Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Synthesis and Phase-transition of 4-alkoxycarbonylphenyl 4′-n-alkoxy-2,3,5,6-tetrafluorobiphenyl-4-carboxylates

J. Wen [a], M. Tian [a], Z. Guo [a] & Q. Chen [a]
[a] Shanghai Institute of Organic Chemistry, Academia Sinica, 354 Fenglin Lu, Shanghai, 200032, China
Version of record first published: 24 Sep 2006.

To cite this article: J. Wen , M. Tian , Z. Guo & Q. Chen (1996): Synthesis and Phase-transition of 4-alkoxycarbonylphenyl 4′-n-alkoxy-2,3,5, 6-tetrafluorobiphenyl-4-carboxylates, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 275:1, 27-36

To link to this article: http://dx.doi.org/10.1080/10587259608034059

*Mol. Cryst. Liq. Cryst.*, 1996, Vol. 275, pp. 27–36
Reprints available directly from the publisher
Photocopying permitted by license only





# Synthesis and Phase-transition of 4-alkoxycarbonylphenyl 4′-n-alkoxy-2, 3, 5, 6-tetrafluorobiphenyl-4-carboxylates

J. WEN, M. TIAN, Z. GUO and Q. CHEN

*Shanghai Institute of Organic Chemistry, Academia Sinica, 354 Fenglin Lu, Shanghai, 200032 (China)*

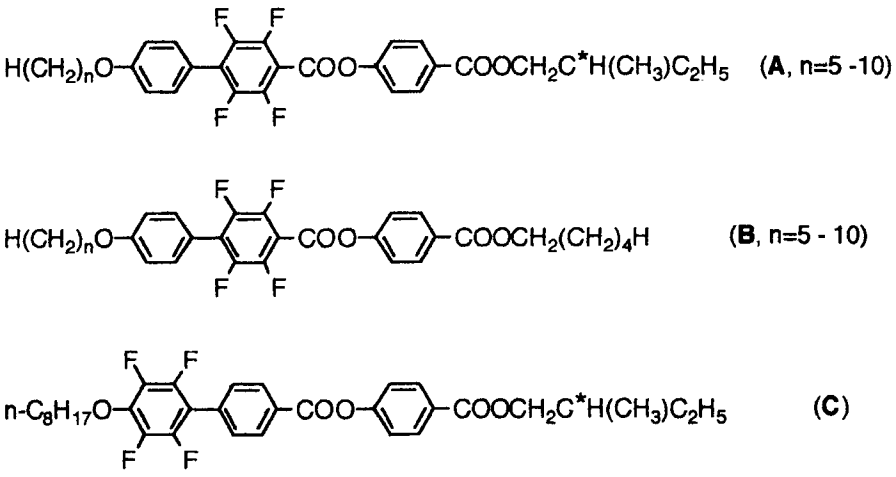
*(Received March 23, 1994; in final form March 23, 1994)*

Two new homologous series of compounds containing symmetrically tetrafluorinated phenyl units, 4-[(s)-2-methylbutoxycarbonyl]phenyl and 4-n-pentyloxyphenyl 4′-n-alkoxy-2, 3, 5, 6-tetrafluorobiphenyl-4-carboxylates ($n = 5$–10) have been synthesized from 1-pentafluorophenyl-2-trimethylsilylacetylene as a starting material, and studied by thermal polarizing microscopy. The members of the chiral series display enantiotropic cholesteric and monotropic smectic C ($S_C^*$) phases for $n = 5$–9, and the homolog of $n = 10$ shows enantiotropic smectic C ($S_C^*$), smectic A and cholesteric phases. However, the homologs of the achiral series exhibit enantiotropic nematic and smectic A phases for $n = 5, 7, 8$ and 9, and the member of $n = 6$ displays only a nematic phase, whereas the homolog of $n = 10$ shows enantiotropic smectic A and monotropic smectic C phases. 4-[(s)-2-methylbutoxycarbonyl]phenyl 4′-n-octyloxy-2′, 3′, 5′, 6′-tetrafluorobiphenyl-4-carboxylate has also been prepared and found not to be thermotropic mesogen. It is showed by comparison that the symmetrical tetrafluorination of biphenyl has a destabilizing effect on the mesophase, and the effect differs at the different substituted positions.

*Keywords: Tetrafluorobiphenyl, chiral smeetic phase, thermal polarizing microscopy, fluorinated liquid crystals*

## 1. INTRODUCTION

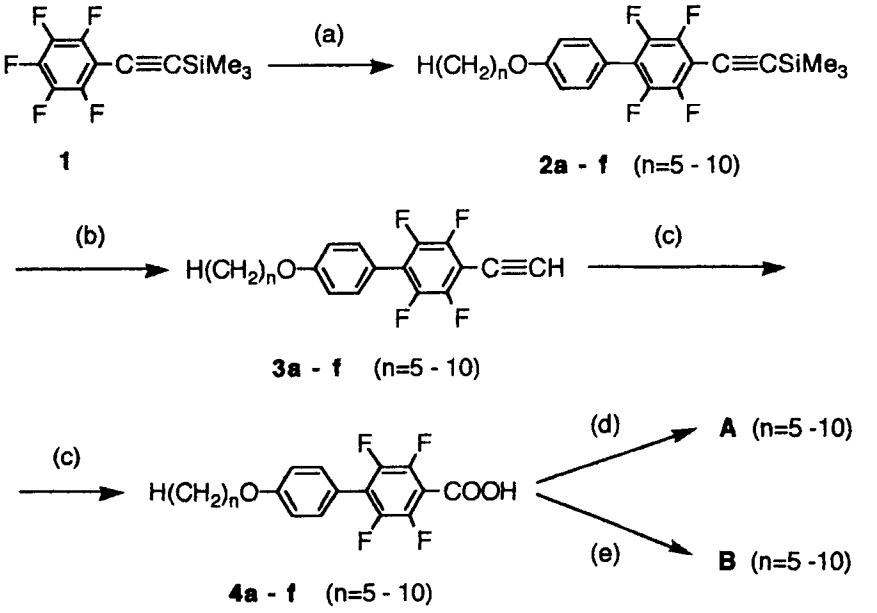
Since the survey and synthesis of new liquid crystal compounds can bring about further development in the scientific understanding of liquid crystals and their device application, more ad more research attention has occurred on fluorinated liquid crystals,[1–9] which are of tremendous interest due to the tendency of the fluorine substituent(s) to transform smectic A ($S_A$) into smectic C ($S_C$) mesophases[1–2], to suppress and eliminate more ordered smectic mesophases[1–3] and to influence the dielectric anisotropy,[1–3] viscosity, birefringence and the melting point. Up to now, hundreds of liquid crystalline molecules with monofluoro or difluoro substituted phenyls have been prepared.[1–9] Nevertheless, only a limited number of liquid crystalline molecules with symmetrically tetrafluorinated phenyl units have been reported.[10–22] In our previous studies, we have reported several types of new liquid crystals with 1, 4-tetraflurophenylene moiety.[23,24] In this paper, we wish to report the synthesis and mesomorphic behaviour of some new symmetrically tetrafluorinated 4′-alkoxybiphenyl-4-carboxylate (compounds **A**, **B** and **C**).




## 2. SYNTHESIS

The target compounds were prepared according to scheme 1 and 2.

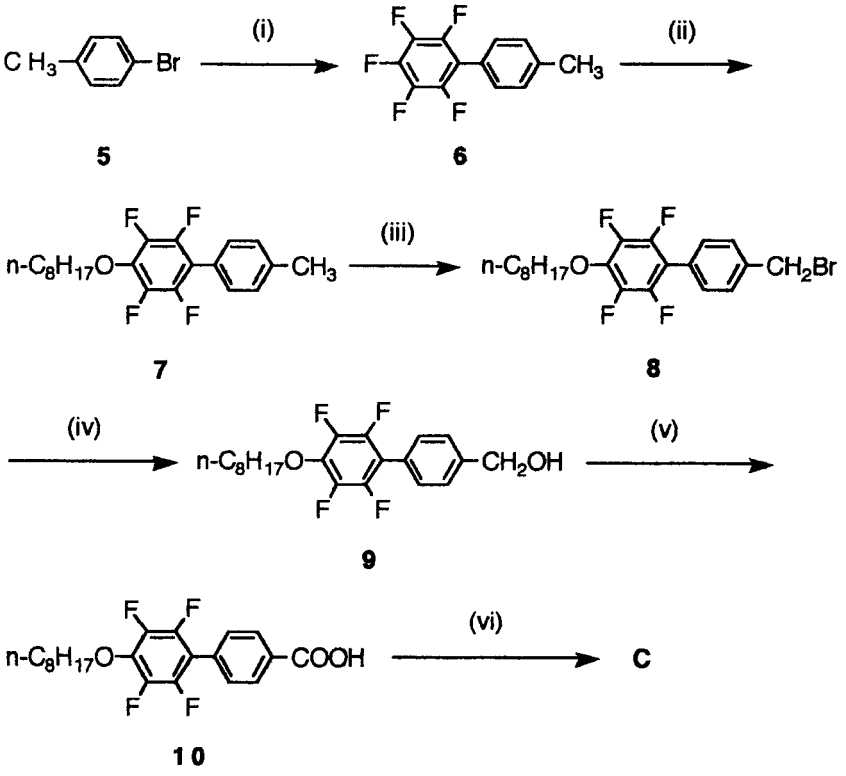
In our previous studies, we have reported the synthesis and mesomorphic properties of 4′-n-alkoxy-2, 3, 5, 6-tetrafluorobiphenyl-4-carboxylic acids[24] (see Scheme 1). The




SCHEME 1 (a) p-H(CH$_2$)$_n$O—C$_6$H$_4$—MgBr, THF, reflux; (b) CH$_3$OH/CH$_3$COCH$_3$, NaOH/H$_2$O, R.T.; (c) KMnoO$_4$/NaOH, 1,4-dioxane/H$_2$O, reflux; (d) 4-HO-C$_6$H$_4$-COOCH$_2$C*H(CH$_3$)C$_2$H$_5$, DCC. PPY, Et$_2$O, R.T.; (e) 4-HO—C$_6$H$_4$—COO(CH$_2$)$_5$H, DCC, PPY, Et$_2$O, R.T..

starting material (compound **1**) was prepared by the method[25] reported previously. The nucleophilic substitution of parasubstituted phenyl magnesium bromide on compound **1** in dry THF gave compound **2a–f**,[26] from which polyfluoro substituted biphenylacetylenes (compounds **3a–f**) were obtained after the removal of trimethylsilyl group under the action of methanol and aqueous NaOH in acetone. The oxidation of compounds **3a–f** by potassium permanganate in alkaline 1,4-dioxane/water solution afforded the polyfluoro substituted aromatic carboxylic acids (compounds **4a–f**). Then the mild one pot esterification[27] between compounds **4a–f** and (s)-2-methylbutyl 4-hydroxybenzoate, and n-pentyl 4-hydroxybenzoate in the presence of both dicyclohexylcarbodiimide (**DCC**) and 4-pyrrolidinopyridine (**PPY**) catalyst in dry ether gave the desired compounds **A** and **B**.

The desired compound **C** was synthesized by the route described in scheme 2. In the first step, p-tolyl lithium which was prepared from 4-bromotoluene reacted with hexafluorobenzene[28] to yield 4-pentafluorophenyltoluene (compound **6**). The nucleophilic substitution reaction between compound **6** and 1-octanol in THF with NaOH as base gave compound **7**, which was brominated using NBS and AIBN in anhydrous




SCHEME 2 (i) 1, Li/$Et_2O$; 2, $C_6H_6/Et_2O$; (ii) $n$-$C_8H_{17}OH$/THF, NaOH, 35–40°C, 17 hr; (iii) NBS/AIBN, $CCl_4$, reflux; (iv) NaOH/$H_2O$, THF; (v) $KMnO_4$/NaOH, 1,4-dioxane/$H_2O$, reflux; (vi) 4-HO—$C_6H_4$—$COOCH_2C^*H(CH_3)C_2H_5$, DCC, PPY, $Et_2O$, R.T..

carbontetrachloride to produce compound **8**. Subsequently, 4-n-octyloxy-2,3,5,6-tetrafluorobiphenyl-4'-methanol (**9**) was prepared through the hydrolysis of compound **8**. The oxidation of compound **9** using potassium permanganate gave the required compound **10**. Finally, the desired compound **C** was obtained from the esterification reaction between compound **10** and (s)-2-methylbutyl 4-hydroxybenzoate.[27]

All of the final compounds were purified by chromatography on silica gel with petroleum ether (bp 60–90°C)/ethyl acetate (30:1) as eluent and were recrystallized from acetone-methanol. Their structures were characterized by elemental analyses, $^1H$ and $^{19}F$ NMR, IR and MS spectral methods. Phase transitions were studied using a Mettler FP52 hot stage and control unit in conjunction with an Olympus BH2 polarizing microscope, while phase identification was made by comparing the observed textures with those in the literature.[29,30]

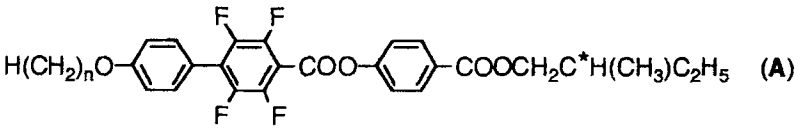
## 3. RESULTS AND DISCUSSION

The transition temperatures of these new fluorinated materials are listed in Tables **1**, **2** and **3**.

As for the chiral series, most of the new compounds exhibit enantiotropic cholesteric and monotropic chiral smectic C ($S_C^*$) phases. However, the compound for $n = 10$ (**A-10**) display enantiotropic Ch, $S_A$ and $S_C^*$ phases. As far as the influence of the end chain is concerned, the melting points of compounds **A** increase first as the number of carbon atoms in the normal alkoxy chain increases from 5 to 7, and then decrease as the chain length is further increased. So does the general alteration of the temperature window of the cholesteric phase, and the tendency for the smectic phase formation increases as the alkoxy chain is lengthened. Moreover, the cholesteric-isotropic transition temperatues of compounds A increase from 5 to 7, and then decrease from

TABLE 1

Phase transition temperatures (°C) of compounds **A**



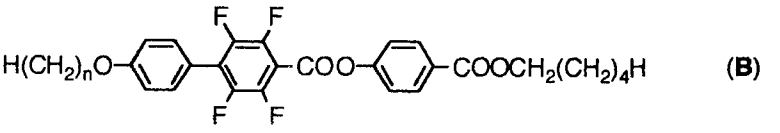

**(A)**

| $n$ | C-Ch | $S_C^*$-Ch | $S_A$-Ch | Ch-I | recryst. |
|---|---|---|---|---|---|
| 5 | 90.0 | (90.0) | / | 99.6 | 72.3 |
| 6 | 95.1 | (89.2) | / | 109.9 | 79.0 |
| 7 | 105.5 | (101.2) | / | 112.8 | 93.3 |
| 8 | 101.6 | (100.4) | / | 112.0 | 81.9 |
| 9 | 89.2 | (80.9) | / | 94.9 | 70.8 |
| 10 | 90.0[a] | 96.1[b] | 98.7 | 103.9 | 70.6 |

[a] The phase-transition at the temperature is C-Sc*.
[b] The phase-transition at the temperature is $S_C^*$-$S_A$.

TABLE 2

Phase transition temperatures (°C) of compounds **B**



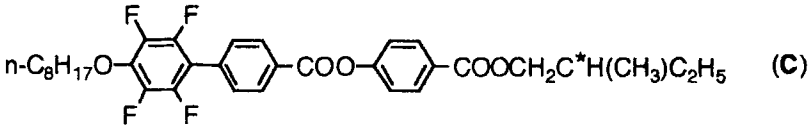

**(B)**

| $n$ | C-$S_A$ | $S_C$-$S_A$ | $S_A$-N | N-I | recryst. |
|---|---|---|---|---|---|
| 5 | 97.8 | / | 101.0 | 121.0 | 67.5 |
| 6 | 82.4[a] | / | / | 102.8 | 75.7 |
| 7 | 98.4 | / | 108.7 | 119.0 | 90.0 |
| 8 | 100.4 | / | 116.0 | 121.8 | 88.0 |
| 9 | 93.2 | / | 113.9 | 117.5 | 84.0 |
| 10 | 87.0 | (86.8) | / | 113.3[b] | 81.7 |

[a] The phase-transition at the temperature is C-N.
[b] The phase-transition at the temperature is $S_A$-I

TABLE 3

Phase transition temperatures (°C) of compound **C**




**(C)**

| C-I | I-C |
|---|---|
| 85.1 | 84.0 |

7 to 9, but increase again from 9 to 10, indicating that the normal odd-even effect is not observed.

As with the achiral series, the phase-transition behaviour with the lengthening of the alkoxy chain is more complicated. The compounds for $n = 5, 7, 8$ and 9 exhibit enantiotropic nematic and smectic A phases, and the member of $n = 6$ display only a nematic phase, whereas the homolog of $n = 10$ shows enantiotropic smectic A and monotropic smectic C phases, but no nematic phase. We believe that the symmetrical tetrafluorinated biphenyl group possesses a non-planar conformation,[12,31] and the interplanar angles may differ from one to another due to the different effect of the normal alkoxy chain. This effect results in the irregular phase-transition behaviour of the two above-described series of fluorinated compounds. It is also clear that a branched terminal alkoxy chain decreases the temperature window of smectic A phase, but conduces to the smectic C phase formation.

For compound **C**, no mesophase exists in the process of heating and cooling. The comparison of the transition temperatures between compounds **A-8**, **C** and the unfluorinated homolog, 4-(2-methylbutoxycarbonyl)phenyl 4′-n-octyloxybiphenyl-4-carboxylate (compound **D**),[32] is shown in Table 4.

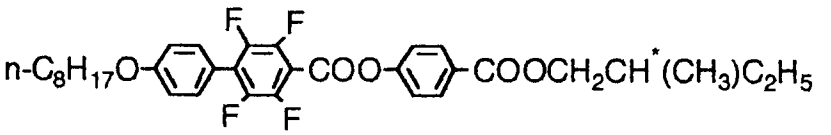
From Table 4, we can see that the symmetrical tetrafluorination of the biphenyl group has a destabilizing effect on the mesophase, especially on smectic phases, and the effect differs at the different substituted positions. It is remarkable that the symmetrical tetrafluorination of the phenyl which is far from the center of the molecule more greatly destroys the mesophase thermal stability. In our opinion, the breadth-increasing effect of fluorine substituents may account for the fact that the mesophase is destabilized. Besides, the symmetrical tetrafluorination of the biphenyl group does destroy the coplanarity of the two phenyl rings,[12,31] and the non-coplanar conformation of the substituted biphenyl plays a more important role in the mesophase formation, thus the symmetrical tetrafluorination of the phenyl ring that is far from the center more greatly destroys the coplanarity of the molecule, and results in the worse thermal stability of mesophase. The more appropriate reasons for these facts are being studied by the theoretical calculation of quantum chemistry.

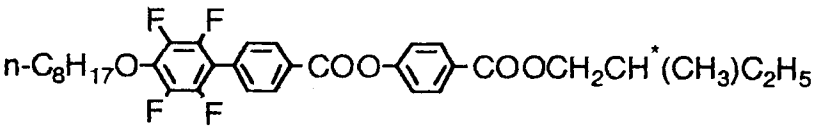
## 4. EXPERIMENTAL

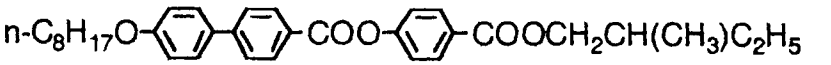
IR spectra were recorded on a Shimadzu IR-440 spectrophotometer, using KBr pellets of solids or films of liquids. $^1$H NMR spectra with TMS as internal standard and

TABLE 4

The effect of lateral polyfluoro-substitution of 4′-alkoxybiphenyl-4-carboxylate (Transition temperatures:°C)

**A-8** 

**C** 

**D** 

| Compound | m.p. | c.p. | Ch[a] | $S_A$ | $S_C/S_C^*$ |
|---|---|---|---|---|---|
| A-8 | 101.6 | 112.0 | 10.4 | / | (18.5)[b] |
| C | 85.1 | 85.1 | / | / | / |
| D | 67.0 | 187.0 | / | 48.0 | 72.0 |

[a] The temperature window of mesophase.
[b] The mesophase or phase transition is monotropic.

$^{19}F$ NMR spectra with trifluoroacetic acid (TFA) as external standard were recorded on a Varian EM-360L spectrometer (60 MHz) or a FX-90 spectrometer (90 MHz). For $^{19}F$ NMR spectra, high field is positive. Mass spectra were recoded on a Finnigan-4021 spectrometer.

Compounds 4a–f were prepared as described in a previous publication.[24]

*1. 4-[(s)-2-Methylbutoxycarbonyl]phenyl 4'-n-heptyloxy-2,3,5,6-tetrafluorobiphenyl-4-carboxylate* (**A-7**)

Quantities: compound 4c (250 mg, 0.65 mmol), (s)-2-methylbutyl 4-hydroxybenzoate (190 mg, 0.91 mmol), N, N-dicyclohexylcarbodiimide (202 mg, 0.98 mmol), 4-pyrrolidinopyridine (10 mg, 0.068 mmol) and anhydrous diethyl ether (15 mL); reaction time: 96 h. The experimental procedure was as described in reference 27. Analysis by TLC revealed the completion of the reaction. The crude product was purified by column chromatography on silica gel using petroleum ether (bp 60–90°C)/ethyl acetate (30:1 v:v) to yield a pale yellow solid which was recrystallized from acetone-methanol to give white flaky crystals of (**A-7**).

Yield 309 mg (82.7%); m.p. 105.5°C, $^1H$ NMR($CDCl_3$/TMS): $\delta$ 0.75–1.20 (m, 9H, 3 × $CH_3$), 1.20–2.20 (m, 13H), 4.08 (t, 2H, J = 6.0 Hz, $OCH_2$), 4.23 (d, 2H, J = 6.0 Hz, $COOCH_2$), 7.05 (d, 2H)/7.51 (d, 2H) (AA'BB', J = 8.0 Hz, O—$C_6H_4$—$C_6F_4$—), 7.38 (d, 2H)/8.20 (d, 2H) (AA'BB', J = 8.0 Hz, COO—$C_6H_4$—COO); $^{19}F$ NMR ($CDCl_3$/TFA): $\delta$ 61.13 (m, 2F, $F_{arom}$). 65.00 (m, 2F, $F_{arom}$); IR(KBr): 2950, 2890, 2820, 1740, 1715, 1605, 1520, 1497, 1462, 1410, 1390, 1320, 1268, 1222, 1194, 1160, 1105, 1010, 980, 838, 798, 745, 680, 620 $cm^{-1}$; MS m/z (rel int): 574 ($M^+$, 5.93), 367 (100.00), 269 (33.33); Elem. anal., Found: C 66.32%, H 5.79%, F 13.29%; Calcd. for $C_{32}H_{34}F_4O_5$: C 66.18%, H 6.09%, F 13.51%.

The other new fluorinated compounds of series **A** and series **B** were prepared by a similar procedure. All of them had satisfactory elemental analyses and appropriate $^1H$ and $^{19}F$ NMR, IR and MS spectral data.

Compound **6** was prepared by the method described in the literature.[28] Its NMR data were shown as follows: $^1H$ NMR ($CCl_4$/TMS): $\delta$ 2.48 (s, 3H, $CH_3$), 7.40 (s, 4H, $H_{arom}$); 19F NMR ($CCl_4$/TMS): $\delta$ 66.30 (d, 2F, J = 18.8 Hz, $F_{arom}$), 79.30 (t, 1F, J = 18.8 Hz, $F_{arom}$), 85.30 (d, 2F, J = 18.8 Hz, $F_{arom}$).

*2. 4'-Methyl-4-n-octyloxy-2, 3, 5, 6-tetrafluorobiphenyl* (**7**)

A mixture of compound **6** (400 mg, 1.55 mmol), 1-octanol (1.30 ml, 1.08 g, 8.33 mmol), sodium hydroxide (200 mg, 5.0 mmol) and THF (3 ml) was stirred at 35–40°C for 17 h. Analysis by $^{19}F$ NMR revealed a complete reaction. Then 20 ml of water was added to the resulting mixture and the product was extracted with ether (3 × 20 ml). The combined ethereal extracts were washed with water and dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel using petroleum ether (bp 60–90°C) as eluent to give a white flaky crystal of (**7**).

Yield 507 mg (88.9%); $^1H$ NMR ($CCl_4$/TMS): $\delta$ 0.95 (t, 3H, J = 5.0 Hz, $CH_3$), 1.15–2.15 (m, 12H), 2.47 (s, 3H, —$C_6H_4$—$CH_3$), 4.25 (t, 2H, J = 6.0 Hz, $OCH_2$), 7.35 (s, 4H, $H_{arom}$); $^{19}F$ NMR ($CCl_4$/TFA): 69.90 (m, 2F, $F_{arom}$), 82.31 (m, 2F, $F_{arom}$).

*3. 4'-Bromomethyl-4-n-octyloxy-2,3,5,6-tetrafluorobiphenyl* (**8**)

A mixture of compound **7** (507 mg, 1.38 mmol), N-bromosuccinimide (NBS) (250 mg, 1.39 mmol), α,α'-azobis(isobutyronitrile) (AIBN) (30 mg, 0.18 mmol) and anhydrous carbontetrachloride (5 ml, dried over phosphorus pentaoxide) was stirred and refluxed for 13 h while isolated from air, and then cooled down to room temperature. TLC analysis revealed a completion of the reaction. The resulting white suspended solid was filtered off and washed with carbontetrachloride. The filtrate was condensed and the residue was purified by column chromatography on silica gel with petroleum ether (bp 60–90°C) as eluent to give a white flaky crystal of (**8**) with 79 mg of compoung **7** recovered.

Yield 453 mg (87.1%); $^1$H NMR ($CCl_4$/TMS): δ 0.81 (t, 3H, J = 5.0 Hz, $CH_3$), 1.00–2.00 (m, 12H), 4.17 (t, 2H, J = 6.0 Hz, $OCH_2$), 4.37 (s, 2H, $CH_2Br$), 7.33 (s, 4H, $H_{arom}$); $^{19}$F NMR ($CCl_4$/TFA): 67.85 (m, 2F, $F_{arom}$), 80.01 (m, 2F, $F_{arom}$).

*4. 4-n-Octyloxy-2,3,5,6-tetrafluorobiphenyl-4'-methanol* (**9**)

A mixture of compound **8** (453 mg, 1.01 mmol), sodium hydroxide (200 mg, 5.0 mmol), water (3 ml) and THF (5 ml) was stirred and refluxed for 10 h (TLC analysis revealed the saturation of the reaction) and then cooled to room temperature. The product was extracted with ether (3 × 20 ml), and the combined ethereal extracts were washed with water and dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel using petroleum ether (bp 60–90°C)/ethyl acetate (3:1 v:v) as eluent to give a white solid of (**9**) with 290 mg of compoung **8** recovered.

Yield 105 mg (75.0%); $^1$H NMR ($CCl_4$/TMS): δ 0.77 (t, 3H, J = 5.0 Hz, $CH_3$), 0.93–2.00 (m, 12H), 2.72 (s, 1H, OH), 4.10 (t, 2H, J = 6.0 Hz, $OCH_2$), 4.60 (s, 2H, $CH_2OH$), 7.20 (s, 4H, $H_{arom}$); $^{19}$F NMR ($CCl_4$/TFA): 67.80 (m, 2F, $F_{arom}$), 80.02 (m, 2F, $F_{arom}$).

*5. 4-n-Octyloxy-2,3,5,6-tetrafluorobiphenyl-4'-carboxylic acid* (**10**)

A mixture of compound **9** (100 mg, 0.26 mmol), potassium permanganate (400 mg, 2.53 mmol), sodium carbonate (200 mg, 1.89 mmol). water (5 ml) and 1,4-dioxane (10 ml) was stirred and refluxed for 12 h (TLC analysis revealed the completion of the reaction) and then cooled to room temperature. The resulting brown precipitate was dissolved by the dropwise addition of saturated aqueous $Na_2SO_3$ and concentrated hydrochloric acid while stirring. The product was extracted with ether (3 × 20 ml), and the combined ethereal extracts were washed with water and dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue was purified by recrystallization from ether–petroleum ether (bp 60–90°C) to give a white solid of (**10**).

Yield 99 mg (90.8%); m.p. 174.0°C; $^1$H NMR ($CD_3COCD_3$/TMS): δ 0.52 (t, 3H, J = 5.0 Hz, $CH_3$), 0.68–1.87 (m, 12H), 3.00 (s, 1H, COOH), 3.92 (t, 2H, J = 6.0 Hz, $OCH_2$), 7.22 (d, 2H)/7.78 (d, 2H) (AA'BB', J = 80 Hz, $H_{arom}$); $^{19}$F NMR ($CD_3COCD_3$/TFA): 69.15 (m, 2F, $F_{arom}$), 81.33 (m, 2F, $F_{arom}$); IR (KBr): 2940, 2850, 1700, 1615, 1500, 1482, 1425, 1404, 1390, 1321, 1300, 1284, 1260, 1195, 1090, 990, 862, 805, 760 $cm^{-1}$; MS m/s (rel int): 398 ($M^+$, 6.54), 286 (100.00), 269 (10.50).

*6. 4-[(s)-2-Methylbutoxycarbonyl]phenyl 4'-n-octyloxy-2',3',5',6'-tetrafluorobiphenyl-4-carboxylate* (**C**)

Compound **C** was prepared by a similar procedure described for compound **A-7**, and had satisfactory elemental analyses.

Yield 74.5%; m.p. 84.1°C; $^1$H NMR ($CCl_4$/TMS): $\delta$ 0.75–1.95 (m, 24H), 4.10 (m, 4H, 2 × $OCH_2$), 7,13 (d, 2H)/7.98 (d, 2H) (AA'BB', J = 8.0 Hz, $C_6F_4$—$C_6H_4$—COO), 7.47 (d, 2H)/8.17 (d, 2H) (AA'BB', J = 8.0 Hz, COO—$C_6H_4$—COO); $^{19}$F NMR ($CCl_4$/TFA): $\delta$ 69.45 (m, 2F, $F_{arom}$), 81.63 (m, 2F, $F_{arom}$); IR (KBr): 2950, 2910, 2850, 1740, 1712, 1602, 1500, 1480, 1405, 1390, 1270, 1208, 1164, 1092, 1020, 980, 890, 855, 762, 725, 702 $cm^{-1}$; MS m/s (rel int): 588 ($M^+$, 1.26), 381 (100.00), 269 (26.13).

## Acknowledgements

Financial support from the 863 R&D Program of China is gratefully acknowledged.

## References

1. V. Reiffenrath, J. Krause, H. F. Plach and G. Weber, *Liq. Cryst.*, **5**, 159 (1989).
2. G. W. Gray, M. Hird, D. Lacey and K. J. Toyne, *J. Chem. Soc. Perkin Trans.* **II**, 2041 (1989).
3. M. Chambers, R. Clemitson, D. Coates, S. Greenfield, J. A. Jenner and I. C. Sage, *Liq. Cryst.*, **5**, 153 (1989).
4. S. Sugawara, Jpn. Kokai Tokkyo Koho, JP 01, 294, 653 [89, 294, 653].
5. S. Saito, H. Inoue, K. Terashima, T. Inukai and K. Furukawa, *U.S. Patent*, US 4, 737 313.
6. Y. Goto and K. Kitano, *Eur. Pat. Appl.*, EP (1991) 387, 032.
7. M. F. Nabor, H. T. Nguyen, C. Destrade and J. P. Marcerou, *Liq. Cryst.*, **10**, 785 (1991).
8. C. Pugh, S. K. Andersson and V. Percec, *Liq. Cryst.*, **10**, 229 (1991).
9. M. Hird, G. W. Gray and K. J. Toyne, *Liq. Cryst.*, **4**, 531 (1992).
10. J. Goldmacher and L. A. Barton, *J. Org. Chem.*, **32**, 476 (1967).
11. M. M. Murza, G. P. Tataurov, L. I. Popov and V. Svetkin Yu, *Z. Org. Khim.*, **13**, 1046 (1977).
12. G. W. Gray, *Mol. Cryst. Liq. Cryst.*, **7**, 127 (1969).
13. A. Beguin and J. C. Dubois, *J. Phys. (Paris)*, **40**, 9 (1979).
14. R. Sirutkaitis and P. Adomenas, *Advances in Liquid Crystals Research and Applications*, edited by Lajos Bata (Pergamon Press, Oxford, 1980), p. 1023.
15. P. Le Barny, G. Ravaux and J. C. Dubois, *Mol. Cryst. Liq. Cryst.*, **127**, 413 (1985).
16. C. Baillon-Moussel, D. Broussoux, J. C. Dubois and P. Le Barny, *Eur. Pat. Appl.*, EP 360, 683.
17. H. Takeshita and A. Mori, *Jpn. Kokai Tokyo Koho*, JP 02, 237, 962 (90, 237, 962).
18. C. Baillon-Moussel, D. Broussoux, P. Le Barny and F. Soyer, *Eur. Pat. Appl.*, EP 418, 140.
19. S. Sugawara, *Jpn. Kokai Tokkyo Koho*, JP 101, 09, 959, [89, 09, 959].
20. S. Sugawara, *Jpn. Kokai Tokkyo Koho*, JP 01, 272, 552 [89, 272, 552].
21. S. Sugawara, *Jpn. Kokai Tokkyo Koho*, JP 01, 283, 258 [89, 283, 258].
22. S. Sugawara, *Jpn. Kokai Tokkyo Koho*, JP 02, 32, 057 [90, 32, 057].
23. Novel Fluorinated Liquid Crystals. J. X. Wen, Y. L. Xu and Q. Chen, *J. Fluorine Chem.*, in press (1994); J. X. Wen, M. Q. Tian and Q. Chen, *Liq. Cryst.*, in press (1994); J. X. Wen, M. Q. Tian, H. B. Yu, Z. H. Guo and Q. Chen, *J. Mater. Chem.*, in press (1994); Y. L. Xu, Q. Chen and J. X. Wen, *Mol. Cryst. Liq. Cryst.*, in press (1994); Y. L. Xu, Q. Chen and J. X. Wen, *Chinese J. Chem.*, in press (1994); Y. L. Xu, Q. Chen and J. X. Wen, *Liq. Cryst.*, in press (1994); J. X. Wen, M. Q. Tian and Q. Chen, *J. Fluorine Chem.*, in press (1994).
24. J. X. Wen, M. Q. Tian and Q. Chen, *J. Fluorine Chem.*, in press (1994).
25. J. D. Zhang and J. X. Wen, *J. Fluorine Chem.*, **47**, 533 (1990).
26. Y. D. Zhang and J. X. Wen, *J. Fluorine Chem.*, **49**, 293 (1990).
27. A. Hassner and V. Alexanian, *Tetrahedron Lett.*, **46**, 4475 (1978).

28. L. A. Wall, W. J. Pummer, J. E. Fearn and J. M. Antonucci, *J. Res. Natl. Bur. Std.*, **67A**(5), 481 (1963).
29. D. Demus and L. Richter, *Textures of Liquid Crystals*, Verlag Chemie, Weinheim, 1978.
30. G. W. Gray and J. W. Goodby, *Smectic Liquid Crystals–Textures and Structures*, Leonard Hill, 1984.
31. G. W. Gray, *Molecular Structure and the Properties of Liquid Crystals*, Academic Press, London and New York, 1962, p. 154.
32. D. Coates, *Liq. Cryst.*, **2**, 63 (1987).