Synthesis and Properties of Deuterated Antiferroelectric Liquid Crystals

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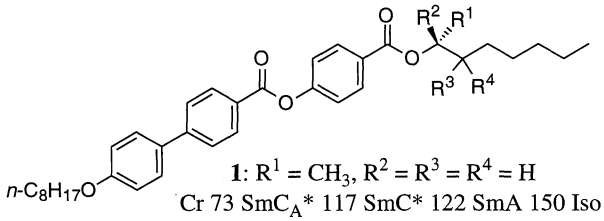
Optically active compounds containing a deuterated chiral alkyl ester group [(*R*)-ArCOOCD(CD_3)CD_2-*n*-C_5H_{11}, ArCOOCH(CD_3)CD_2-*n*-C_5H_{11}, ArCOOCD(CH_3)-*n*-C_6H_{13}: Ar = *n*-C_8H_{17}-$OC_6H_4C_6H_4COOC_6H_4$] were prepared from 2-octanone and were proved to exhibit liquid crystal phases (Cr 73 SmC_A* 117 SmC* 122 SmA 149 Iso) same as the parent compound [(*R*)-ArCOOCH(CH_3)-*n*-C_6H_{13}].

Antiferroelectric liquid crystals (AFLCs) are materials expected to be applicable to high speed display device.[1,2] In spite of synthetic efforts for preparing new AFLC materials, few AFLC materials are known other than **1** and its derivatives. Thus, it appears to be hard to design new AFLC materials. The difficulty may be attributed to the fact that conformational molecular ordering in SmC_A* phase is not well understood. Recently ^{2}H-NMR is shown to be an excellent tool for studying the alignment of molecules in liquid crystal phase,[3] but only a few deuterated liquid crystalline materials have been prepared.[3,4] Accordingly we designed and synthesized **2-4**, deuterated analogs of **1**, for studying isotope effect on AFLC properties. Herein we report their synthesis and properties.



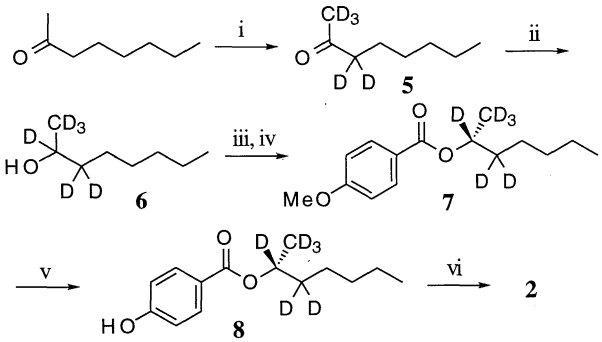
1: $R^1 = CH_3$, $R^2 = R^3 = R^4 = H$
Cr 73 SmC_A* 117 SmC* 122 SmA 150 Iso

2: $R^1 = CD_3$, $R^2 = R^3 = R^4 = D$
Cr 73 SmC_A* 117 SmC* 122 SmA 149 Iso

3: $R^1 = CD_3$, $R^2 = H$, $R^3 = R^4 = D$
Cr 73 SmC_A* 117 SmC* 122 SmA 149 Iso

4: $R^1 = CH_3$, $R^2 = D$, $R^3 = R^4 = H$
Cr 73 SmC_A* 118 SmC* 122 SmA 149 Iso

Hexadeuterated liquid crystalline compound **2** was prepared according to the route shown in Scheme 1. The pentadeuterated 2-octanone **5** (>97% D), obtained by the H-D exchange reaction of 2-octanone with D_2O in the presence of *t*-BuOK and *n*-Bu_4NBr, was reacted with $LiAlD_4$ to give hexadeuterated 2-octanol **6**. Esterification of **6** with 4-methoxybenzoic acid followed by resolution of the resulting 4-methoxybenzoate by HPLC (Daicel, CHIRALPAK AD, hexane : 2-propanol = 150 : 1) afforded **7** (>98% *e.e.*). Demethylation of **7** was effected with Me_2S and $AlCl_3$ to give phenol **8**, which was esterified with 4-(4-octyloxyphenyl)benzoic acid to give rise to **2**. Compounds **3** and **4** were prepared by reducing **5** with $LiAlH_4$ and by reducing 2-octanone with $LiAlD_4$, respectively, followed by the same sequence of reactions in Scheme 1.



i: D_2O, *t*-BuOK, *n*-Bu_4NBr, C_6H_6; ii: $LiAlD_4$; iii: $MeOC_6H_4COCl$, NEt_3; iv: separation by HPLC (CHIRALCEL AD); v: $AlCl_3$, SMe_2; vi: *n*-$C_8H_{17}OC_6H_4C_6H_4COOH$, DCC, DMAP

Scheme 1.

Phase transition temperatures[5] of **2-4** are shown below each structure of **2-4**. All compounds we prepared exhibited SmA, SmC*, and SmC_A* phases with the same temperature ranges as those of **1**.[1] It was reported that **1** exhibited SmCα* phase between SmA and SmC* phases, and SmCγ* phase between SmC* and SmC_A* phases respectively.[6] In the case of **2-4**, SmCα* and SmCγ* phases could be determined by DSC. The electric-field-induced SmC_A*-SmC* phase transition of **2-4** was exactly the same as those of **1**. Thus, isotope effect on AFLC properties are shown to be negligible.

In summary, we have synthesized deuterated antiferroelectric liquid crystalline materials and demonstrated that introduction of deuterium atoms does not change the properties of liquid crystals. Thus, these deuterated materials should be useful for studying conformational molecular ordering of antiferroelectric liquid crystals by ^{2}H-NMR.

References and Notes

1 A. D. L. Chandani, E. Gorecka, Y. Ouchi, H. Takezoe, and A. Fukuda, *Jpn. J. Appl. Phys.*, **28**, L1265 (1989).
2 "Future Liquid Crystal Display and Its Materials," ed by A. Fukuda, CMC, Tokyo (1992).
3 D. J. Photinos, C.-D. Poon, E. T. Samulski, and H. Toriumi, *J. Phys. Chem.*, **96**, 8176 (1992).
4 Synthesis and properties of deuterated antiferroelectric, ferroelectric, and nematic liquid crystalline materials were reported at the 21th Jpn. Liquid Crystal Conf. (Sendai, 1995); B. Jin (2C14), M. Yoshida (3C01), J. Sano (1B07), S. Takehara (3D17, 3D18, 3D19).
5 Given in °C. Cr: crystalline phase, SmC_A*: antiferroelectric chiral smectic C phase, SmC*: ferroelectric chiral smectic C phase, SmA: smectic A phase, Iso: isotropic liquid phase.
6 T. Isozaki, T. Fujikawa, H. Takezoe, A. Fukuda, T. Hagiwara, Y. Suzuki, and I. Kawamura, *Phys. Rev. B*, **48**, 13439 (1993).