Antiferroelectric Liquid Crystals Having a Chiral Ring Structure

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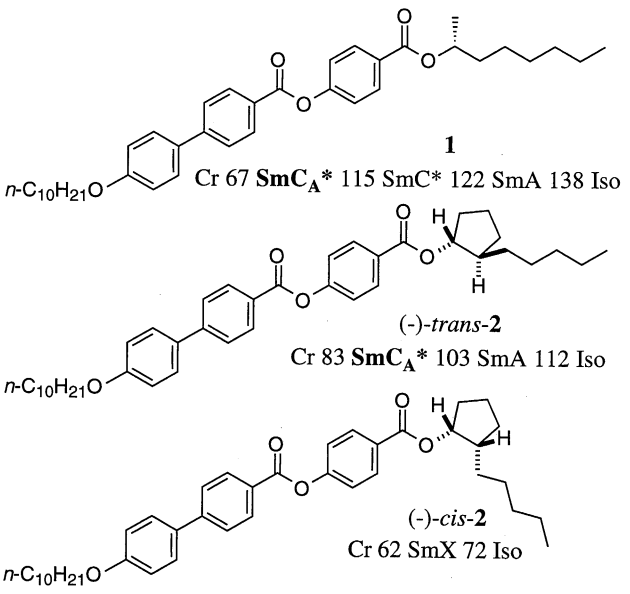
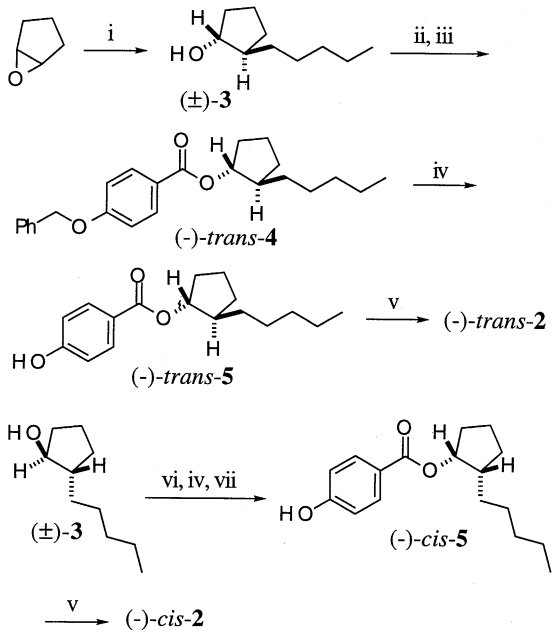
Liquid crystalline compound having a chiral *trans*-2-pentylcyclopentyl ester group exhibited stable antiferroelectric chiral smectic C phase whereas its cis isomer showed an unidentified smectic phase.

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 ((±)-**3**) was prepared by the reaction of pentylmagnesium bromide with cyclopentene oxide. Esterification of (±)-**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 (±)-**3**. Esterification of (±)-**3** by Mitsunobu reaction followed by debenzylation gave (±)-*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**.



i: *n*-$C_5H_{11}MgBr$, CuI; ii: $PhCH_2OC_6H_4COOH$, DCC, DMAP; iii: separation by HPLC (CHIRALCEL OD); iv: H_2, Pd-C; v: *n*-$C_{10}H_{21}O$-$C_6H_4C_6H_4COOH$, DCC, DMAP; vi: $PhCH_2OC_6H_4COOH$, $(NCOOEt)_2$, PPh_3; vii: separation by HPLC (CHIRALPAK AD)

Scheme 1.

Phase transition temperatures[8] 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 (±)-*cis*-**2** showed typical fan-shaped and *schlieren* textures of SmC phase (Figure 1). Similar phenomena were found in 5-(2-fluoroalkyl)-2-(4-

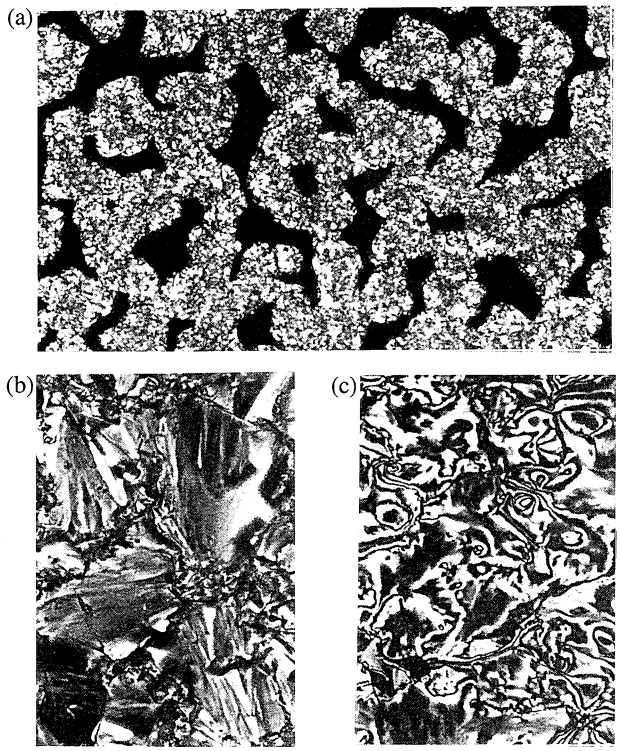


Figure 1. Optical micrographs of (a): (-)-*cis*-**2** at 65 °C, (b): fan-shaped texture of (±)-*cis*-**2** at 71 °C, and (c): *schlieren* texture of (±)-*cis*-**2** at 71 °C.

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.

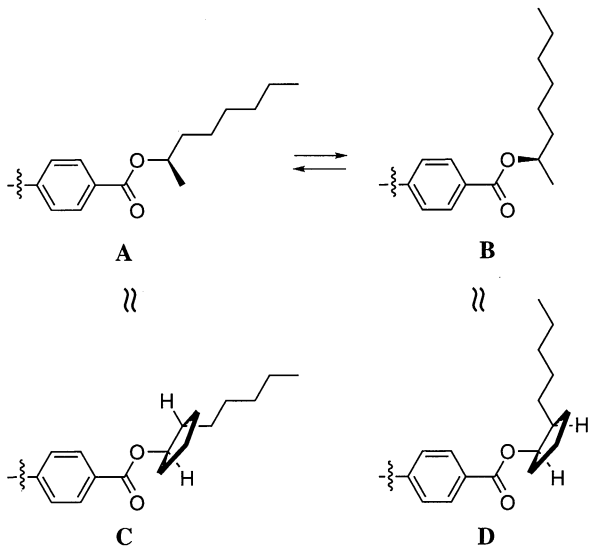


Figure 2. Structural correlation of **1** (**A** and **B**) and **2** (**C** and **D**).

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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