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Preliminary communication

Synthesis and mesomorphic properties of steroidal liquid crystals containing perfluoroalkoxycarbonylphenyl units

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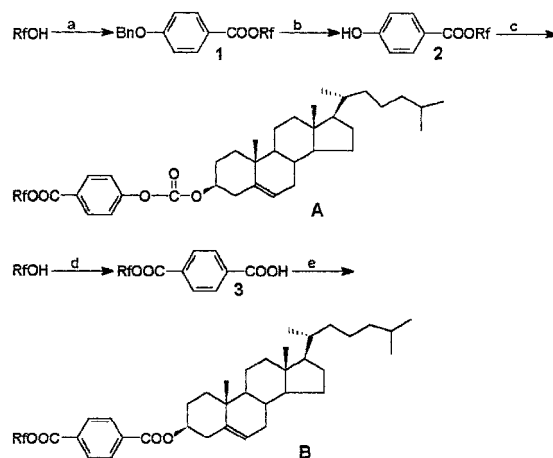
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Two cholesteryl esters liquid crystals containing perfluoroalkoxy terminal chains, and benzoate and carbonate moieties, have been synthesized. Their mesomorphic properties were observed and measured by optical polarizing microscopy and differential scanning calorimetry. The results show that the two liquid crystals exhibit smectic A and B phases. No chiral tilted smectic phase was observed.

Steroids offer a cheap chiral resource, so steroidal liquid crystals exhibiting a good ferroelectric phase would be valuable as potential components of mixtures for ferroelectric liquid crystals displays (FLCDs). Vill *et al.* reported that steroidal liquid crystals containing a long alkyl chain, e.g. cholesteryl *p*-hexadecylbenzoate and cholesteryl *p*-hexadecyloxyphenylcarbonate, display a monotropic ferroelectric phase [1]. We also know that liquid crystals containing highly fluorinated alkyl or alkoxy terminal groups may form a tilted smectic phase of increased temperature range [2, 3]. We therefore synthesized cholesteryl *p*-perfluoroalkylbenzoate and cholesteryl *p*-perfluoroalkylphenylcarbonate, but found no ferroelectric phase [4, 5]. Janulis *et al.* have shown that $(\text{CH}_2)_n$ as a spacer between the fluorinated tail and the rigid core influences the nature of the mesomorphic phase, especially with regard to obtaining a smectic C phase [6]. Hence steroidal liquid crystals containing semifluorinated terminal chains appear desirable. This paper reports results on two series of liquid crystals, cholesteryl 4-(perfluoroalkoxycarbonylphenyl)carbonate (**A**) and cholesteryl 4-(perfluoroalkoxycarbonyl)benzoate (**B**); their structures and preparation paths are outlined in the scheme.

The mesomorphic properties of the new compounds were studied by thermal optical polarizing microscopy using a polarizing microscope (Olympus PM-6) fitted with a heating stage (Mettler FP-80) and a temperature control unit (FP-82), and by differential scanning calorimetry (DSC, Shimadzu-50 calorimeter with a data system, heating and cooling rate 5°C min^{-1}). Phase



Reagents and Conditions: (a) *p*-benzyloxybenzoic acid, DCC, cat. DMAP, THF; (b) Pd/C, H₂ (1atm), ethyl acetate; (c) cholesteryl chloro-formate, Et₃N, CH₂Cl₂; (d) *p*-dibenzoyl chloride, then H₂O, THF; (e) cholesterol, DCC, cat. DMAP, THF.

Scheme.

identification was made by comparing the observed textures with those reported in the literatures [7, 8]. Two compounds were prepared; their transition temperatures are summarized below ($^\circ\text{C}$).

A, $R_f = \text{CH}_2\text{CH}_2(\text{CF}_2)_8\text{F}$: Cr 121.7 SmA 196.5 I 190.6 SmA 90.4 Recr.

B, $R_f = \text{CH}_2(\text{CF}_2)_4\text{H}$: Cr 160.9 SmA 212.4 I 209.5 SmA 147.3 SmB 121.4 Recr.

No chiral smectic C phase or other ferroelectric phases were seen, but some interesting results have been obtained. First, these two compounds both exhibit an enantiotropic smectic A phase, but **B** also shows a

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monotropic smectic B phase, a highly ordered smectic phase. Second, the carbonate linkage is softer than the benzoate linkage, and in general a mesomorphic core containing a carbonate is shorter than one containing a benzoate linkage, causing the mesomorphic properties of the former to be worse than those of the latter. In this case, however, **A** exhibits better mesomorphic properties than **B**; this must be caused by the longer highly fluorinated alkyl terminal chains and a more advantageous terminal fluorine atom.

Although many steroidal liquid crystals containing highly fluorinated alkyl terminal chains have been synthesized by our group [4, 5, 9], no chiral tilted smectic phase have been obtained. But no modifications on the steroidal core have been made yet in these compounds, so liquid crystals containing a different steroidal core should be studied. Fluorination of the steroidal core, which has been used in the synthesis of many drug, hormone and other biologically active molecules, may lead to liquid crystals with unique mesomorphic properties.

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Appendix

The following are results of identification analyses on target compounds.

Cholesteryl 4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hepta-decafluorodecaoxycarbonylphenyl)carbonate **A**, $Rf = CH_2CH_2(CF_2)_8F$. MS (m/z): 368 (Ch^+ , 100.00), 353 ($Ch^+ - CH_3$), 260, 147, 121. Anal. for $C_{45}H_{53}F_{17}O_5$ calc. C 54.21, H 5.36, F 32.40; found C 54.28, H 5.45, F 32.43%. 1H NMR ($CDCl_3/TMS$, 90 MHz) δH (ppm): 0.65–0.75 (s, 6H), 0.85–2.08 (m, 35H), 2.40–2.87 (m, 4H), 4.69 (m, 3H), 5.45 (m, 1H), 7.10 (d, 2H, $J = 9$ Hz), 8.10

(d, 2H, $J = 9$ Hz). ^{19}F NMR ($CDCl_3/TFA$, 56.4 MHz) δF (ppm): 2.9 (m, 3F), 35.9 (m, 2F), 43.7–46.3 (m, 10F), 48.5 (m, 2F), IR (KBr, ν_{max} , cm^{-1}): 2950, 1721, 1616, 1533, 1351, 1292, 1214, 1151, 1029, 836, 655, 535.

Cholesteryl 4-(2,2,3,3,4,4,5,5-octafluoropentoxycarbonyl)benzoate **B**, $Rf = CH_2(CF_2)_4H$. MS (m/z): 749 ($M^+ + 1$, 0.30), 3.68 (Ch^+ , 100.00), 147 (39.33). Anal. for $C_{40}H_{52}F_8O_4$ calc. C 64.19, H 6.96, F 20.30; found C 64.47, H 7.17, F 19.95%. 1H NMR ($CDCl_3/TMS$, 90 MHz) δH (ppm): 0.65–0.75 (s, 6H), 0.85–2.08 (m, 35H), 2.50 (m, 2H), 4.70 (m, 3H), 5.45 (m, 1H), 6.09 (tt, 1H, $J_1 = 52$ Hz, $J_2 = 5$ Hz), 8.15 (s, 4H). ^{19}F NMR ($CDCl_3/TFA$, 56.4 MHz) δF (ppm): 42.1 (m, 2F), 48.0 (m, 2F), 52.7 (m, 2F), 59.9 (d, 2F, $J = 50$ Hz). IR (KBr, ν_{max} , cm^{-1}): 2938, 1734, 1713, 1627, 1501, 1466, 1275, 1175, 876, 846, 808.

References

- [1] VILL, V., THIEM, J., and ROLLIN, P., 1992, *Z. Naturforsch., A*, **47**, 515.
- [2] JANULIS, E. P., NOVACK, J. C., PAPAPOLYMEROU, G. A., TRISTANI-KENDRA, M., and HUFFMAN, W. A., 1988, *Ferroelectrics*, **85**, 375.
- [3] IVASHCHENKO, A. V., KOVSHEV, E. I., LAZAREVA, V. T., PRUDNIKOVA, E. K., TITOV, V. V., ZVERKOVA, T. I., BARNIK, M. I., and YAGUPOLSKI, L. M., 1981, *Mol. Cryst. liq. Cryst.*, **67**, 235.
- [4] WEN, J., CHEN, H., and SHEN, Y., 1999, *Liq. Cryst.*, **26**, 1833.
- [5] SHEN, Y., CHEN, H., and WEN, J., *J. Fluorine. Chem.* (to be published).
- [6] JANULIS, E. P., OSTEN, D. W., RADCLIFFE, M. D., NOVACK, J. C., TRISTANI-KENDRA, M., EPSTEIN, K. A., KEYES, M., JOHNSON, G. C., SAVU, P. M., and SPAWN, T. D., 1992, *Proc. SPIE*, **1665**, 146.
- [7] DEMUS, D., and RICHTER, L., 1978, *Textures of Liquid Crystals* (Weinheim: Verlag Chemie).
- [8] GRAY, G. W., and GOODBY, J. W., 1984, *Smectic Liquid Crystals: Textures and Structures* (Philadelphia: Heyden).
- [9] WANG, K., LI, H., and WEN, J., *J. Fluorine. Chem.* (to be published).