-to-tail dimer structure to cancel their dipole–dipole repulsion. However, the polar mesomorphic groups in a dimer could hardly change their orientation since they are connected by a spacer. Recently, we observed that unsymmetrical calamitic liquid crystalline dimers with a troponoid and benzenoid core showed smectic phases while the corresponding benzenoid twins were not mesomorphic [3]. The presence of a troponoid core is essential for mesomorphism in the dimers with monocyclic cores. Furthermore, we have previously reported mesomorphic properties of liquid crystalline dimers with two troponoid cores, and the corresponding benzenoid dimers, to investigate the role of the direction of the dipole moments of the troponoid cores [4].

Unsymmetric troponoid dimers **1** (see scheme 1) showed smectic A (SmA) phases. They can form head-to-tail arrangements by canceling their dipole moments. Two types of symmetric dimers **2** and **3**, where two tropone carbonyl groups direct outwards, were non-mesomorphic. Symmetric dimers **4**, where two tropone carbonyl groups direct inwards, had smectic C (SmC) phases. It is expected that symmetric dimers would rarely form perpendicular arrangements because of the repulsive dipole–dipole interactions. In the case of **4**, they formed tilted phases to avoid the perpendicular alignment. The corresponding benzenoid dimers **5** were non-mesomorphic. However, since the melting points of **5** are higher than the clearing temperatures of the corresponding mesomorphic troponoid dimers, we could not evaluate the thermal stabilities of the benzenoid twins because the high melting point sometimes hides the existence of mesophases. In order to increase the thermal stability of dimers with a two-ring system, we added one benzene ring into the each core part of the dimers.

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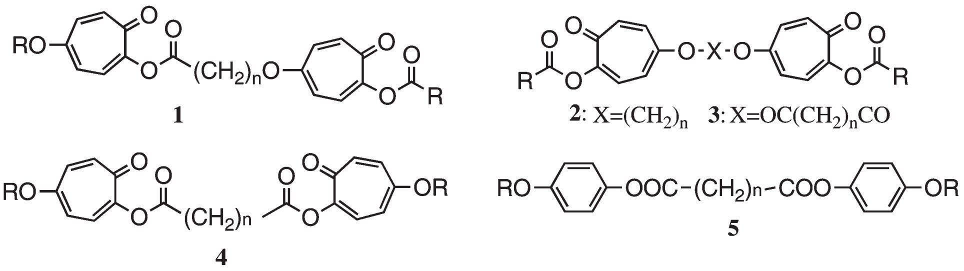


Scheme 1. Structures of dimers **1**–**5**.

In this study, we synthesize compounds **6** [5] with two 5-(4-alkoxybenzoyloxy)tropone cores and compounds **7** [6] with two 4-(4-alkoxybenzoyloxy)phenyl cores to discuss their thermal stability. Packing models are proposed from the results of layer spacings, which were obtained in X-ray diffraction (XRD) measurements. We evaluated the contribution of the core, the spacer, and the side chains to the layer spacing by changing the lengths of the spacer (*n*) and the side chains (*m*).

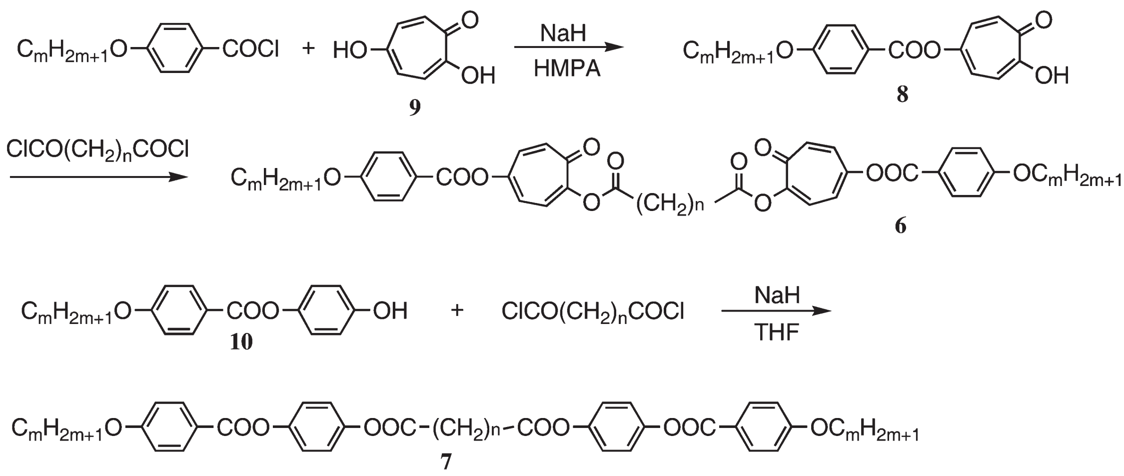
## 2. Synthesis

Compounds **6** were synthesized from the reaction of dialkanoyl dichlorides and 5-(4-alkoxybenzoyloxy)-tropolones (**8**), which were obtained from the reaction of 5-hydroxytropolone (**9**) and 4-alkoxybenzoyl chlorides. The corresponding benzenoids **7** were synthesized from the reaction of dialkanoyl dichlorides and 4-hydroxyphenyl 4-alkoxybenzoates (**10**), as depicted in scheme 2.

## 3. Results and discussion

### 3.1. *Mesomorphic properties of troponoid 6 and benzenoid dimers 7*

Transition temperatures were determined by differential scanning calorimetry (DSC). Thermal behaviour and microscopic textures were observed using a polarizing optical microscope (POM) equipped with a hot stage. The POM observation of compound **6a** ($m$=10, $n$=4) showed two kinds of mesophase, one of which was a SmC phase, from the observation of a schlieren and focal-conic fan texture. The other was a nematic (N) phase, because it had two- and four-brush schlieren textures and threaded textures. We have already observed that compounds **6** with short alkoxy side chains show SmA and N phases [5]. The transition temperatures and entropy changes are summarized in table 1. When the transition temperatures of troponoid dimers **6** with an even spacer and with an odd spacer



Scheme 2. Synthesis routes to compounds **6** and **7**.

Table 1. Transition temperatures (°C) and enthalpy changes ($\Delta H$/kJmol$^{-1}$, in parentheses) of troponoid dimers **6**.

| Compound **6** | *m* | *n* | Cr | SmC | N | I |
|---|---|---|---|---|---|---|
| **a** | 10 | 4 | • 120 (50.5) | • 142 | • 155 | • |
| **b** | 12 | 4 | • 113 (54.4) | • 158 (19.5) | | • |
| **c** | 12 | 5 | • 123 (93.1) | (• 112) | | • |
| **d** | 13 | 4 | • 109 (42.5) | • 161 (21.9) | | • |
| **e** | 13 | 5 | • 126 (89.1) | (• 120 (19.4)) | | • |
| **f** | 14 | 3 | • 111 (64.0) | • 137 (19.1) | | • |
| **g** | 14 | 4 | • 112 | • 166 (25.3) | | • |
| **h** | 14 | 5 | • 121 | • 126 | | • |
| **i** | 14 | 6 | • 122 (49.5) | • 149 (26.8) | | • |
| **j** | 14 | 7 | • 113 (90.8) | (• 111 (17.3)) | | • |
| **k** | 14 | 8 | • 103 (53.5) | • 123 (19.1) | | • |
| **l** | 14 | 10 | • 102 (104.9) | • 113 (12.9) | | • |
| **m** | 15 | 4 | • 114 (73.5) | • 165 (21.0) | | • |
| **n** | 15 | 5 | • 118 (68.6) | • 130 (21.8) | | • |
| **o** | 15 | 6 | • 117 (48.9) | • 150 (24.8) | | • |
| **p** | 15 | 7 | • 110 | • 118 | | • |
| **q** | 15 | 8 | • 97 (110.0) | • 127 (22.4) | | • |
| **r** | 15 | 10 | • 102 (117.2) | • 116 (20.0) | | • |
| **s** | 16 | 4 | • 114 (90.2) | • 169 (24.6) | | • |
| **t** | 16 | 5 | • 118 (72.0) | • 132 (22.5) | | • |
| **u** | 17 | 5 | • 118 (73.2) | • 134 (22.1) | | • |

were compared, the former had higher transition temperatures, as shown in figure 1. Figure 2 shows the dependence of SmC–isotropic (I) phase transition temperatures of compounds **6** with the side chain length ($m=14$) on the length of the spacer, which indicates a remarkable odd–even effect.

The textures of benzenoid dimers **7** indicated a SmC phase because of the observation of schlieren and focal-conic fan textures. Some homologues had two phases, one of which was SmC. At the lower temperature region, the schlieren textures of the SmC phase of compound **7l** ($m=14$, $n=8$) changed to schlieren–mosaic, as shown in figure 3, which suggested that the second phase is a smectic F (SmF) phase rather than smectic I [7]. The thermal behaviours of compounds **7** with $m=12$ and 16 and $n=2$–8 have been reported to show N, SmC and smectic X (SmX) phases [6]. The transition temperatures summarized in table 2 are dependent on the length of the side chains as shown in figure 4. Figure 5 shows the dependence of the SmC–I transition temperatures of compounds **7**, which shows an odd–even effect. When the thermal stabilities of troponoids **6** and benzenoids **7** were compared, the latter benzenoids had higher transition temperatures. This is a remarkable contrast because we have observed that monomeric 5-(4-alkoxybenzoyloxy)-2-alkanoyloxytropones (**11**) have more stable mesophases than the corresponding benzenoid 4-(4-alkoxybenzoyloxy)phenyl alkanoates (**12**) (see scheme 3) [8].

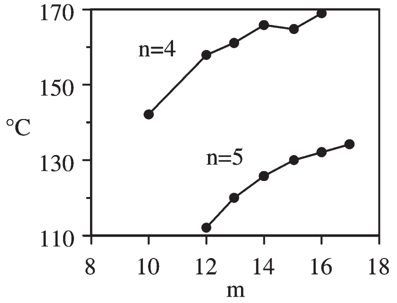


Figure 1. Dependence of SmC-I temperatures of **6** ($n=4$ and $n=5$) on $m$.

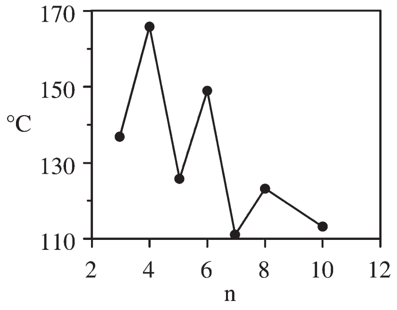


Figure 2. Dependence of SmC-I temperatures of **6** ($m=14$) on $n$.

The entropy values of the benzenoids were larger than those of the troponoids, which indicated that benzenoids had a larger number of conformers in their mesophases [9]. We have already observed that the troponoids with an alkanoyloxy group at the C-2 position showed a [[1,9]] sigmatropy to restrict the number of the conformers because at least the carbonyl group of the alkanoyloxy group remained within the molecular width [10]. In contrast, since the benzenoids do not have such a structural restriction, they could have a larger number of conformers than the troponoids. Furthermore, the benzenoids showed large entropy changes of the SmC–I transition. This is because the molecular shape of the benzenoids changes with the parity of the spacer.

### 3.2. *X-ray diffraction study*

In order to discuss the thermal stability of the liquid crystalline states, we elucidated a packing model of the SmC phase. We determined the layer spacing from an XRD study to summarize the layer spacings of troponoid twins **6** with an even spacer, as shown in table 3. After checking that the layer spacings are independent of temperature, we plotted the layer spacings of troponoid twins as a function of the length $m$ when the length $n$ is fixed to 4. The data follow a straight line as shown in figure 6. The contribution of

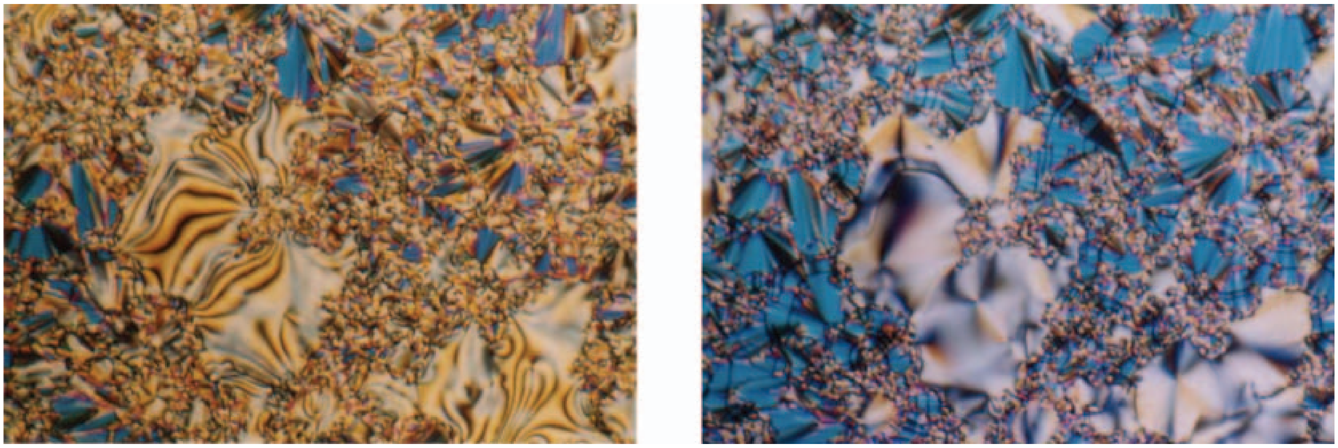

(*a*) (*b*)

Figure 3. Textures of **7l**: (*a*) SmC phase at 146°C (cooling), (*b*) SmF phase at 125.5°C (cooling).

the core part including the spacer to the layer spacing of the SmC phase is estimated to be approximately 18.2 Å by extrapolation.

To estimate the contribution of the spacer to the layer spacing, the layer spacing is plotted as a function of the length *n* when the length *m* is fixed to 15. From figure 7, the intercept is 34.0 Å for $m=15$ and 33.0 Å for $m=14$. Since the layer spacing of compound **6m** ($m=15$, $n=4$) is observed to be 36.2 Å, the contribution of the spacer to the layer spacing is estimated to be 2.2 Å when the spacer is fixed at 4. The spacer is also tilted, because the calculated length of the spacer is 6.4 Å. We estimate that

Table 2. Transition temperatures (°C) and enthalpy changes ($\Delta H/\mathrm{kJmol}^{-1}$ in parentheses) of benzenoid dimers **7**.

| Compound **7** | *m* | *n* | Cr | SmF | SmC | N | I |
|---|---|---|---|---|---|---|---|
| **a** | 10 | 4 | • 134 (51.7) | | • 178 | • 183 | • |
| **b** | 10 | 5 | • 138 | | | • 139 | • |
| **c** | 12 | 4 | • 127 (53.1) | | • 183 (27.4) | | • |
| **d** | 12 | 5 | • 131 (85.5) | | • 136 | • 138 | • |
| **e** | 13 | 4 | • 119 | • 123 | • 182 (29.1) | | • |
| **f** | 13 | 5 | • 131 (86.9) | | • 138 (21.3) | | • |
| **g** | 14 | 3 | • 138 (85.5) | | • 153 (24.9) | | • |
| **h** | 14 | 4 | • 122 (58.0) | (• 117 (45.2)[a]) | • 183 (29.5) | | • |
| **i** | 14 | 5 | • 128 (90.6) | | • 140 (22.4) | | • |
| **j** | 14 | 6 | • 137 (45.7) | | • 166 (32.6) | | • |
| **k** | 14 | 7 | • 128 (79.7) | | • 133 (26.2) | | • |
| **l** | 14 | 8 | • 127 (49.3) | • 132 (10.0) | • 152 (36.1) | | • |
| **m** | 14 | 10 | • 130 (47.4) | • 136 (15.8) | • 140 (38.4) | | • |
| **n** | 15 | 3 | • 137 (96.4) | | • 154 (28.1) | | • |
| **o** | 15 | 4 | • 118 (60.5) | | • 183 (30.7) | | • |
| **p** | 15 | 5 | • 126 (92.6) | | • 142 (24.4) | | • |
| **q** | 15 | 6 | • 135 (50.0) | | • 167 (34.5) | | • |
| **r** | 15 | 7 | • 127 (97.9) | | • 135 (28.7) | | • |
| **s** | 15 | 8 | • 123 (46.5) | • 132 (13.6) | • 153 (38.1) | | • |
| **t** | 15 | 10 | • 128 (48.1) | • 134 (16.3) | • 140 (39.7) | | • |
| **u** | 16 | 4 | • 122 (70.2) | | • 183 (32.9) | | • |
| **v** | 16 | 5 | • 127 (94.9) | | • 142 (25.7) | | • |

[a] SmG phase.

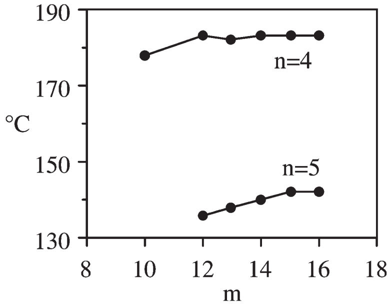


Figure 4. Dependence of SmC-I temperatures of **7** ($n=4$ and $n=5$) on *m*.

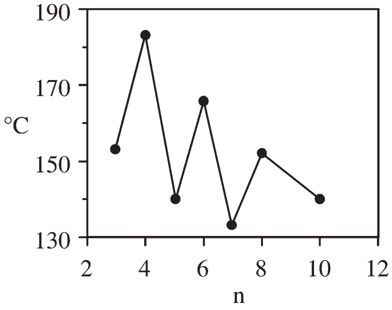


Figure 5. Dependence of SmC-I temperatures of **7** ($m=14$) on *n*.

**11** **12**

Scheme 3. Structures of monomers **11** and **12**.

Table 3. Layer spacing (*d*) of the SmC phase of **6** with an even spacer.

| Compound **6** | *m* | *n* | *d*/Å (*T*/°C) |
|---|---|---|---|
| **a** | 10 | 4 | 30.2 (130, 145) |
| **b** | 12 | 4 | 32.5 (130), 32.9 (140) |
| **d** | 13 | 4 | 34.0 (130) |
| **g** | 14 | 4 | 35.0 (100, 130) |
| **i** | 14 | 6 | 35.6 (125, 136) |
| **k** | 14 | 8 | 36.8 (103, 110) |
| **l** | 14 | 10 | 38.0 (100) |
| **m** | 15 | 4 | 36.2 (125, 150) |
| **o** | 15 | 6 | 36.8 (120, 130) |
| **q** | 15 | 8 | 38.2 (110) |
| **r** | 15 | 10 | 39.2 (106) |
| **s** | 16 | 4 | 37.4 (120, 130) |

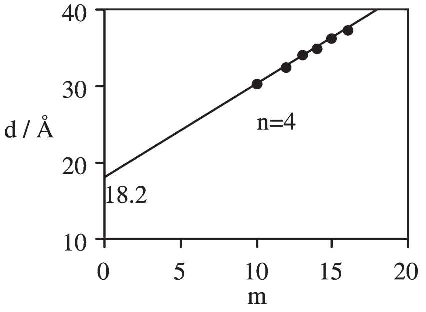


Figure 6. A plot of layer spacing (*d*) vs. the length (*m*) of the side chain for compounds **6**.

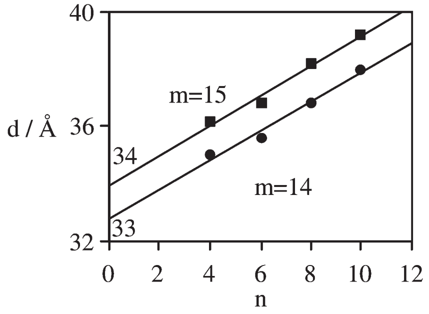


Figure 7. Plots of layer spacing (*d*) vs. the length (*n*) of the spacer for compounds **6**.

the contribution of the core part including the spacer to the whole layer spacing of **6m** ($m$=15, $n$=4) is 18.2 Å, so that the contribution of the each core part is 8.0 Å [(18.2–2.2)/2]. The tilt angle of the core is, therefore, calculated to be 53°. Next, the contribution of the side chains is calculated to be 18 Å [36.2–18.2]. Since the length of the side chains ($m$=15) is calculated to be 19.9 Å by the MM2 method, the side chain should be tilted by 63° [$\cos^{-1}(9/19.9)$] to the layer plane. Figure 8 shows a possible packing model of **6m**.

As another possible packing model, an interdigitated arrangement should be considered. However, since the packing model of the core structure is the same whether the alkyl side chains are interdigitated or not, we discuss the difference in thermal stability between troponoids **6** and benzenoids **7** by considering the packing model with no interdigitation of the side chains, as shown in figure 8. Furthermore, when the alkyl chains are interdigitated, the molecule has a zig-zag shape, which might be less favoured than the nearly linear shape of the molecule shown in figure 8.

On the other hand, when we calculate the tilt angle of the whole molecule of troponoid **6m** ($m$=15, $n$=4) by using the layer spacing of 36.2 Å and the calculated molecular length of 72.6 Å, the result is 60°. This is larger than the tilt angle (53°) of the core.

Table 4 summarizes the layer spacing of benzenoid dimers with an even spacer. The contribution of the core structure of compound **7o** ($m$=15, $n$=4) was estimated to be 23.4 Å from the plot of the layer spacing against the length $m$, which is longer than that (18.2 Å) of the corresponding troponoid **6m** ($m$=15, $n$=4), to indicate that the tilt angle (40°) of **7o** is smaller than that (53°) of compound **6m**. Since the layer spacing of the core of **7o** was estimated to be 38.4 Å when the length $n$ is zero and the length $m$ is fixed to 15, the contribution of the spacer to the layer spacing is 4.0 Å. The packing model of **7o** ($m$=15, $n$=4) is proposed as shown in figure 9. The benzenoid core has a smaller tilt angle than the troponoid core. Similarly, we calculate the tilt angle of the whole molecule of **7o**, to be 54°. This is also larger than the tilt angle (40°) of the core.

Next, we evaluated the packing model of troponoid and benzenoid dimers with an odd spacer. Table 5 summarizes the layer spacings of compounds **7** with an odd spacer. The core part has a contribution of 26.1 Å

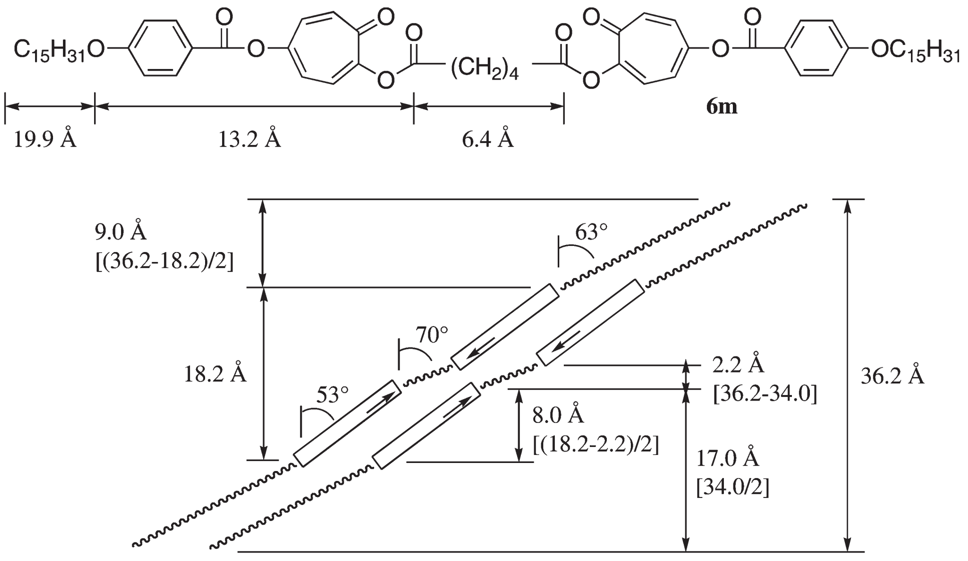


Figure 8. Proposed packing model for the SmC phase of **6m**.

to the layer spacing from the plot of the layer spacings against the length *m* when the length *n* is 5.

We estimated the contribution of the spacer to the layer spacing. The layer spacing of the core was estimated to be 41.8 Å from the plot of the layer spacing against the length *m* when the length *n* is zero. The contribution of the spacer should be 2.4 Å (44.2–41.8 Å) because the observed layer spacing of compound **7p** ($m$=15, $n$=5) is 44.2 Å. Since the value is less than the calculated length (7.4 Å) of the spacer ($n$=5) by the MM2 method, a molecular packing model where the spacer directs perpendicularly to the layer plane should be excluded. Therefore, we propose the packing model of benzenoid dimers with an odd spacer as shown in figure 10.

Table 4. Layer spacing ($d$) of the SmC phase of **7** with an even spacer.

| Compound **7** | $m$ | $n$ | $d$/Å ($T$/°C) |
|---|---|---|---|
| **a** | 10 | 4 | 35.9 (150), 36.2 (160) |
| **c** | 12 | 4 | 38.6 (155), 38.8 (165) |
| **e** | 13 | 4 | 39.8 (130), 39.9 (160) |
| **h** | 14 | 4 | 41.2 (125), 41.1 (135) |
| **j** | 14 | 6 | 43.2 (140), 43.3 (155) |
| **l** | 14 | 8 | 44.3 (140) |
| **m** | 14 | 10 | 49.8 (138) |
| **o** | 15 | 4 | 42.4 (130), 42.2 (160) |
| **q** | 15 | 6 | 44.2 (145) |
| **s** | 15 | 8 | 46.4 (135), 46.3 (148) |
| **t** | 15 | 10 | 48.3 (138) |
| **u** | 16 | 4 | 43.4 (130), 43.3 (160) |

Table 6 summarizes the layer spacings of troponoids **6** with an odd spacer. Since the plot of the layer spacing as a function of the length *m* did not show a straight line, the contribution of the layer spacing of the core structure could not be estimated.

### 3.3. *Thermal stability*

Except for troponoid dimers with an odd spacer, we could propose a packing model. Both troponoid and benzenoid twins had tilted mesophases such as a SmC and SmF phase. In the case of troponoid dimers, the dipole moments directed inwards. They should tilt to avoid the repulsive interaction of the dipole moment when they form a perpendicular layer structure.

We have observed that 5-(4-alkoxybenzoyloxy)-2-alkanoyloxytropones (**11**) have more stable mesophases than the corresponding benzenoids 4-(4-alkoxybenzoyloxy)phenyl alkanoates (**12**) [8]. As shown in tables 1 and 2, troponoid dimers have lower transition temperatures than benzenoid dimers. As discussed, the tilt angle of the core structure of troponoid dimers is 53° whereas that of benzenoid dimers is 40°. The larger tilt angle means that the overlapping area of the core part of troponoid dimers is smaller than in the benzenoid dimers. In addition, when the tilt angle becomes larger, the overlapping area between the polar troponoid core and the less polar alkyl chains of the neighbouring molecules would also increase to destabilize the layer structure. These are reasons why the mesophases of troponoid dimers are less stable than those of benzenoid dimers. This would result from the loss of orientational freedom of the polar core parts in dimers since they are connected by a spacer.

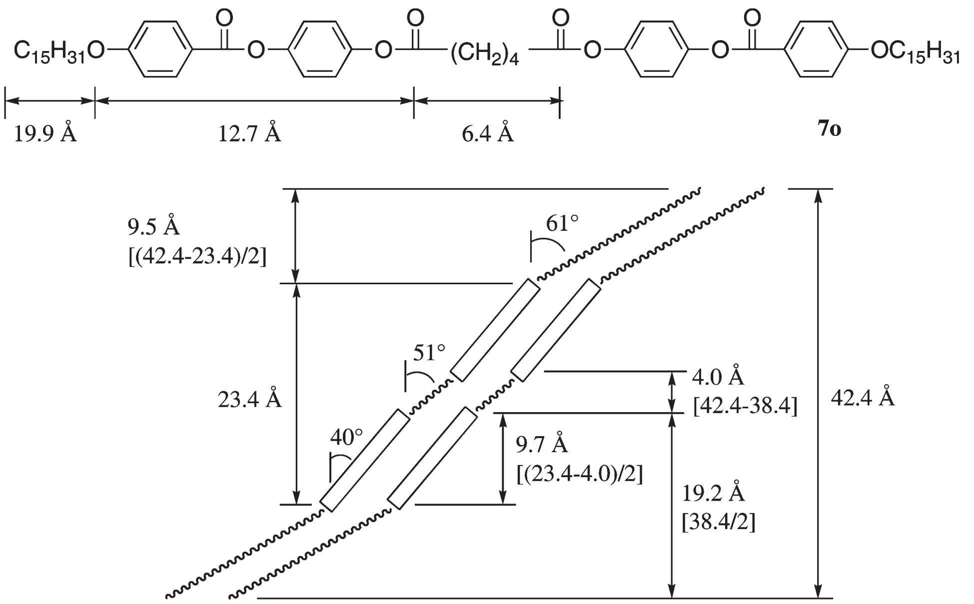


Figure 9. Proposed packing model for the SmC phase of **7o**.

### 3.4. *Mesomorphic properties of compounds 8 and 10*

Table 7 summarizes the transition temperatures of monomeric tropolones **8** and phenols **10** of the dimers. Troponoids **8** showed SmA phases, and benzenoids **10** had N phases. The XRD study of **8d** ($m=14$) showed that the layer spacing is 40.3 Å. The calculated molecular length is 29.8 Å. The X-ray crystallographic study of tropolone showed that the molecule forms a dimer through intermolecular hydrogen bonding, and the intermolecular length between the two oxygen atoms is 2.746 Å [11]. When compound **8d** forms a dimer through intermolecular hydrogen bonding by the tropolones, the molecular length of its dimer structure is calculated to be *ca.* 62 Å. Since the calculated molecular length exceeds the value of the layer spacing of 40.3 Å, it might be possible to show the packing model as in figure 11, where the core part would tilt a little to the layer plane and the side chains would partially melt in the mesophases.

The thermal behaviour of compounds **8** and **10** are parallel to the previous results that troponoids have an enhanced tendency to exhibit smectic phases [12]. The thermal stability of the mesophases of **8** is higher than for those of **10** although they have different types of

Table 5. Layer spacing ($d$) of the SmC phase of **7** with an odd spacer.

| Compound **7** | $m$ | $n$ | $d$/Å ($T$/°C) |
|---|---|---|---|
| **d** | 12 | 5 | 40.9 (135) |
| **f** | 13 | 5 | 41.7 (133) |
| **g** | 14 | 3 | 41.8 (143) |
| **i** | 14 | 5 | 42.6 (131) |
| **k** | 14 | 7 | 44.7 (130) |
| **n** | 15 | 3 | 43.2 (144) |
| **p** | 15 | 5 | 44.2 (138) |
| **r** | 15 | 7 | 45.1 (129) |
| **v** | 16 | 5 | 45.7 (138) |

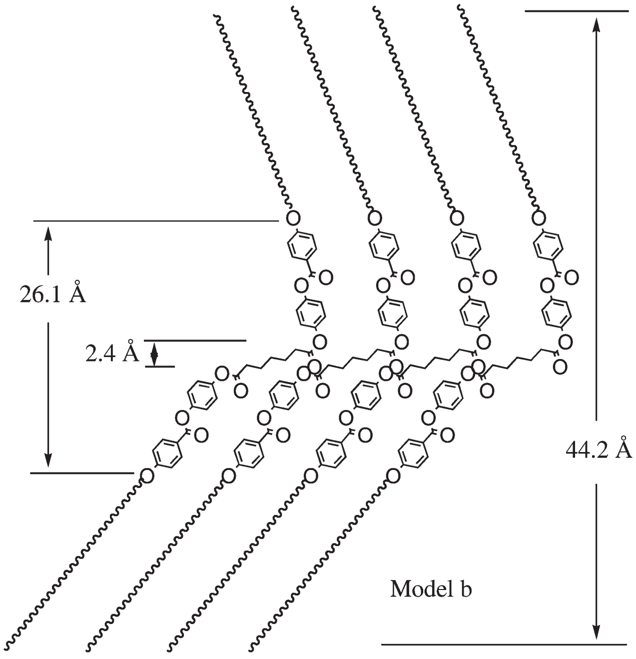


Figure 10. Proposed packing model for the SmC phase of benzenoid **7p**.

Table 6. Layer spacing (*d*) of the SmC phase of **6** with an odd spacer.

| Compound **6** | *m* | *n* | *d*/Å (*T*/°C) |
|---|---|---|---|
| **c** | 12 | 5 | 27.7 (110) |
| **e** | 13 | 5 | 28.7 (118) |
| **f** | 14 | 3 | 35.0 (120, 130) |
| **h** | 14 | 5 | 35.5 (110, 118) |
| **j** | 14 | 7 | 35.9 (100) |
| **n** | 15 | 5 | 36.0 (120) |
| **p** | 15 | 7 | 37.2 (113), 37.1 (108) |
| **t** | 16 | 5 | 37.7 (120) |
| **u** | 17 | 5 | 39.1 (120) |

Table 7. Transition temperatures (°C) of compounds **8** and **10**.

|  | *m* | **8** | **10** |
|---|---|---|---|
| **a** | 10 | Cr • 113 • I | Cr • 106 • (N • 96 •) I [15] |
| **b** | 12 | Cr • 113 • I | Cr • 108 • (N • 95 •) I [16] |
| **c** | 13 | Cr • 101 • SmA • 127 • I | Cr • 113 • I [17] |
| **d** | 14 | Cr • 98 • SmA • 133 • I | Cr • 119 • (N • 106 •) I [18] |
| **e** | 16 | Cr • 110 • I | Cr • 114.8 • I [19] |

mesophase. The former makes a stronger packing model because it can form a dimeric structure as observed in the single crystalline structure of tropolone [11] and the p$K_a$ value of tropolone is reported to be 6.92 [13], which is stronger than that of phenol (10.0) [14].

## 4. Conclusion

Two types of symmetric troponoid and benzenoid dimers showed tilted smectic phases. Whole molecule tilt angles were determined from XRD measurements: 60° for troponoid **6m** ($m$=15, $n$=4) and 54° for benzenoid **7o** ($m$=15, $n$=4). Packing models are proposed from the XRD studies by changing the length of the side chains and the spacer. We estimated the contribution of the core part, the spacer and the side chain to the layer spacing, from which the tilt angles were determined. The tilt angles of the core structure of **6m** and **7o** are 53° and 40°, respectively. The difference (13°) in the tilt angles is more than twice the difference of the tilt angle (6°) of the whole molecule. The large tilt angle of troponoid **6m** decreased overlapping areas of the core part, which led to lower transition temperatures. The corresponding monomeric troponoids **11** had higher transition temperatures than monomeric benzenoids **12**. This can be explained by the fact that troponoids **11** form a head-to-tail arrangement in a mesophase [8]. In the case of symmetric dimers **6**, however, no head-to-tail arrangement could be formed since the polar troponoid cores are connected by a spacer.

The entropy changes listed in tables 1 and 2 indicate that troponoids have a smaller number of conformers than benzenoids. This parallels what we have proposed, that the number of conformers of troponoids with an alkanoyloxy group at the C-2 position is limited due to [[1,9]] sigmatropy [10].

## 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 $\delta$ units. Mass spectra were obtained 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 by 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-$K_\alpha$ radiation at various temperatures controlled with a Linkam HFS-91 hot stage.

### 5.2. *5-(4-Alkoxybenzoyloxy)tropolones (8)*

A DMF solution (0.5 cm$^3$) of 4-decyloxybenzoic acid (810 mg, 2.9 mmol) and thionyl chloride (2 cm$^3$) was heated under reflux for 5 h. An HMPA solution (10 cm$^3$) of 5-hydroxytropolone (400 mg, 2.9 mmol)

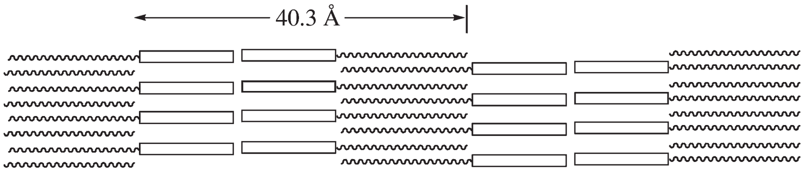


Figure 11. Packing model of the SmA phase of **8d**.

and 60% NaH (125 mg, 3.1 mmol) was stirred at room temperature for 1h. The synthesized 4-decyloxybenzoyl chloride was added to the HMPA solution and stirred at room temperature for 2 h. The reaction mixture was poured into 2M aqueous HCl and extracted by AcOEt. The organic layer was washed with NaCl saturated solution, dried over $Na_2SO_4$, and evaporated under reduced pressure. The residue was chromatographed on a silica gel column (hexane/AcOEt=1/1) to give **8a**: (306 mg, 27%), m.p. 114.1°C. $^1$H NMR $\delta$ 0.89 (3H, t, $J=6.8$ Hz), 1.28–1.48 (14H, m), 1.83 (2H, m), 4.05 (2H, t, $J=6.4$ Hz), 6.98 (2H, d, $J=8.8$ Hz), 7.27 (2H, $J=10.9$ Hz), 7.34 (2H, $J=10.9$ Hz), and 8.08 (2H, $J=8.8$ Hz). Found, C 72.50, H 7.62; calcd for $C_{24}H_{30}O_5$, C 72.34, H 7.59. **8b**: 32%, m.p. 113°C. Found, C 73.10, H 8.03; calcd for $C_{26}H_{34}O_5$, C 73.21, H 9.03%. **8c**: 38%, m.p. 101°C. Found, C 73.10, H 8.03; calcd for $C_{27}H_{36}O_5$ 1/4$H_2O$, C 72.86, H 8.27% **8d**: 45%, m.p. 114.1°C. Found, C 73.79, H 8.46; calcd for $C_{28}H_{38}O_5$, C 73.98 H 8.42%. **8e**: 27%, m.p. 113.2°C. Found, C 74.43, H 8.62; calcd for $C_{29}H_{40}O_5$, C 74.33, H 8.60%. **8f**: 38%, m.p. 110.9°C. Found, C 74.45, H 8.78; calcd for $C_{30}H_{42}O_5$, C 74.66, H 8.77%. **8g**: 32%, m.p. 112.9°C. Found, C 75.08, H 8.96; calcd for $C_{31}H_{44}O_5$, C 75.00, H 8.93%.

### 5.3. *Synthesis of troponoid dimers (6)*

A THF solution (2 cm$^3$) of 5-(4-decyloxybenzoyloxy)-tropolone (**8a**, 50 mg, 0.13 mmol) and 60% NaH (6 mg, 0.15 mmol) was stirred at room temperature for 1h under nitrogen. To the mixture was added adipoyl dichloride (0.01 cm$^3$, 0.07 mmol) and the mixture was stirred at room temperature for 15 h. It was then poured into aqueous NaCl and extracted by AcOEt. The organic layer was washed with aqueous NaCl and dried on $Na_2SO_4$. The solvent was removed under reduced pressure and the residue chromatographed on a silica gel column (hexane/AcOEt=3/2–1/1) to give **6a**: (19 mg, 32%), m.p. 120°C. $^1$H NMR $\delta$: 0.89 (6H, t, $J=6.8$ Hz), 1.28–1.51 (28H, m), 1.82 (4H, m), 1.94 (4H, m), 2.72 (4H, m), 4.05 (4H, t, $J=6.5$ Hz), 6.97 (4H, d, $J=8.8$ Hz), 7.03 (4H, d, $J=11.7$ Hz), 7.23 (4H, d, $J=11.7$ Hz), and 8.08 (4H, d, $J=8.8$ Hz). Calcd for $C_{54}H_{66}O_{12}$, C 71.50, H 7.33; found, C 71.37, H 7.32%. **6b**: m.p. 113°C, 23%. Calcd for $C_{58}H_{74}O_{12}$, C 72.32, H 7.74; found, C 72.04, H 7.68%. **3c**: m.p. 123°C, 17%. Calcd for $C_{59}H_{76}O_{12}$, C 72.51, H 7.84; found, C 72.43, H 7.84%. **6d**: 25%, m.p. 109°C. Calcd for $C_{60}H_{78}O_{12}$, C 72.70, H 7.93; found, C 72.46, H 7.92%. **6e**: 24%, m.p. 126°C. Calcd for $C_{61}H_{80}O_{12}$, C 72.88, H 8.02; found, C 72.69, H 8.02%. **6f**: 25%, m.p. 111°C. Calcd for $C_{61}H_{80}O_{12}$, C 72.88, H 8.02; found, C 72.75, H 7.99%. **6g**: 45%, m.p. 112°C. Calcd for $C_{62}H_{82}O_{12}$, C 73.06, H 8.11; found, C 72.88, H 8.11%. **6h**: 44%, m.p. 121°C. Calcd for $C_{63}H_{84}O_{12}$, C 73.23, H 8.19; found, C 73.14, H 8.18%. **6i**: 60%, m.p. 122°C. Calcd for $C_{64}H_{86}O_{12}$, C 73.39, H 8.28; found, C 73.15, H 8.26%. **6j**: 58%, m.p. 113°C. Calcd for $C_{65}H_{88}O_{12}$, C 73.55, H 8.36; found, C 73.29, H 8.46%. **6k**; 32%, m.p. 103°C. Calcd for $C_{66}H_{90}O_{12}$, C 73.71, H 8.44; found, C 73.57, H 8.41%. **6l**: 27%, m.p. 102°C. Calcd for $C_{68}H_{94}O_{12}$, C 74.02, H 8.59; found, C 73.77, H 8.61%. **6m**: 25%, m.p. 104°C. Calcd for $C_{64}H_{86}O_{12}$, C 73.39, H 8.28; found, C 73.20, H 8.30%. **6n**: 33%, m.p. 108°C. Calcd for $C_{65}H_{88}O_{12}$, C 73.55, H 8.36; found, C 73.46, H 8.33%. **6o**: 44%, m.p. 117°C. Calcd for $C_{66}H_{90}O_{12}$, C 73.71, H 8.44; found, C 73.57, H 8.42%. **6p**: 47%, m.p. 110°C. Calcd for $C_{67}H_{92}O_{12}$, C 73.87, H 8.51; found, C 73.70, H 8.50%. **6q**: 45%, m.p. 97°C. Calcd for $C_{68}H_{94}O_{12}$, C 74.02, H 8.59; found, C 73.78, H 8.59%. **6r**: 22%, m.p. 102°C. Calcd for $C_{70}H_{98}O_{12}$, C 74.30, H 8.73; found, C 74.08, H 8.75%. **6s**: 32%, m.p. 114°C. Calcd for $C_{66}H_{90}O_{12}$, C 73.71, H 8.44; found, C 73.41, H 8.39%. **6t**: 36%, m.p. 118°C Calcd for $C_{67}H_{92}O_{12}$, C 73.87, H 8.51; found, C 73.62, H 8.47%. **6u**: 46%, m.p. 118°C Calcd for $C_{69}H_{96}O_{12}$, C 74.16, H 8.66; found, C 73.87, H 8.55%.

### 5.4. *Synthesis of benzenoid dimers (7)*

A THF solution (3 cm$^3$) of 4-hydroxyphenyl 4-decyloxybenzoate (50 mg, 0.14 mmol) and 60% NaH (6 mg, 0.15 mmol) was stirred at room temperature for 1h under nitrogen. To the mixture was added adipoyl dichloride (0.01 cm$^3$, 0.07 mmol) and the mixture was stirred at room temperature for 5 h. It was then poured into aqueous NaCl and was extracted by AcOEt. The organic layer was washed with aqueous NaCl and dried over $Na_2SO_4$. The solvent was removed under reduced pressure and the residue chromatographed on a silica gel column ($CHCl_3$) to give **7a**: (50 mg, 84%), m.p. 134°C, $^1$H NMR $\delta$ 0.89 (6H, t, $J=6.8$ Hz), 1.28–1.49 (28H, m), 1.82 (4H, m), 1.89 (4H, m), 2.65 (4H, m), 4.03 (4H, t, $J=5.7$ Hz), 6.96 (4H, d, $J=8.9$ Hz), 7.14 (4H, d, $J=9.2$ Hz), 7.22 (4H, d, $J=9.2$ Hz), and 8.13 (4H, d, $J=8.9$ Hz). Calcd for $C_{52}H_{66}O_{10}$, C 73.38, H 7.82; found, C 73.37, H 7.75%. **7b**: 54%, m.p. 138°C. Calcd for $C_{53}H_{68}O_{10}$, C 73.58, H 7.92; found, C 73.55, H 7.85%. **7c**: 90%, m.p. 127°C. Calcd for $C_{56}H_{74}O_{10}$, C 74.14, H 8.22; found, C 74.14, H 8.16%. **7d**: 57%, m.p. 131°C. Calcd for $C_{57}H_{76}O_{10}$, C 74.32, H 8.32; found, C 74.32, H 8.25%. **7e**: 92%, m.p. 119°C. Calcd for $C_{58}H_{78}O_{10}$, C 74.49, H 8.41; found, C 74.49, H 8.42%. **7f**: 96%, m.p. 131°C. Calcd for $C_{59}H_{80}O_{10}$, C 74.65, H 8.49; found, C 74.52, H 8.47%. **7g**: 83%, m.p. 138°C. Calcd for $C_{59}H_{80}O_{10}$, C 74.65, H 8.49; found, C 74.59, H 8.44%. **7h**: 77%, m.p. 122°C. Calcd for $C_{60}H_{82}O_{10}$, C 74.81, H 8.58; found, C 74.67, H 8.53%. **7i**: 66%, m.p.

128°C. Calcd for $C_{61}H_{84}O_{10}$, C 74.97, H 8.66; found, C 74.91, H 8.66%. **7j**: 71%, m.p. 137°C. Calcd for $C_{62}H_{86}O_{10}$, C 75.12, H 8.74; found, C 75.05, H 8.70%. **7k**: 63%, m.p. 128°C. Calcd for $C_{63}H_{88}O_{10}$, C 75.26, H 8.82; found, C 75.18, H 8.82%. **7l**: 66%, m.p. 127°C. Calcd for $C_{64}H_{90}O_{10}$, C 75.41, H 8.90; found, C 75.32, H 8.78%. **7m**: 82%, m.p. 130°C. Calcd for $C_{66}H_{94}O_{10}$, C 75.68, H 9.04; found, C 75.73, H 9.01%. **7n**: 89%, m.p. 137°C. Calcd for $C_{61}H_{84}O_{10}$, C 74.97, H 8.66; found, C 74.92, H 8.61%. **7o**: 64%, m.p. 122°C. Calcd for $C_{62}H_{86}O_{10}$, C 75.12, H 8.74; found, C 74.92, H 8.74%. **7p**: 93%, m.p. 126°C. Calcd for $C_{63}H_{88}O_{10}$, C 75.26, H 8.82; found, C 75.20, H 8.84%. **7q**: 82%, m.p. 135°C. Calcd for $C_{64}H_{90}O_{10}$, C 75.41, H 8.90; found, C 75.28, H 8.84%. **7r**: 87%, m.p. 128°C. Calcd for $C_{65}H_{92}O_{10}$, C 75.55, H 8.97; found, C 75.51, H 8.92%. **7s**: 82%, m.p. 123°C. Calcd for $C_{66}H_{94}O_{10}$, C 75.68, H 9.04; found, C 75.59, H 8.98%. **7t**: 84%, m.p. 134°C. Calcd for $C_{68}H_{98}O_{10}$, C 75.94, H 9.18; found, C 75.80, H 9.11%. **7u**: 89%, m.p. 122°C. Calcd for $C_{64}H_{90}O_{10}$, C 75.41, H 8.90; found, C 75.27, H 8.90%. **7v**: 53%, m.p. 127°C. Calcd for $C_{65}H_{92}O_{10}$, C 75.55, H 8.97; found, C 75.56, H 9.02%.

## References

[1] C.T. Imrie, G.R. Luckhurst. In *Handbook of Liquid Crystals*, Vol. 2B, p. 801, D. Demus, J. Goodby, G.W. Gray, H.-W. Spiess, V. Vill (Eds), Wiley-VCH, Weiheim (1998).

[2] C.T. Imrie, P.A. Henderson. *Curr. Opin. colloid interface Sci.*, **7**, 298 (2002).

[3] A. Mori, K. Kubo, M. Takemoto, S. Ujiie. *Liq. Cryst.*, **32**, 1021 (2005).

[4] M. Takemoto, A. Mori, V. Vill. *Chem. Lett.*, 617 (1998); M. Takemoto, A. Mori and S. Ujiie. *Chem. Lett.*, 1177 (1999); M. Takemoto, A. Mori, S. Ujiie and V. Vill. *Liq. Cryst.*, **29**, 687 (2002).

[5] A. Mori, M. Takemoto, S. Ujiie. *Mol. Cryst. liq. Cryst.*, **411**, 1205 (2004).

[6] R. Achten, A.T.M. Marcelis, A. Koudijs, Sudhölter. *Mol. Cryst. liq. Cryst.*, **411**, 1219 (2004).

[7] G.W. Gray, J.W. Goodby. In *Smectic Liquid Crystals*, Chaps. 6 and 9, Leonard Hill, Heyden & Son (1984).

[8] A. Mori, M. Isobe, unpublished results.

[9] R.W. Date, C.T. Imrie, G.R. Luckhurst, J.M. Seddon. *Liq. Cryst.*, **12**, 203 (1992).

[10] A. Mori, K. Uno, H. Takeshita, Y. Kakihara, S. Ujiie. *Liq. Cryst.*, **29**, 1539 (2002).

[11] H. Shimanouchi, Y. Sasada. *Tetrahedron Lett.*, 2421 (1970).

[12] A. Mori, H. Taya, M. Uchida, H. Takeshita. *Chem. Lett.*, 699 (1996); M. Hashimoto, S. Ujiie and A. Mori. *Chem. Lett.*, 758 (2000).

[13] N. Yui, T. Nozoe. *Sci. Repts. Tohoku Univ., I*, **35**, 83 (1951); W.v.E. Doering and L.H. Knox. *J. Am. chem. Soc.*, **73**, 828 (1951).

[14] J.F. Dippy. *Chem. Rev.*, **25**, 151 (1939).

[15] I. Rensch. PhD thesis, Halle University, Germany (1988).

[16] S. Köhler. PhD thesis, Halle University, Germany (1987).

[17] R. Deschinaux. *Helv. Chim. Acta.*, **76**, 865 (1993).

[18] A. Mori, H. Kitaura, unpublished results.

[19] M.M. Naoum. *Liq. Cryst.*, **23**, 247 (1997).