

Antiferroelectric Liquid Crystals Having a Chiral Ring Structure

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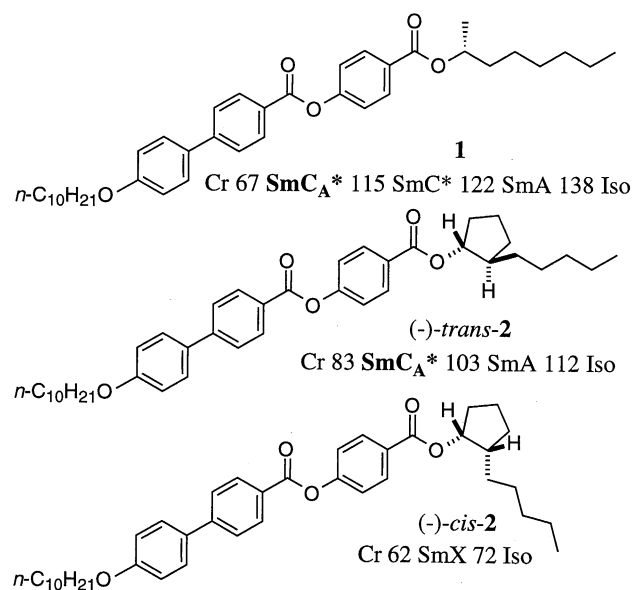
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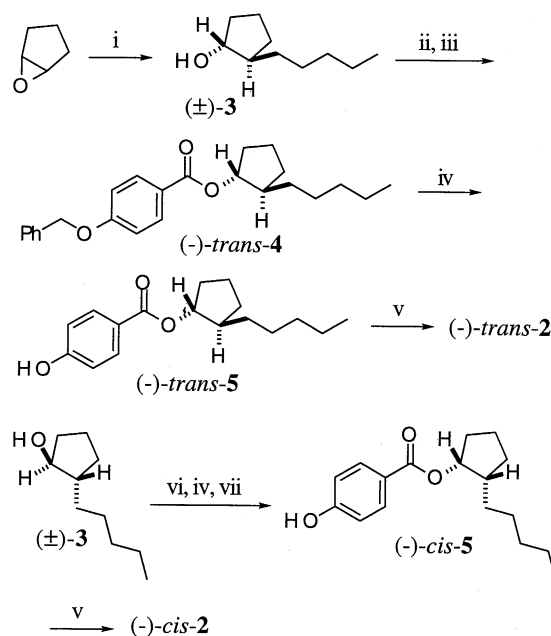
Liquid crystalline compound having a chiral *trans*-2-pentylcyclopentyl ester group exhibited stable antiferroelectric chiral smectic C phase whereas its *cis* isomer showed an unidentified smectic phase.

Antiferroelectric liquid crystal (AFLC) materials are expected to be applicable to high speed display device.¹⁻⁴ The most important requirements for achievement of practical AFLC display are design and synthesis of new compounds which exhibit stable antiferroelectric chiral smectic C (SmC_A^*) phase over a wide range of temperatures. Although a lots of studies on the synthesis of new AFLC materials have been conducted, few compounds with SmC_A^* phase were found except **1** and its derivatives. Because conformational molecular ordering in SmC_A^* phase is not well established yet,⁵⁻⁷ it is hard to design new AFLC materials. To study in details the conformational effect of **1** and to develop new AFLC materials, we designed *trans*-**2** and *cis*-**2** whose conformations around the chiral centers were fixed by a cyclopentane ring structure. Herein we report their synthesis and properties.



Synthesis of *(-)-trans*-**2** and *(-)-cis*-**2** were carried out according to the route shown in Scheme 1. 2-Pentylcyclopentanol ($\pm$)-**3** was prepared by the reaction of pentylmagnesium bromide with cyclopentene oxide. Esterification of ($\pm$)-**3** with 4-benzyloxybenzoic acid using dicyclohexylcarbodiimide (DCC) followed by resolution of the resulting 4-benzyloxybenzoate by HPLC (Daicel, CHIRALCEL OD, hexane

: 2-propanol = 60 : 1) afforded ($-$)- and ($+$)-enantiomers of *trans*-**4**. Debenzylation of ($-$)-*trans*-**4** (100% *de*, >98% *ee*) afforded ($-$)-*trans*-**5**, which was condensed with 4-(4-decyloxyphenyl)-benzoic acid to give rise to ($-$)-*trans*-**2**. ($-$)-*Cis*-**2** also was synthesized starting with ($\pm$)-**3**. Esterification of ($\pm$)-**3** by Mitsunobu reaction followed by debenzylation gave ($\pm$)-*cis*-**5** which was resolved into ($-$)- and ($+$)-*cis*-**5** by HPLC (Daicel, CHIRALPAC AD, hexane : 2-propanol = 20 : 1). Esterification of ($-$)-*cis*-**5** (100% *de*, >98% *ee*) with 4-(4-decyloxyphenyl)-benzoic acid gave ($-$)-*cis*-**2**.



Scheme 1.

Phase transition temperatures⁸ of **1**, *(-)-trans*-**2**, and *(-)-cis*-**2** are shown below each structural formula. Of the compounds we prepared, *(-)-trans*-**2** exhibited SmA and SmC_A^* phases and did not exhibit SmC^* phase. This should be ascribed to the fact that the SmC_A^* phase is stabilized by the conformational effect of *trans*-cyclopentyl group. On the other hand, *(-)-cis*-**2** exhibited unidentified smectic phase caused by poor molecular orientation. Noteworthy is that the texture of *(-)-cis*-**2** was totally different from SmC_A^* or SmC^* phase, whereas ($\pm$)-*cis*-**2** showed typical fan-shaped and *schlieren* textures of SmC phase (Figure 1). Similar phenomena were found in 5-(2-fluoroalkyl)-2-(4-

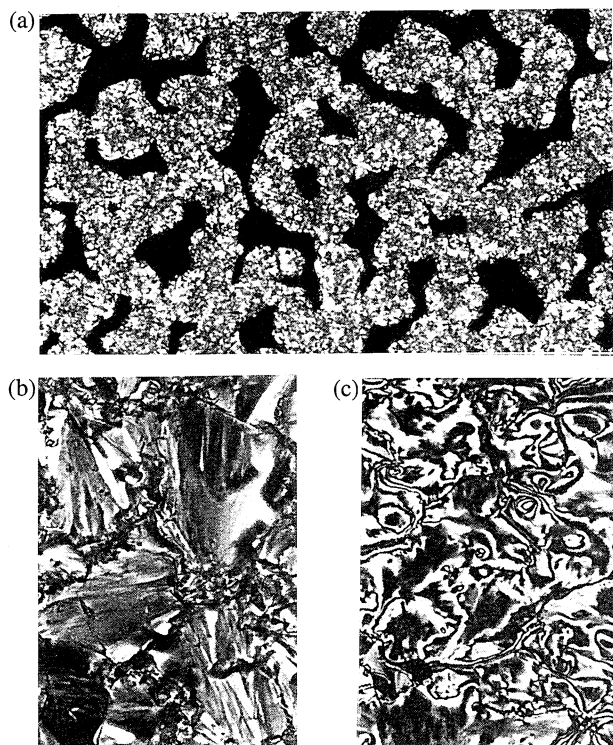


Figure 1. Optical micrographs of (a): (-)-*cis*-**2** at 65 °C, (b): fan-shaped texture of (±)-*cis*-**2** at 71 °C, and (c): *schlieren* texture of (±)-*cis*-**2** at 71 °C.

alkoxyphenyl)pyrimidines also.⁹

In Figure 2 the conformers **A** and **B** of **1** is schematically drawn. *Trans*-**2** (**C**) and *cis*-**2** (**D**) are models corresponding to conformers **A** and **B** of **1**, respectively. Ouchi *et al.* proposed that the terminal hexyl chain connected to the chiral carbon of **1** should be bent away from the molecular long axis, as shown in **B**, the bent molecular structure being necessary for the appearance of stable SmC_A^* phase.¹⁰ In contrast, we consider that the bent structure **B** is not effective for stabilizing SmC_A^* phase because (-)-*trans*-**2** (**C**) exhibited SmC_A^* phase, but (-)-*cis*-**2** (**D**) did not.

In summary, we have synthesized new antiferroelectric liquid crystalline materials having a chiral 2-pentylcyclopentyl ester group and demonstrated that the *trans*-isomer exhibits stable SmC_A^* phase and the *cis*-isomer an unidentified smectic phase. These observations should be useful for designing new antiferroelectric liquid crystalline materials.

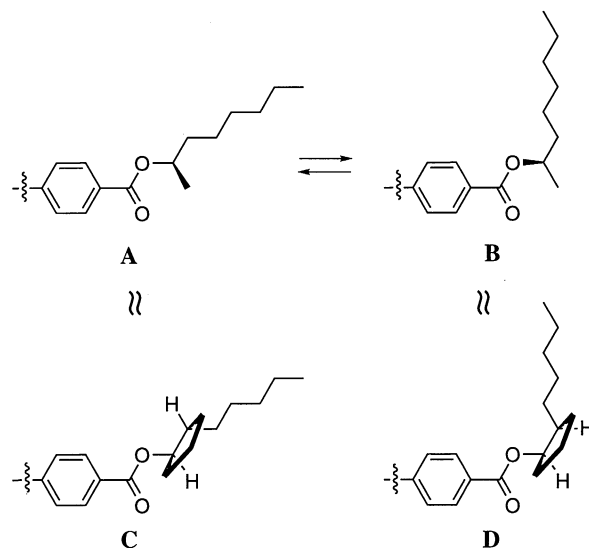


Figure 2. Structural correlation of **1** (**A** and **B**) and **2** (**C** and **D**).

References and Notes

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- 8 Given in °C. Cr: crystalline phase, SmC_A^* : antiferroelectric chiral smectic C phase, SmC^* : chiral smectic C phase, SmA: smectic A phase, Iso: isotropic liquid phase, SmX: an unidentified smectic phase.
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