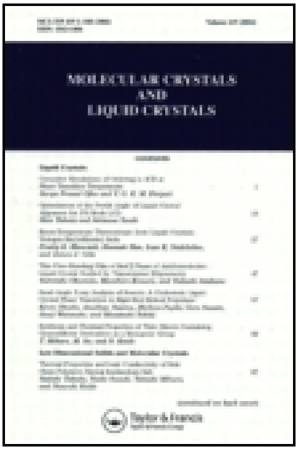

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# The First Synthesis of the Rod-Type Monocyclic Liquid Crystals With 2-Acyloxytropone Structure

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# The First Synthesis of the Rod-Type Monocyclic Liquid Crystals with 2-Acyloxytropone Structure

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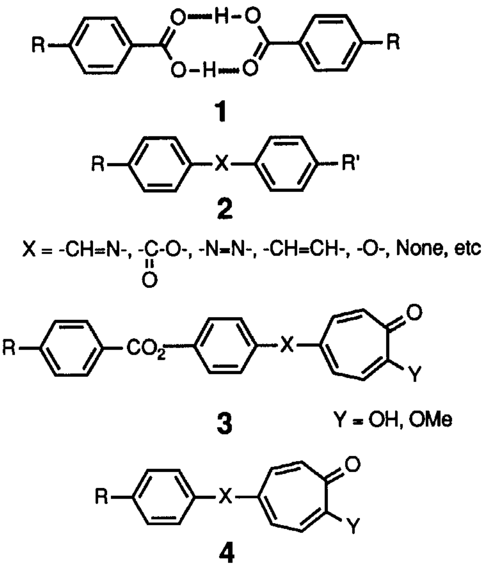
The acyloxy groups of 2-acyloxytropones are known to migrate between two oxygen atoms. This dynamic motion in the 2-alkanoyloxy-5-alkoxytropones did not disturb the orientation of the side chains, but induced the dipole moment along the averaged direction of the longer molecular axis. The present work disclosed that this unique property in 2-acyloxytropones made it possible to disclose the mesophase even in a monocyclic system.

*Keywords: monocyclic LCs, troponoid*

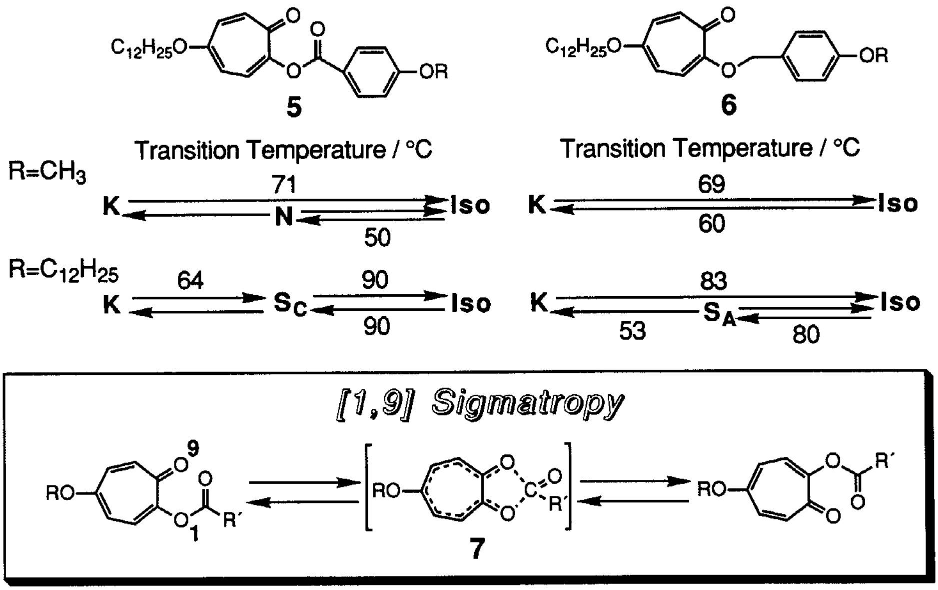
Except for benzoic acids **1**[1] and carbohydrate derivatives,[2] examples of rod-type monocyclic liquid crystals are rare. Usually, the core structure of rod-type liquid crystals contains benzene rings connected either directly or through a linking unit to gain the rigidity in the molecule **2**.[3] On the other hand, the preparation of other ring systems has rarely been examined. One example is the work of Kusabayashi *et al.* who have prepared liquid crystals with a tropolone ring as a terminal component. Their three-ring systems **3** showed nematic phases whereas two-ring systems were non-mesogenic **4**.[4]

Recently, we prepared some new liquid crystals containing a tropone ring; 5-alkoxy-2-(4-alkoxybenzoyloxy)tropones **5** and 5-alkoxy-2-(4-alkoxybenzyloxy) tropones **6**.[5] When the mesomorphic properties of these 2 series with the same alkyl groups were compared, the former showed mesophases while the latter did not.

Masamune *et al.* in 1973 and Minkin *et al.* in 1981 reported that the acetyl group of 2-acetoxytropones and the benzoyl group of 2-benzoyloxytropones could migrate between two oxygen atoms at C-1 and C-2.[6] Independently, we studied this acetyl migration with various polyacetoxytropones by means of ordinary- and high-

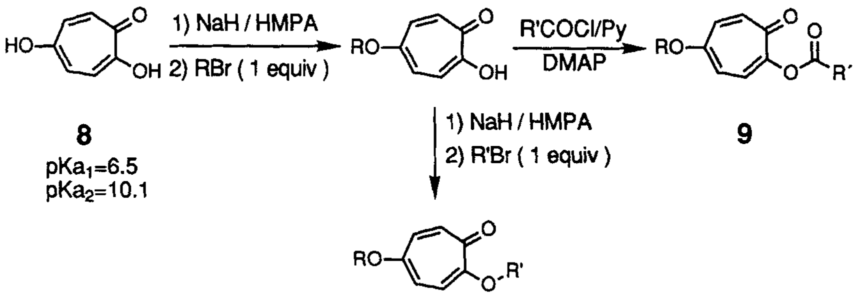


SCHEME 1



SCHEME 2

pressure kinetic analyses. From the solvent and substituent effects, we concluded that this migration is a concerted process, that is a Woodward-Hoffmann Rule-allowed [1,9] sigmatropy.[7–9] Since the migration of the benzoyl group of 2-(4-dodecyloxybenzoyloxy)-5-dodecyloxytropone was operative in solutions and even in a mesophase, which was confirmed by $^{13}C$ CPMAS,[10] it is clear that 1) a cyclic transition geometry is retained during the acylotropy and 2) an induced dipole moment along with the longer molecular axis should be significantly large. Obviously, these two features can not be expected in the benzenoid skeleton. This paper describes the first synthesis of rod-like monocyclic liquid crystals with 2-



**8**
$pKa_1$=6.5
$pKa_2$=10.1

**9**

**10**

SCHEME 3

TABLE I

Yields, transition temperatures, and enthalpies of **9**

| | R | R′ | Yield (%) | Transition Temp. / °C ( ΔH / kJ·mol$^{-1}$ ) | ΔS / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| **9a** | $C_{12}H_{25}$ | $C_9H_{19}$ | 56 | $\mathrm{K} \xrightarrow{48\,(55.1)} \mathrm{Iso}$<br>$\mathrm{K} \xleftarrow[37\,(21.2)]{} \mathrm{S_A} \xrightleftharpoons[46\,(11.7)]{} \mathrm{Iso}$ | 30.7 |
| **9b** | $C_{12}H_{25}$ | $C_{11}H_{23}$ | 45 | $\mathrm{K} \xrightarrow{58} \mathrm{Iso}$<br>$\mathrm{K} \xleftarrow[41]{} \mathrm{S_A} \xrightleftharpoons[45]{} \mathrm{Iso}$ | — |
| **9c** | $C_{12}H_{25}$ | $C_{13}H_{27}$ | 65 | $\mathrm{K} \xrightarrow{63} \mathrm{Iso}$<br>$\mathrm{K} \xleftarrow[48]{} \mathrm{S_A} \xrightleftharpoons[51]{} \mathrm{Iso}$ | — |
| **9d** | $C_{15}H_{31}$ | $C_7H_{15}$ | 20 | $\mathrm{K} \xrightarrow{41\,(56.9)} \mathrm{Iso}$<br>$\mathrm{K} \longleftarrow \mathrm{S_A} \xrightleftharpoons[39\,(9.7)]{} \mathrm{Iso}$ | 31.1 |
| **9e** | $C_{15}H_{31}$ | $C_9H_{19}$ | 56 | $\mathrm{K} \xrightarrow{48\,(64.4)} \mathrm{Iso}$<br>$\mathrm{K} \xleftarrow[25\,(28.1)]{} \mathrm{S_A} \xrightleftharpoons[47\,(12.6)]{} \mathrm{Iso}$ | 39.4 |
| **9f** | $C_{15}H_{31}$ | $C_{11}H_{23}$ | 38 | $\mathrm{K} \xrightarrow{60\,(73.9)} \mathrm{Iso}$<br>$\mathrm{K} \xleftarrow[47]{} \mathrm{S_A} \xrightleftharpoons[52]{} \mathrm{Iso}$ | 33.5 |
| **9g** | $C_{15}H_{31}$ | $C_{13}H_{27}$ | 88 | $\mathrm{K} \xrightleftharpoons[60\,(57.7)]{67\,(83.7)} \mathrm{Iso}$ | — |
| **9h** | $C_{18}H_{37}$ | $C_7H_{15}$ | 33 | $\mathrm{K} \xrightarrow{49\,(64.2)} \mathrm{Iso}$<br>$\mathrm{K} \xleftarrow[32\,(49.1)]{} \mathrm{S_A} \xrightleftharpoons[39\,(10.1)]{} \mathrm{Iso}$ | 32.4 |
| **9i** | $C_{18}H_{37}$ | $C_9H_{19}$ | 50 | $\mathrm{K} \xrightarrow{53\,(71.1)} \mathrm{Iso}$<br>$\mathrm{K} \xleftarrow[29\,(20.3)]{} \mathrm{S_A} \xrightleftharpoons[46\,(14.9)]{} \mathrm{Iso}$ | 46.7 |
| **9j** | $C_{18}H_{37}$ | $C_{11}H_{23}$ | 25 | $\mathrm{K} \xrightarrow{60\,(62.2)} \mathrm{Iso}$<br>$\mathrm{K} \xleftarrow[44\,(36.5)]{} \mathrm{S_A} \xrightleftharpoons[52\,(17.0)]{} \mathrm{Iso}$ | 52.3 |
| **9k** | $C_{18}H_{37}$ | $C_{13}H_{27}$ | 56 | $\mathrm{K} \xrightleftharpoons[61]{72} \mathrm{Iso}$ | — |

K: Crystals, Iso: Isotropic, $S_A$: Smectic A Phase.

TABLE II

Yields, transition temperatures, and enthalpies of **10**

| | R | R′ | Yield (%) | Transition Temp. / °C ( ΔH / kJ·mol$^{-1}$ ) |
|---|---|---|---|---|
| **10a** | $C_{12}H_{25}$ | $C_{12}H_{25}$ | 25 | $K \underset{61\ (73.8)}{\overset{63\ (74.3)}{\rightleftarrows}} Iso$ |
| **10b** | $C_{15}H_{31}$ | $C_{12}H_{25}$ | 38 | $K \underset{57\ (82.9)}{\overset{63\ (78.3)}{\rightleftarrows}} Iso$ |
| **10c** | $C_{18}H_{37}$ | $C_{12}H_{25}$ | 18 | $K \overset{64-66}{\rightleftarrows} Iso$ |

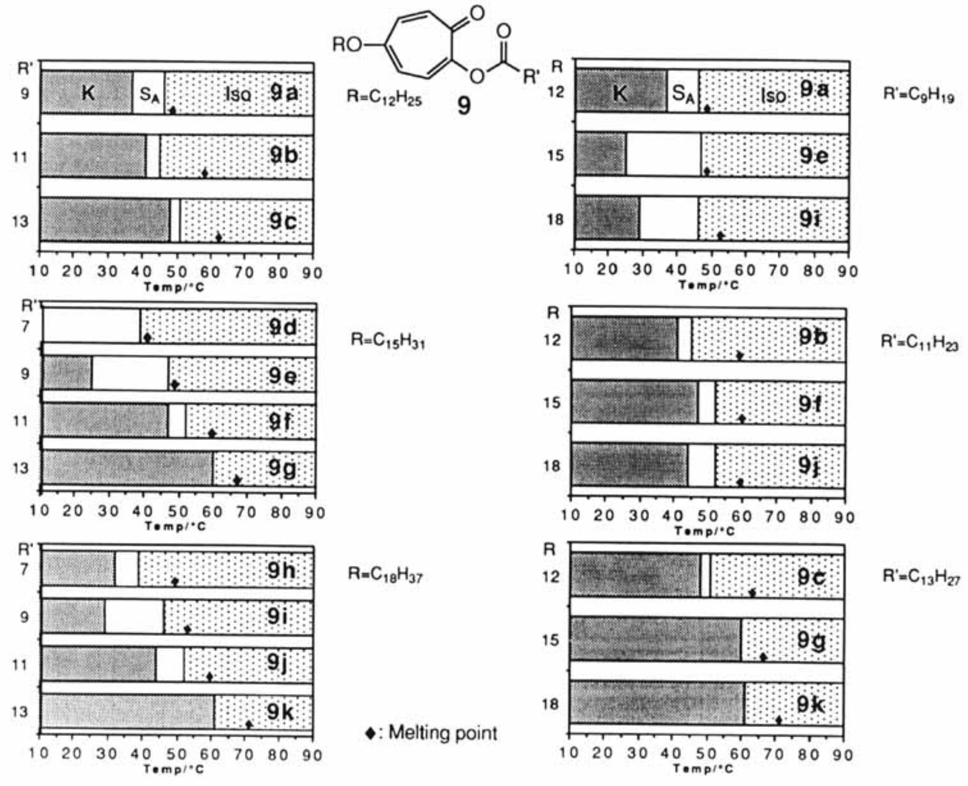


FIGURE 1

acyloxytropone structure, whose molecular dynamic properties may reflect on the appearance of the mesophase.

Based on the pKa difference between the two hydroxy groups of 5-hydroxytropolone (**8**) ($pKa_1 = 6.5$; $pKa_2 = 10.1$),[11] 2-acyloxy-5-alkoxytropones (**9**) were prepared by monoalkylation at the C-5 position of compound **8** and subsequent acylation at the C-2 position. The phase transition temperatures were measured using a differential scanning calorimeter (DSC) and the mesomorphic phases were observed by a polarized microscope equipped with a hot stage. The results are summarized in Table I.

Compound **9** showed a monotropic smectic A phase except for **9g** and **9k**. The enthalpies of the $S_A$-I transition are almost within those of the typical $S_A$-I transition except for **9j**.[12] The entropies of this transition except for **9j** are almost twice those of the typical $S_A$-I transition.[12] On the other hand, the 2,5-dialkoxytropones (**10a**, mp 63°C; **10b**, mp 63°C; **10c**, mp 64-66°C) were non-mesogenic. The NMR spectra of **10** in $CDCl_3$ showed the sharp signals at 27°C indicating that no migration occurred under these conditions. Thus, it appears that the rod-type monocyclic tropone derivatives **9** are liquid crystals because of their molecular dynamic property.

Figure 1 shows the effect of the alkyl chain length on the appearance of the smectic A phase. When the length of R′ was constant and that of R was changed, the $S_A$-I transition and the clearing temperatures were roughly constant. While the length of R was constant and that of R′ was changed, the $S_A$-I transition and the clearing temperatures changed. The chain length of the migrating part, R′, was more effective than that of R on the mesophase; the longer the alkyl chain, the higher the melting point and the larger the entropy change of the $S_A$-I transition.

Aromatic acids[1] and monosaccharide derivatives[2] show mesophases since a stable dimer can form through hydrogen bonding. It is quite interesting that the monocyclic troponoid **9**, in which an intermolecular hydrogen bonding is impossible, showed the smectic A phase even though it was monotropic. This can not be explained only by the stacking forces of the alkyl chain. It is concluded that through the [1,9] sigmatropy, the monocyclic ester **9** formed linear rod-type geometry **7** with an induced dipole moment along the longer molecular axis to exhibit the liquid crystal phase.

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