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Liquid Crystals

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Jianxun Wen; Hao Chen; Yuehai Shen

Online publication date: 06 August 2010

To cite this Article Wen, Jianxun , Chen, Hao and Shen, Yuehai(1999) 'The first series of ferroelectric steroidal fluorinated liquid crystals', Liquid Crystals, 26: 12, 1833 — 1834

To link to this Article: DOI: 10.1080/026782999203472

URL: http://dx.doi.org/10.1080/026782999203472

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LIQUID CRYSTALS, 1999, VOL. 26, NO. 12, 1833–1834

Preliminary communication

The first series of ferroelectric steroidal fluorinated liquid crystals

JIANXUN WEN*, HAO CHEN, YUEHAI SHEN
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences,
354 Fenglin Lu, Shanghai 200021, PR China

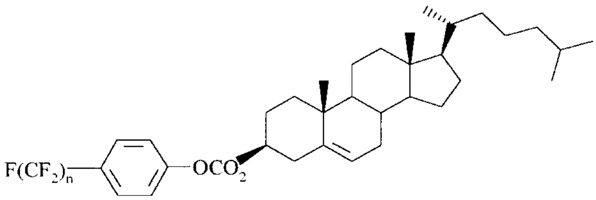
(*Received 18 June 1999; accepted 1 July 1999*)

A series of cholesteryl *p*-perfluoroalkylphenyl carbonate (CPC) [$C_{27}H_{45}OCO_2C_6H_4(CF_2)_nF$, $n = 1, 4, 6, 8$] liquid crystals was synthesized and their phase transition behaviours were studied. The results show that the compounds containing a not too long perfluoroalkyl chain ($n = 6, 8$) have monotropic chiral smectic C phases.

Owing to their excellent characteristics, such as the memory effect and high response speed, ferroelectric liquid crystals, especially those having chiral smectic C phases (SmC*), have been intensely studied in recent years. Generally, the structure of ferroelectric liquid crystalline (FLC) compounds consists of rod-like molecule of three aromatic or cyclohexyl rings containing one or more chiral centres. However, the traditional concept recently has been changed. In 1992, Vill *et al.* reported that steroidal liquid crystals containing a long alkyl chain, e.g. cholesterly *p*-hexdecyl benzoate and cholesteryl *p*-hexadecyloxyphenyl carbonate, displayed monotropic ferroelectric phases [1]. Solladie *et al.* also reported the first smectic C* liquid crystals with a rigid twisted biphenyl core and axial chirality [2].

Recently, fluorinated liquid crystal materials have been the focus of investigation, and it is found that some of them are FLCs. In 1992, Tournilhac *et al.* observed ferroelectric phases in liquid crystals having perfluoroalkyl chains and no chiral centres [3]; representative work has also been done by Nguyen's group [4, 5]. In our earlier studies on the synthesis of the three-ring FLCs, it was also found that although the fluorinated terminal chain may inhibit liquid crystal phases, it can be conductive to forming ferroelectric phases and increasing their temperature range. Therefore, we wanted to introduce perfluoroalkyl chains into steroidal mesomorphic molecules in order to obtain FLCs.

Similar compounds, such as cholesterly ω-monohydrofluoroalkanoates (CHFA) and cholesteryl perfluoroalkanoates (CPFA), have been synthesized but few of them show mesomorphic phases and no ferroelectric phase was observed [7]. In the present work, we introduced a phenylene group into the molecule to stabilize mesophases and synthesized a series of cholesterly *p*-perfluoroalkylphenyl carbonates (CPCs).



CPC, $n = 1, 4, 6, 8$.

The CPC compounds were conveniently by condensation reactions, from cholesterol chloroformates and the appropriate *p*-perfluoroalkyl phenols. The identity of all samples was confirmed from IR, ^1H NMR, ^{19}F NMR and elemental analysis. The phase transition temperatures of the target compounds were measured visually by optical microscopy using a polarizing microscope (Olympus PM-6) fitted with a heating stage (Mettler FP-80) and a control unit (FP-82), and by differential scanning calorimetry (DSC, Shimadzu DSC-50 calorimeter with a data system, heating and cooling rate of 5°C min^{-1}). The phase transition temperatures were summarized in the table.

Table. The phase transition temperatures of the CPC compounds on heating and subsequent cooling.

n	Phase transition temperatures/°C
1	Cr 126.3 I 112.8 Ch 78.7 Recr
4	Cr 105.4 SmA 112.0 Ch 119.4 I 117.3 Ch 109.8 SmA 29.7[a]
6	Cr 100.3 SmA 148.3 I 146.5 SmA 45.4 SmC* − 39.2[a]
8	Cr 125.3 SmA 175.0 I 171.6 SmA 83.4 SmC* − 34.1[a]

[a] Crystallizations were not observed above these temperatures.

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*Author for correspondence.

Journal of Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 1999 Taylor & Francis Ltd
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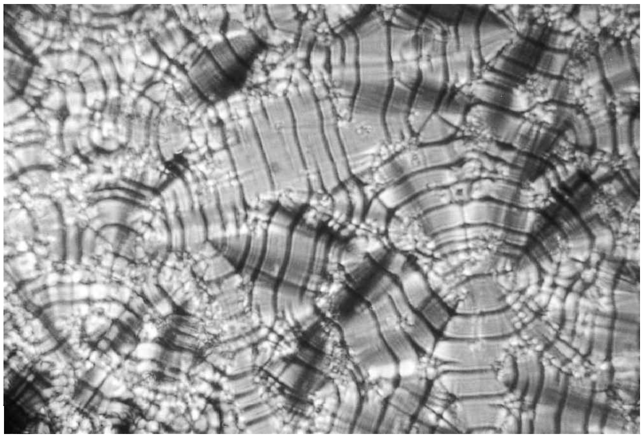

Figure. Photomicrograph of the texture of a CPC compound ($n = 8$) in the SmC* phase, at 25.0°C (×40).

Through studying the mesomorphic properties of CPC compounds, some interesting results have been obtained. The sample with $n = 1$ shows a monotropic cholesteric phase; the sample with $n = 4$ exhibits enantiotropic SmA and Ch phases. For $n = 6$ and 8, no cholesteric phase but smectic A and monotropic smectic C* phases are observed, and the samples do not crystallize even when cooled to − 40°C. So we can conclude that this kind of liquid crystal displays cholesteric phases as the perfluoroalkyl chain is shortened, and SmA and SmC* phases as the chain is lengthened.

This outcome is certainly appropriate to the properties of perfluoroalkyl chains, which are known to be more rigid than the corresponding alkyl chains. In addition, strong electrostatic interactions, such as fluorophilic interactions around the perfluoroalkyl groups, are expected to facilitate the layer arrangement of molecules. When the chain is short ($n = 1$), the molecules can easily form a cholesteric phase because the effect of lateral forces among molecules is weaker than that of terminal forces. When the perfluoroalkyl chain becomes longer ($n = 4, 6, 8$), the molecules tend to form a layer arrangement owing to the increase of lateral forces. As a result, the SmA phases form and the Ch phases disappear. As the temperature decreases further, the molecular arrangement tends to be more orderly because of reduced thermal motion, so the SmC* phases appear.

This work was supported by National Natural Science Foundation of China. The authors also thank Daikin Co. for the support of our research by gifts of 1-perfluoroalkyl iodides.

Appendix

The following are results of identification analyses on CPC compounds.

$n = 1$. ^{1}H NMR ($CDCl_3$/TMS): 0.61–0.78 (s, 6H), 0.80–2.15 (m, 35H), 2.40–2.55 (m, 2H), 4.51–4.55 (m, 1H), 5.40–5.50 (m, 1H). 7.20–7.70 (AA′BB′, 4H, $J_1 = 100$ Hz). ^{19}F NMR ($CDCl_3$/TFA): 14.70 (s, 3F); IR (KBr) ν (cm^{-1}): 2920, 1765, 1320, 1220, 1160, 1130, 1060. Elemental analysis for $C_{35}H_{49}F_3O_3$: found H 8.68, C 72.86, F 9.76 (calc. H 8.59, C 73.14, F 9.92%).

$n = 4$. ^{1}H NMR ($CDCl_3$/TMS): 0.65–0.80 (s, 6H), 0.82–2.10 (m, 35H), 2.42–2.60 (m, 2H), 4.50–4.55 (m, 1H), 5.40–5.50 (m, 1H). 7.30–7.70 (AA′BB′, 4H, $J_1 = 9$ Hz, $J_2 = 89$ Hz). ^{19}F NMR ($CDCl_3$/TFA): 4.03 (m, 2F), 45.58 (m, 2F), 48.55 (m, 2F). IR (KBr) ν (cm^{-1}): 2920, 1760, 1220, 1130, 1095. Elemental analysis for $C_{38}H_{49}F_9O_3$: found H 6.76, C 62.84, F 23.27 (calc. H 6.81, C 62.91, F 23.59%).

$n = 6$. ^{1}H NMR ($CDCl_3$/TMS): 0.65–0.75 (s, 6H), 0.85–2.08 (m, 35H), 2.45–2.55 (m, 1H), 4.55–4.65 (m, 1H), 5.40–5.45 (m, 1H). 7.35–7.65 (AA′BB′, 4H, $J_1 = 9$ Hz, $J_2 = 90$ Hz). ^{19}F NMR ($CDCl_3$/TFA): 3.78 (t, 3F, $J = 9.32$ Hz), 33.26 (m, 2F), 44.39–44.70 (m, 4F), 45.73 (m, 2F), 49.04 (m, 2F). IR (KBr) ν (cm^{-1}): 2920, 1760, 1220, 1140. Elemental analysis for $C_{40}H_{49}F_{13}O_3$: found H 5.92, C 58.04, F 29.84 (calc. H 5.99, C 58.25, F 29.94%).

$n = 8$. ^{1}H NMR ($CDCl_3$/TMS): 0.60–0.70 (s, 6H), 0.85–2.10 (m, 35H), 2.40–2.50 (m, 2H), 4.55–4.65 (m, 1H), 5.40–5.45 (m, 1H). 7.32–7.60 (AA′BB′, 4H, $J_1 = 9$ Hz, $J_2 = 89$ Hz). ^{19}F NMR ($CDCl_3$/TFA): 3.75–3.82 (t, 3F, $J = 9.84$ Hz), 33.22–33.33 (t, 3F, $J = 14.35$ Hz), 44.18–45.64 (m, 10F), 49.04 (m, 2F). IR (KBr) ν (cm^{-1}): 2920, 1760, 1220, 1150. Elemental analysis for $C_{42}H_{49}F_{17}O_3$: found H 5.32, C 54.54, F 34.97 (calc. H 5.34, C 54.55, F 34.92%).

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