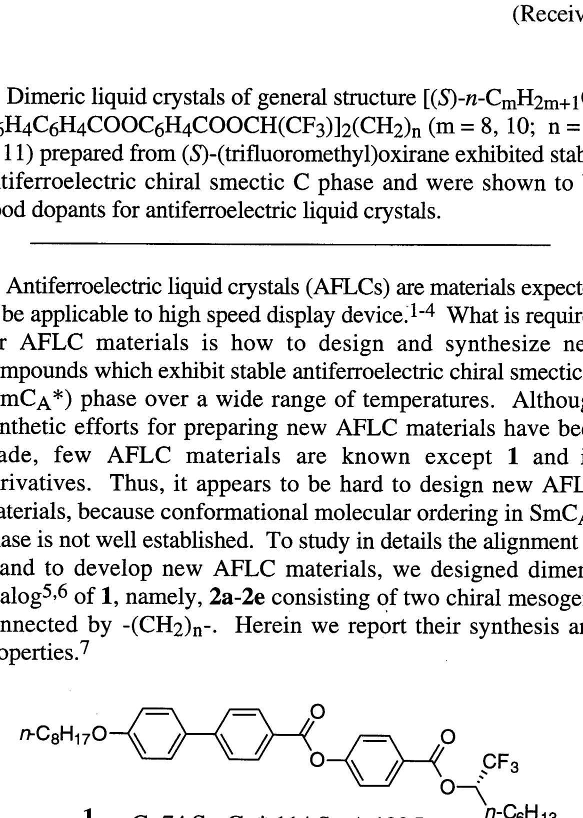
Synthesis and Properties of Dimeric Antiferroelectric Liquid Crystals

Yoshiichi Suzuki, Tadaaki Isozaki, Tetsuo Kusumoto,*† and Tamejiro Hiyama††
Central Research and Development Laboratory, Showa Shell Sekiyu K.K., 123-1 Shimokawairi, Atsugi, Kanagawa 243-02
†*Sagami Chemical Research Center, 4-4-1 Nishiohnuma, Sagamihara, Kanagawa 229*
††*Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, Kanagawa 226*

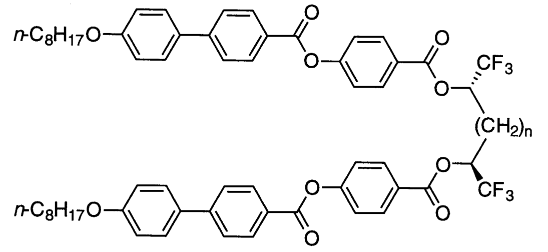
(Received May 26, 1995)

Dimeric liquid crystals of general structure $[(S)\text{-}n\text{-}C_mH_{2m+1}O\text{-}C_6H_4C_6H_4COOC_6H_4COOCH(CF_3)]_2(CH_2)_n$ ($m = 8, 10$; $n = 7, 9, 11$) prepared from (*S*)-(trifluoromethyl)oxirane exhibited stable antiferroelectric chiral smectic C phase and were shown to be good dopants for antiferroelectric liquid crystals.

Antiferroelectric liquid crystals (AFLCs) are materials expected to be applicable to high speed display device.[1-4] What is required for AFLC materials is how to design and synthesize new compounds which exhibit stable antiferroelectric chiral smectic C (SmC$_A$*) phase over a wide range of temperatures. Although synthetic efforts for preparing new AFLC materials have been made, few AFLC materials are known except **1** and its derivatives. Thus, it appears to be hard to design new AFLC materials, because conformational molecular ordering in SmC$_A$* phase is not well established. To study in details the alignment of **1** and to develop new AFLC materials, we designed dimeric analog[5,6] of **1**, namely, **2a**-**2e** consisting of two chiral mesogens connected by -(CH$_2$)$_n$-. Herein we report their synthesis and properties.[7]



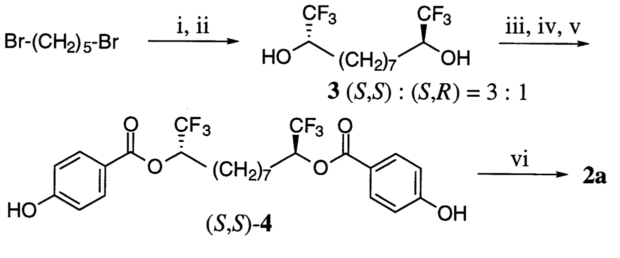
1 Cr 74 **SmC$_A*$** 114 SmA 123 Iso



2

a:	n =	7	Cr 145 **SmC$_A*$** 179 Iso
b:		8	Cr 154 SmC* 166 SmA 173 Iso
c:		9	Cr 145 **SmC$_A*$** 169 Iso
d:		10	Cr 140 SmC* 158 SmA 166 Iso
e:		11	Cr 125 **SmC$_A*$** 161 Iso

Dimeric liquid crystalline compound **2a** was prepared according to the route shown in Scheme 1. The diol **3** was prepared by the reaction of Grignard reagent obtained from 1,5-dibromopentane with (*S*)-(trifluoromethyl)oxirane (75% *e.e.*).[8-10] Esterification of **3** with 4-benzyloxybenzoic acid followed by debenzylation of the resulting 4-benzyloxybenzoate afforded bisphenol **4** as a diasteromeric mixture (*S*,*S* : *S*,*R* = 3 : 1). Resolution by HPLC (Daicel, CHIRALPAK AD, hexane : 2-propanol = 7 : 1) afforded (*S*,*S*)-**4** which was condensed with 4-(4-octyloxyphenyl)benzoic acid to give rise to **2**. In a similar manner, **2b**-**2e** were obtained.

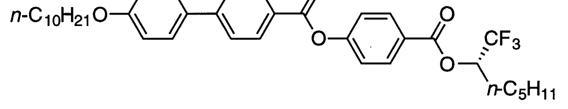


i: Mg; ii: CuI, (*S*)-3,3,3-trifluoro-1,2-epoxypropane (75% *e.e.*); iii: PhCH$_2$OC$_6$H$_4$COOH, PPE; iv: H$_2$, 10% Pd-C; v: separation by HPLC (CHIRALCEL AD); vi: *n*-C$_8$H$_{17}$OC$_6$H$_4$C$_6$H$_4$COOH, DCC, DMAP

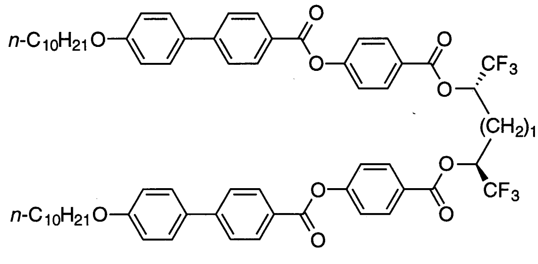
Scheme 1.

Phase transition temperatures[11] of **2a**-**2e** are shown below each structure of **2a**-**2e**. Of the compounds we prepared, **2a**, **2c**, and **2e** with odd number of n exhibited only SmC$_A$* phase, and **2b** and **2d** with even number of n exhibited SmA and SmC* phase. These results may suggest that two mesogenic units, -C$_6$H$_4$C$_6$H$_4$COOC$_6$H$_4$COO-, tend to align anticlinically or parallel in the dimer compounds **2a**-**2e** depending on the odd or even number of n, respectively. In Figure 1 the conformational effect of the spacer -(CH$_2$)$_n$- is schematically drawn.[5-7] Although we attempted to observe the electric-field-induced SmC$_A$*-SmC* phase transition in the compounds of **2a**, **2c**, and **2e**, the electro-optic switching did not take place. This should be ascribed to the fact that the SmC$_A$* phase is highly stabilized by the conformational effect.

The dopant effect of dimeric liquid crystals was next studied. Compound **5** selected as a host liquid crystal, exhibited SmA, SmC*, and SmC$_A$* phase. Dimeric compound **6** prepared in a similar manner, was added to **5** (**5** : **6** = 95 : 5 by weight), and the properties of the resulting mixture were measured and



5 Cr 53 **SmC$_A*$** 97 SmC* 110 SmA 116 Iso



6 Cr 62 **SmC$_A*$** 144 Iso

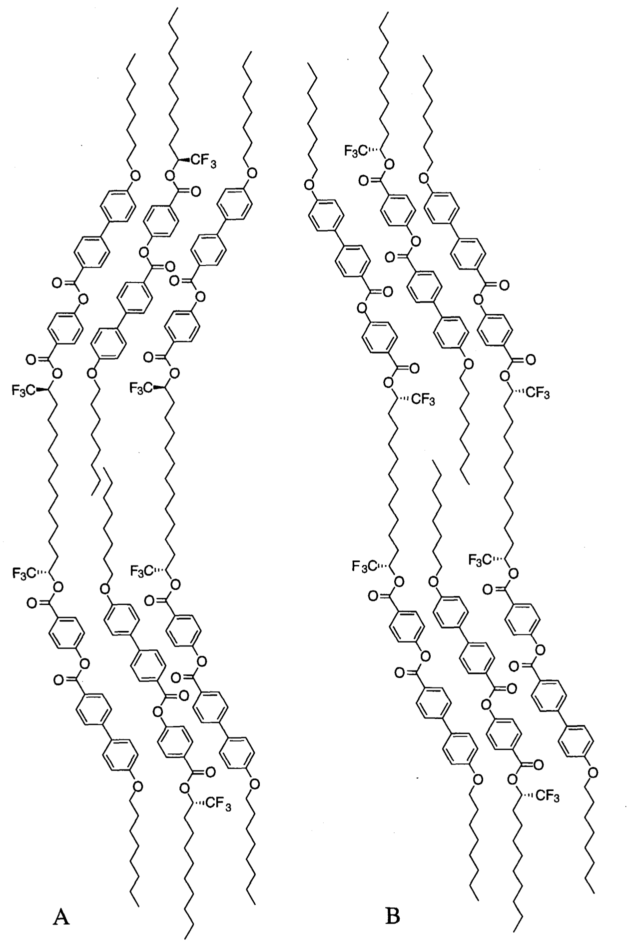


Figure 1. Illustration of the alignment of **2e** (n = 11) in SmC$_A$* phase (A) and **2d** (n = 10) in SmC* phase (B).

compared with those of pure **5**. The mixture showed SmA and SmC$_A$* phase and did not exhibit SmC* phase; Cr 52 SmC$_A$* 111 SmA 117 Iso. The SmC$_A$* phase was well stabilized by the coexisting dimer **6**. The electric-field-induced SmC$_A$*-SmC* phase transition of **5** and the one of the **6** containing mixture are shown in Figure 2.[12] The electro-optic response of these samples exhibited the antiferroelectric double-loop-hysteresis. The hysteresis of the mixture (b, Figure 2) is clearer than that of pure **5** (a, Figure 2). This means that the SmC$_A$* phase of the mixture is much more stabilized against electric field than that of **5**. Thus, dimeric AFLC material **6** is shown to be useful as a dopant for stabilizing SmC$_A$* phase.

In summary, we have synthesized new antiferroelectric liquid crystalline materials having a dimeric structure and demonstrated these exhibit stable SmC$_A$* phase and stabilize SmC$_A$* phase as a dopant. These observations should be useful for designing new antiferroelectric liquid crystalline materials.

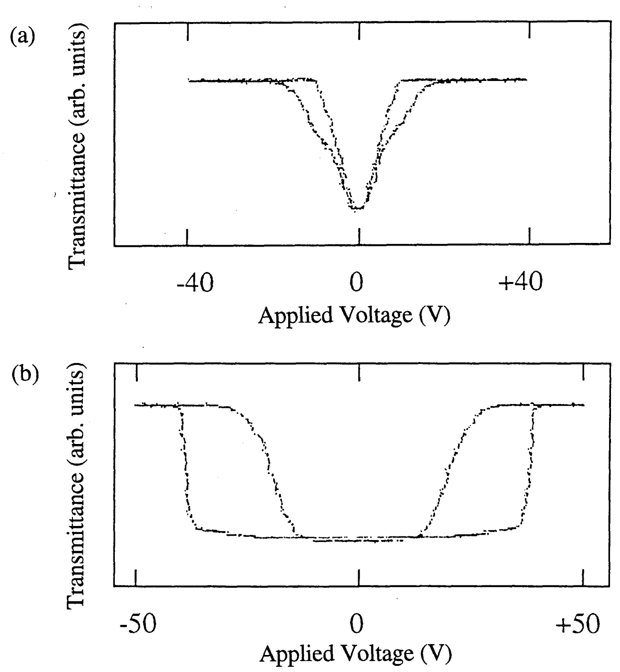


Figure 2. Electro-optic switching characteristics at 90 °C; (a): compound **5** and (b): the mixture containing 5 wt% of **6** with 95 wt% of **5**.

The authors are grateful to Professor A. Fukuda, Professor H. Takezoe, and Dr. Y. Takanishi, Tokyo Institute of Technology, for assignment of the liquid crystalline phases. The present work was partially supported by a Grant-in-Aid for Developmental Scientific Research No. 05555238 from the Ministry of Education, Science and Culture.

References and Notes

1 A. D. L. Chandani, T. Hagiwara, Y. Suzuki, Y. Ouchi, H. Takezoe, and A. Fukuda, *Jpn. J. Appl. Phys.*, **27**, L729 (1988).
2 A. D. L. Chandani, E. Gorecka, Y. Ouchi, H. Takezoe, and A. Fukuda, *Jpn. J. Appl. Phys.*, **28**, L1265 (1989).
3 "Future Liquid Crystal Display and Its Materials," ed by A. Fukuda, CMC, Tokyo (1992).
4 I. Nishiyama, *Adv. Mater.*, **6**, 966 (1994).
5 J. Watanabe, H. Komura, and T. Niiori, *Liq. Cryst.*, **13**, 455 (1993).
6 Y. Nakata and J. Watanabe, *J. Mater. Chem.*, **4**, 1699 (1994).
7 T. Kusumoto, T. Isozaki, Y. Suzuki, Y. Takanishi, H. Takezoe, A. Fukuda, and T. Hiyama, *Jpn. J. Appl. Phys.*, in press.
8 (*S*)-(Trifluoromethyl)oxirane (*ca.* 75% *e.e.*) was purchased from Japan Energy Co. and used directly.
9 O. Takahashi, K. Furuhashi, M. Hurumasa, and T. Hirai, *Tetrahedron Lett.*, **31**, 7031 (1990).
10 Recently, synthesis of chiral (trifluoromethyl)oxirane (96% *e.e.*) was reported: P. V. Ramacheandran, B. Gong, and H. C. Brown, *J. Org. Chem.*, **60**, 41 (1995).
11 Given in °C. Cr: crystalline phase, SmC$_A$*: antiferroelectric chiral smectic C phase, SmA: smectic A phase, Iso: isotropic liquid phase, SmC*: chiral smectic C phase.
12 The transmittance of each cell between crossed polarizer is plotted as a function of an applied voltage in the layer.