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# Liquid Crystals

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# Synthesis and mesomorphic properties of semi-perfluorinated chain liquid crystals

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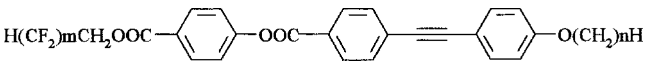
Three homologous series of 4-(*n*-polyfluoroalkoxycarbonyl)phenyl 4-[(4-*n*-alkoxyphenyl)-ethynyl] benzoates have been synthesized from 1,1,3-trihydroperfluoropropanol, 1,1,5-trihydroperfluoropentanol and 1,1,7-trihydroperfluoroheptanol. Polarizing microscopic textural observations and DSC measurements of the phase transitions of these compounds show that most of them are thermotropic liquid crystals with smectic A and very broad smectic C phases; furthermore, several show very narrow monotropic SmB phases. The effect of the terminal polyfluoroalkoxy and alkoxy groups on the mesomorphic behaviour is also discussed.

## 1. Introduction

Self assembly is one of the possible ways to generate novel supermolecular structures. In this way, the amphiphilic character of molecules is one of the parameters permitting us to predict the type of organization for both thermotropic and lyotropic mesogens. Amphiphilic molecules consist of two fragments differing in their chemical nature; for example, hydrophilic/hydrophobic, stiff/flexible, aliphatic/aromatic, polar or polarizable/non-polar or non-polarizable. The liquid crystal molecule with a fluorocarbon tail can also be divided into two parts—fluorophilic/fluorophobic—because the fluoroalkyl chain which has a fluorophilic nature is more rigid than the corresponding alkyl chain. So we can consider liquid crystals with fluorocarbon tails as a potentially novel series of self assembling supermolecules.

Earlier work [1–7] by different groups on liquid crystals with polyfluoroalkyl or polyfluoroalkoxy chains showed enhancement of the smectic mesophases and mesophase thermal stability. Especially for molecules with a biphenyl core and two semi-perfluorinated chains, tilt smectic properties are exhibited. In recent years, with the development of monophenyl liquid crystals, molecules with polyfluoroalkyl or polyfluoroalkoxy terminal chains have become an important topic in the study of liquid crystal materials [8–10]. In our own work [1] it was also found that molecules with a long fluorocarbon tail chain gave rise to a broad smectic C phase. But in that series we could rarely find a relationship between the length of polyfluorocarbon tail and the mesophase. For further study, we have synthesized three series of liquid crystals with the formula shown below.



| | |
|---|---|
| $m=2$; $n=4$–10, 12 | **F4(F4-4–F4-10, F4-12)** |
| $m=4$; $n=5$–10 | **F8(F8-5–F8-10)** |
| $m=6$; $n=6$–9 | **F12(F12-6–F12-9)** |

## 2. Experimental

### 2.1. *Synthesis route*

The synthesis of the target molecules bearing three kinds of fluorinated tail chains is outlined in the scheme.

*Reagents and conditions*: (1) a. Na, benzyl chloride, $C_2H_5OH$, r.t. to reflux; b. NaOH, $C_2H_5OH/H_2O$; (2) $HOCH_2(CF_2)_nH$, DCC/DMAP, THF, 0°C to r.t.; (3) $H_2$ Pd/C, ethyl acetate; (4) *p*-I-benzoic acid, DCC/DMAP, THF, 0°C to r.t.; (5) $Br(CH_2)_nH$, KOH, KI, $C_2H_5OH$, reflux; (6) $Pd(PPh_3)_2Cl_2$, CuI, $Et_3N$, ≡–$SiMe_3$; (7) NaOH, acetone, methanol; (8) $Pd(PPh_3)_2Cl_2$, $Et_3N$, CuI.

The hydroxyl group of methyl 4-hydroxybenzoate was protected with benzyl chloride and the methyl ester was hydrolysed to give the benzoic acid. The protected acid was then esterified with the appropriate alcohol using dicyclohexylcarbodiimide (DCC) as dehydrating agent and *N*,*N*-dimethylaminopyridine as catalyst, in dry tetrahydrofuran solution. The benzyl ether produced was then converted to the corresponding phenol ester by removal of the benzyl protecting group by hydrogenation at room temperature with $H_2$ in the presence of palladium on active carbon in ethyl acetate. Then the phenol was esterified with *p*-iodobenzoic acid using

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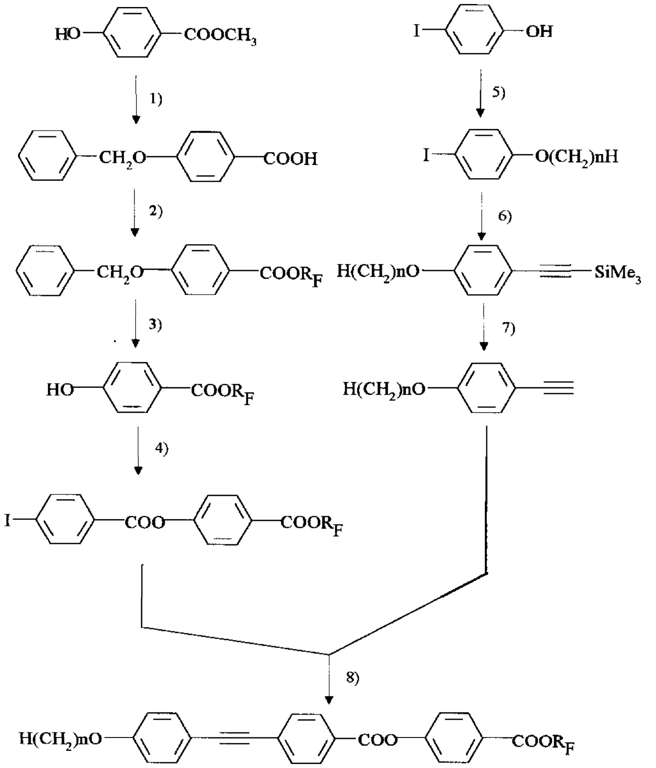

Scheme. Synthesis route.

DCC as dehydrating agent and DMAP as catalyst, in tetrahydrofuran solution. Finally the coupling reaction between the ester and 4-alkoxyphenylacetylene, under the catalysis of bis(triphenylphosphine)palladium dichloride and copper(I) iodide in dried triethylamine, gave the desired polyfluorinated substituted homologous compound.

### 2.2. *Analysis*

All of the product compounds were purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C)/ethyl acetate (20/1) as eluent and then recrystallized from petroleum ether (b.p. 60–90°C) and acetone/methanol.

The structures of the final products and intermediates were determined by a variety of spectral methods. IR spectra were recorded on a PE-983G spectrophotometer, using KBr pellets of the solids, or films of liquids. $^1$H NMR spectra, with TMS as internal NMR standard were recorded on a Varian EM 360L spectrometer (60 MHz) or a Fx-90Q (90 MHz) instrument; $^{19}$F NMR spectra, with trifluoroacetic acid (TFA) as external standard, were recorded on a Varian EM 360L spectrometer (60 MHz). For $^{19}$F NMR spectra the high field was positive. MS spectra were measured with a Finnigan-4021 spectroscope.

The phase transition temperatures of the target compounds were measured by optical microscopy using a polarizing microscope (Olympus PM-6) fitted with a heating stage (Mettler FP-80) and control unit (FP-82), and by differential scanning calorimetry (DSC, Shimadzu DSC-50 calorimeter with a data system, heating and cooling rate 5°C min$^{-1}$). The transition temperatures reported in this paper were the peak values of the transition on DSC traces. Phase identification was made by comparing the observed textures with those reported in the literature [11, 12].

### 2.3. *1-(4-Heptyloxyphenyl)-2-trimethylsilylacetylene*

In a dry 250 ml three-necked flask fitted with a magnetic stirrer, gas inlet and reflux condenser with bubbler, 5.224 g (16.4 mmol) of 4-heptyloxyiodobenzene, 160 mg (0.24 mmol) of bis(triphenylphosphine)palladium dichloride, 640 mg (3.2 mmol) of copper(I) iodide and 120 ml of anhydrous triethylamine were mixed under a slow stream of nitrogen for 5 min. Then 2.543 g (25.9 mmol) of trimethylsilylacetylene was added to the mixture under nitrogen. The reaction mixture was heated at 30–35°C for nearly 24 h, until TLC analysis indicated completion of the reaction. The resulting grey precipitate was then filtered off and washed with diethyl ether. The filtrate was washed with water, dried over anhydrous sodium sulphate, and the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel using petroleum ether as eluent to give a pale yellow liquid product. Yield: 4.561 g (95.3%). $^1$H NMR (60 MHz, $CDCl_3$/TMS) $\delta$; 0.21 (s, 9H), 0.7–2.10 (m, 13H), 3.91 (t, $J = 6$ Hz, 2H), 7.09 (dd, $J = 20$ Hz, 9 Hz, 4H (ppm. IR(KBr): $\nu$ 2929, 2857, 2156, 1567, 1504, 1466, 1251, 869, 845 cm$^{-1}$.

### 2.4. *4-Heptyloxyphenylacetylene*

In a round-bottomed flask, 4.510 g (15.63 mmol) of 1-(4-heptyloxyphenyl)-2-trimethylsilylacetylene was poured into 17.2 ml of acetone and 8.6 ml of methanol and the mixture was stirred for 2 min. Then 8.6 ml of 0.2N aqueous sodium hydroxide was added over a few minutes; the mixture was stirred for further 3 h. Analysis by TLC showed the reaction was complete, and the solvent was removed *in vacuo*. The residue was added to 160 ml of ether, washed with 5% aqueous acetic acid and saturated aqueous sodium chloride, then dried over anhydrous sodium sulphate. The solvent was removed *in vacuo* and the resulting residue purified by column chromatography on silica gel, using petroleum ether as eluent to give the product as a pale yellow liquid. Yield: 3.100 g (91.7%). $^1$H NMR (60 MHz, $CDCl_3$/TMS) $\delta$: 0.7–2.0 (m, 13H), 3.03 (s, 1H), 3.94 (t, $J = 6$ Hz, 2H), 7.11 (dd, $J = 20$ Hz, 9 Hz, 4H) ppm. IR(KBr): $\nu$ 2929, 2857, 2107, 1606, 1503, 1467, 1250, 835 cm$^{-1}$.

### 2.5. *4-(n-1,1,3-Trihydroperfluoropropyloxycarbonyl)-phenyl 4-iodobenzoate*

The experimental procedure was as described in [1]. Quantities: 4-iodobenzoic acid (1.967 g, 7.93 mmol), DCC (1.800 g, 8.72 mmol), DMAP (10 mg), THF (25 ml), 1,1,3-trihydroperfluoropropyl 4-hydroxybenzoate (2.000 g, 7.93 mmol); reaction temperature 0°C–r.t., reaction time 48 h. The crude product was recrystallized from acetone/methanol to give a white flaky crystalline product. Yield: 3.103 g (81.1%). $^1$H NMR (90 MHz, $\mathrm{CDCl_3}$/TMS) $\delta$: 4.82 (t, $J = 14.2$ Hz, 2H), 6.07 (tt, $J = 52.2$ Hz, 6 Hz, 1H), 7.73 (dd, $J = 32.1$ Hz, 9 Hz) 7.9 (s, 4H) ppm. $^{19}$F NMR (60 MHz, $\mathrm{CDCl_3}$/TFA) $\delta$: 45.7 (s, 2F) 59.5 (d, $J = 30$ Hz, 2F) ppm. IR(KBr): $\nu$ 1716, 1588, 1500, 1465, 1289, 1263, 1203, 1169, 832, 817 $\mathrm{cm^{-1}}$.

### 2.6. *4-(n-1,1,5-Trihydroperfluoropentyloxycarbonyl)-phenyl 4-[(4-n-heptyloxyphenyl)ethynyl] benzoate (**F4-7**)*

In a typical procedure, to a mixture of compound 4-heptyloxyphenylacetylene (123 mg, 0.569 mmol), 4-(*n*-1,1,3-trihydroperfluoropentyloxycarbonyl)phenyl 4-iodobenzoate (250 mg, 0.518 mmol), bis(triphenylphosphine)palladium dichloride (20 mg) and copper(I) iodide (60 mg), under dry $\mathrm{N_2}$, was added 20 ml of anhydrous triethylamine. The resulting mixture was heated under reflex while stirring for 2 h. Analysis by TLC revealed completion of the reaction. The precipitate formed was then filtered off and washed with ether, and the filtrate was washed with water and dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue purified by column chromatography in silica gel using petroleum ether (b.p. 60–90°C)/ethyl acetate (20/1) as eluent top give pale yellow crystals. These were recrystallized from petroleum ether (b.p. 60–90°C) and acetone/methanol to yield white flaky crystals of the product. Yield: 221 mg (74.7%). $^1$H NMR (90 MHz, $\mathrm{CDCl_3}$/TMS) $\delta$: 0.70–2.00 (m, 13H), 3.94 (t, $J = 6$ Hz, 2H), 4.82 (t, $J = 14.2$ Hz, 2H), 6.07 (tt, $J = 52.2$ Hz, 1H), 7 6.80–8.20 (m, 12H) ppm. $^{19}$F NMR (60 MHz, $\mathrm{CDCl_3}$/TFA) $\delta$: 46.2 (s, 2F) 59.5 (d, $J = 52$ Hz, 2F) ppm. IR (KBr): $\nu$ 2933, 2856, 2215, 1733, 1598, 1276, 1209, 1111, 1078, 896, 842, 765 $\mathrm{cm^{1}}$. MS ($m/z$): 570 ($\mathrm{M^+}$, 9.05) 319 ($\mathrm{C_7H_{15}O{-}C_6H_4{-}C{\equiv}C{-}C_6H_4{-}CO^+}$, 100.00). Elemental analysis: calculated (for $\mathrm{C_{32}H_{30}O_5F_4}$), C 67.36, H 5.30, F 13.32; found, C 67.36, H 5.20, F 13.28%.

### 2.7. *4-(n-1,1,5-Trihydroperfluoropentyloxycarbonyl)-phenyl 4-[(4-n-heptyloxyphenyl)ethynyl] benzoate (**F8-7**)*

Compound F8-7 was prepared in a similar way to **F4-7**. Yield: 78.5%. $^1$H NMR (90 MHz, $\mathrm{CDCl_3}$/TMS) $\delta$: 0.77-2.00 (m, 13H), 3.98 (t, $J = 6$ Hz, 2H), 4.84 (t, $J = 14.2$ Hz, 2H), 6.07 (tt, $J = 52.2$ Hz, 6 Hz, 1H), 6.80–8.30 (m, 12H) ppm. $^{19}$F NMR (60 MHz, $\mathrm{CDCl_3}$/TFA) $\delta$: 42.1 (s, 2F) 48.0 (s, 2F) 52.7 (s, 2F) 59.9 (d, $J = 52$ Hz, 2F) ppm. IR(KBr): $\nu$ 2931, 2856, 2215, 1738, 1599, 1269, 1167, 1069, 890, 836, 765 $\mathrm{cm^{-1}}$. MS ($m/z$): 671 ($\mathrm{M^+}$, 6.51) 319 ($\mathrm{C_7H_{15}O{-}C_6H_4{-}C{\equiv}C{-}C_6H_4{-}CO^+}$, 100.00). Elemental analysis: calculated (for $\mathrm{C_{36}H_{30}O_5F_8}$), C 60.90, H 4.51, F 22.66; found, C 61.11, H 4.21, F 22.85%.

### 2.8. *4-(n-1,1,7-Trihydroperfluoroheptyloxycarbonyl)-phenyl 4-[(4-n-heptyloxyphenyl)ethynyl] benzoate (**F12-7**)*

Compound F12-7 was prepared in a similar way to **F4-7** and **F8-7**. Yield: 77.9%. $^1$H NMR (90 MHz, $\mathrm{CDCl_3}$/TMS) $\delta$: 0.70–2.30 (m, 13H), 3.94 (t, $J = 6$ Hz, 2H), 4.82 (t, $J = 14.2$ Hz, 2H), 6.07 (tt, $J = 52.2$ Hz, 6 Hz, 1H), 6.80–8.60 (m, 12H) ppm. $^{19}$F NMR (60 MHz, $\mathrm{CDCl_3}$/TFA) $\delta$: 42.1 (s, 2F) 45.1 (s, 2F) 46.3 (m, 4F) 52.5 (s, 2F) 59.9 (d, $J = 52$ Hz, 2F) ppm. IR(KBr): $\nu$ 2931, 2856, 2215, 1734, 1599, 1272, 1167, 1142, 1071, 892, 836, 765 $\mathrm{cm^{-1}}$. MS ($m/z$): 771 ($\mathrm{M^+}$, 3.09) 319 ($\mathrm{C_7H_{15}O{-}C_6H_4{-}C{\equiv}C{-}C_6H_4{-}CO^+}$, 100.00). Elemental analysis: calculated (for $\mathrm{C_{38}H_{30}O_5F_{12}}$), C 56.11, H 3.92, F 29.58; found, C 56.37, H 3.92, F 29.28%.

Other homologues were made by analogous reactions. All of the intermediates and new compounds had satisfactory elemental analysis results and appropriate IR, MS, $^1$H NMR and $^{19}$F NMR spectral data.

Table 1. Transition temperatures of the **F4** series. Cr = crystal; SmA = smectic A; SmC = smectic C; I = isotropic liquid; Recr = recrystallization.

| Compounds | *n* | Transition temperature/°C |
|---|---|---|
| **F4-4** | 4 | Cr 139.9 SmA 222.1 N 224.1 I 222.2 N 219.9 SmA 115.4 Recr[a] |
| **F4-5** | 5 | Cr 125.6 SmC 142.6 SmA 211.1 I 208.8 SmA 139.4 SmC 102.0 Recr |
| **F4-6** | 6 | Cr 122.8 SmC 150.1 SmA 208.3 I 206.6 SmA 147.6 SmC 101.5 Recr |
| **F4-7** | 7 | Cr 115.2 SmC 151.7 SmA 201.3 I 199.7 SmA 149.5 SmC 95.8 Recr |
| **F4-8** | 8 | Cr 108.5 SmC 148.7 SmA 196.9 I 194.9 SmA 145.6 SmC 94.1 Recr |
| **F4-9** | 9 | Cr 108.4 SmC 143.7 SmA 189.7 I 188.0 SmA 141.5 SmC 92.7 Recr |
| **F4-10** | 10 | Cr 109.2 SmC 139.3 SmA 185.1 I 183.6 SmA 136.8 SmC 94.2 Recr |
| **F4-12** | 12 | Cr 108.1 SmC 125.3 SmA 183.2 I 182.5 SmA 122.5 SmC 95.7 Recr |

[a] A very short SmC phase is found on cooling, which can not be determined, even using POM.

Table 2. Transition temperatures of the **F8** and **F12** series. Cr = crystal; SmA = smectic A; SmC = smectic C; SmB = smectic B; I = isotropic liquid; Recr = recrystallization.

| Compounds | *n* | Transition temperature/°C |
|---|---|---|
| **F8-5** | 5 | Cr 116.8 SmC 152.3 SmA 213.5 I 209.9 SmA 147.2 SmC 91.1 Recr |
| **F8-6** | 6 | Cr 105.0 SmC 169.1 SmA 210.2 I 208.0 SmA 166.0 SmC 91.3 SmB 88.3 Recr |
| **F8-7** | 7 | Cr 105.1 SmC 173.2 SmA 200.5 I 198.9 SmA 171.1 SmC 88.5 SmB 77.4 Recr |
| **F8-8** | 8 | Cr 100.6 SmC 173.2 SmA 194.4 I 192.7 SmA 171.1 SmC 90.8 SmB 66.4 Recr |
| **F8-9** | 9 | Cr 88.1 SmC 167.0 SmA 185.0 I 182.9 SmA 164.8 SmC 83.7 SmB 69.1 Recr |
| **F8-10** | 10 | Cr 95.8 SmC 165.2 SmA 180.1 I 178.3 SmA 163.2 SmC 83.1 SmB 73.1 Recr |
| **F12-6** | 6 | Cr 112.8 SmC 182.1 SmA 219.1 I 216.9 SmA 179.0 SmC 93.9 Recr |
| **F12-7** | 7 | Cr 106.3 SmC 184.4 SmA 209.5 I 207.6 SmA 181.9 SmC 92.9 SmB 87.0 Recr |
| **F12-8** | 8 | Cr 106.2 SmC 182.2 SmA 201.5 I 198.9 SmA 179.3 SmC 94.8 SmB 77.7 Recr |
| **F12-9** | 9 | Cr 99.6 SmC 174.3 SmA 189.5 I 186.6 SmA 172.0 SmC 88.5 SmB 72.5 Recr |

## 3. Results and discussion

The phase transition temperatures of all the compounds studied were determined by DSC and the mesomorphic textures were observed on the polarizing optical microscope (POM); the results are summarized in the tables 1 and 2. As shown in these tables, all the compounds display liquid crystallinity. When $m = 2$, $n = 5$–10 and 12, the compounds show enantiotropic broad SmA and broad SmC phases; only **F4-4** shows a very narrow enantiotropic nematic phase. For $m = 4$, $n = 6$–10 and $m = 6$, $n = 7$–9, most of the compounds show not only a very broad enantiotropic SmC phase with an enantiotropic narrow SmA phase, but also a narrow monotropic SmB phase. It is also seen that the smectic C phase is enhanced with the lengthening of the polyfluorocarbon tails. In other work we have found also that compounds similar to these series but without the triple bond, show only enantiotropic SmA phases when $m = 2$, $n = 4$–10 and 12, and show enantiotropic SmA and SmC phases when $m = 4$ and 6, $n = 6$–10 [1]. So we come to the conclusion that the smectic C phase is enhanced by the addition of a triple bond. Moreover, compounds without the triple bond do not show a SmB phase.

From the results shown in tables 1 and 2, it is seen that the SmB phase forms when the alkoxy chains and the fluorocarbon tails are particularly long or short. We believe that these effects can be rationalized by considering lateral molecular interactions and the oleophobic effect. With the lengthening of the alkoxy chain the lateral–lateral interaction is increased, which is favourable for the formation of high-order mesophases. However, when the alkoxy group is long enough, it will interact with the fluorophilic interaction and destablize the layer structure [10]. When the fluorocarbon tail is short the oleophobic effect is too weak to affect the arrangement of the molecules. But when the fluorocarbon tail is a little longer, as in the **F8** series, the oleophobic effect became so strong that the molecular more easily form a layer structure, and the compounds readily form high-order mesophases. On further lengthening of the fluorocarbon tail, as in the **F12** series, the lateral–lateral interaction does not greatly increase and may be a little lower, because the interaction with the fluorocarbon tail is weak [10]. This may be one reason why the SmB phase does not form when $m$ is 6. In polarized microscopy, the samples show typical focal-conic textures in the SmA phase, broken focal-conic textures in the SmC phase, and polygonal textures in the SmB phase.

It is interesting to find that the phase transition temperatures of the new compounds are similar to those of compounds without triple bonds. From this important results we can design and synthesize many useful compounds.

## References

[1] Chen, B. Q., Yang, Y. G., and Wen, J. X., 1998, *Liq. Cryst.*, **24**, 539.

[2] Kromm, P., Cotrait, M., Rouillon, J. C., Barois, P., and Nguyen, H. T., 1996, *Liq. Cryst.*, **21**, 121.

[3] Kromm, P., Cotrait, M., and Nguyen, H. T., 1996, *Liq. Cryst.*, **21**, 95.

[4] Tournilhac, F. G., Bosio, L., Simon, J., Blinov, L. M., and Yablonsky, S. V., 1993, *Liq. Cryst.*, **14**, 405.

[5] Liu, H., and Nohira, H., 1997, *Liq. Cryst.*, **22**, 217.

[6] Tournilhac, F., Blinov, L. M., Simon, J., and Yablonsky, S. V., 1992, *Nature*, **359**, 621.

[7] Nguyen, H. T., Sigaud, G., Achard, M. F., Hardouin, F., Twieg, R. J., and Betterton, K., 1991, *Liq. Cryst.*, **10**, 389.

[8] Johansson, G., Percec, V., Ungar, G., and Smith, K., 1997, *Chem. Mater.*, **9**, 164.

[9] Takenaka, S., 1992, *J. chem. Soc. chem. Commun.*, 1748.

[10] Okamoto, H., Murai, H., and Takenaka, S., 1997, *Bull. chem. Soc. Jpn.*, 3163.

[11] Demus, D., and Richter, L., 1978, *The Texture of Liquid Crystals* (Leipzig: VEB Deutcher Verlag fur Grandstoff Industrie).

[12] Gray, G. W., and Goodby, J. W., 1984, *Smectic Liquid Crystals-Textures and Structures* (Glasgow: Leonard Hill).