Synthesis and mesomorphic properties of mesogens containing 1,1,2,2-tetrahydroperfluorodecaoxy terminal chains

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One series of two-ring and two series of three-ring mesogens with 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10 - heptadecafluorodecaoxy terminal chains containing tolane or biphenyl units have been synthesized. Their mesomorphic properties were observed and measured by optical polarizing microscopy and differential scanning calorimetry. The three-ring mesogens only exhibit a wide smectic C phase when the length of their hydrocarbon chains is intermediate.

1. Introduction

Owing to their excellent switching characteristics, ferroelectric liquid crystals have been intensely studied in recent years. Mesogens containing highly fluorinated alkyl terminal chains are advantageous to the formation of tilted smectic phases [1, 2] and are valuable as potentially important components of mixtures for ferroelectric liquid crystal displays (FLCDs). In previous work [3–5], series of mesogens with 2,2,3,3-tetrafluoropropyl, 2,2,3,3,4,4,5,5-octafluoropentyl and 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl substituted benzoates containing a tolane or biphenyl unit have been synthesized, and their mesomorphic properties studied. From those, it seemed that the increase of the number of the difluoromethylene units stabilized the smectogenic character but it is worth noting that at the same time an increase was recorded for the temperature range of the smectic C phase. This paper therefore reports the results on three series of mesogens containing the 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-hepta - decafluorodecyl group (**An**, **Bn**, **Cn**) as shown in the scheme. The relationships between the molecular structure and the mesomorphic properties are discussed.

2. Experimental

2.1. *Characterization*

The structures of the final products and intermediates were elucidated by a variety of spectral methods. IR spectra were recorded on a PE-983G spectrophotometer, using KBr pellets of solids or films of liquids. ^{1}H NMR spectra with tetramethylsilane (TMS) as internal standard and ^{19}F NMR spectra with trifluoroacetic acid (TFA)
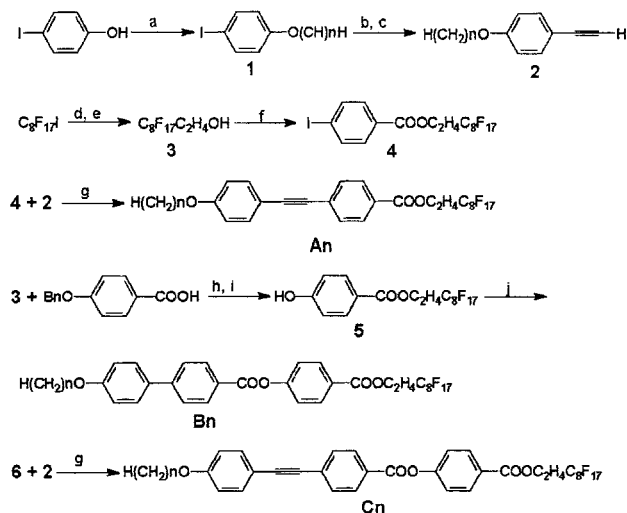
Reagents and conditions: (a) H(CH$_2$)nBr, K$_2$CO$_3$, (CH$_3$)$_2$CO; (b) H-≡-C(CH$_3$)$_2$OH, Pd(PPh$_3$)$_2$Cl$_2$, CuI, PPh$_3$, Et$_3$N; (c) KOH, CH$_3$C$_6$H$_5$; (d) CH$_2$=CH$_2$; (e) fuming H$_2$SO$_4$; (f) p-I-C$_6$H$_4$-COOH, DCC, cat. DMAP, CH$_2$Cl$_2$; (g) Pd(PPh$_3$)$_2$Cl$_2$, CuI, PPh$_3$, Et$_3$N; (h) DCC, cat. DMAP, CH$_2$Cl$_2$; (i) Pd/C, H$_2$ (1 atm), CH$_3$COOC$_2$H$_5$; (j) DCC, cat. DMAP, CH$_2$Cl$_2$.

Scheme.

as external standard were recorded on a Bruker 300 spectrometer (300 MHz), a Varian EM360L spectrometer (60 MHz) or a FX-90Q spectrometer (90 MHz). For ^{19}F NMR spectra the high field was positive. MS spectra were measured with a Finnigan-4021 spectroscope using electrical ionization. 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 (Metter FP-80) and a control unit (FP-82), and by

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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 previously reported [6, 7].

2.2. Synthesis

The paths to the target fluorinated mesogens are outlined in the scheme. The preparation of 4-*n*-alkoxy-phenylacetylene **2** was reported previously [4]. The 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadeca fluorodecanol was prepared from 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-hepta-decafluoro-1-iodo-decane through two reaction steps [8, 9]. Other intermediates can be easily obtained according to a reported procedure [3, 4]. The compounds **4**, **5**, **6**, **B*n*** were prepared by a mild one-pot esterification procedure, between the substituted benzoic acid and substituted phenol or alcohol in the presence of dicyclohexylcarbodiimide (DCC) and *N,N*-dimethyl-aminopyridine (DMAP) as catalyst in anhydrous dichloro-methane or tetrahydrofuran (THF) solution. Finally, a coupling reaction between compound **4** or **6** and **2** with catalysis by bis(triphenylphosphine)palladium dichloride and copper(I) iodide in anhydrous triethylamine solution gave the target compounds **A*n*** and **C*n***.

2.2.1. 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadeca-fluorodecoyl 4-(4-n-alkoxyphenylethyny l)benzoate (*An*, *n* = 4–10, 12, 16)

In a typical procedure, under dry N_2, anhydrous triethylamine (10 ml) was added to a mixture of compound 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decyl 4-iodobenzoate (**4**, 200 mg, 0.29 mmol), bis(triphenyl-phosphine)palladium dichloride (6 mg), copper(I) iodide (10 mg), triphenylphosphine (16 mg) and 4-*n*-butoxy-phenylacetylene (**2**, 70 mg, 0.4 mmol). The resulting mixture was stirred at 60°C for 24 h. The precipitate formed was filtered off and washed with ether, and the filtrate washed with water, then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C)/dichloromethyl (3:1) as eluent. This gave pale yellow crystals which were recrystallized from acetone/methanol to yield white flaky crystals of compound **A4**; yield 193 mg (90%). MS (*m/z*, %): 741 (M$^+$ + 1, 100.00), 685 (M$^+$ − C$_4$H$_8$ + 1, 60.23), 221 (HO−C$_6$H$_4$−≡−C$_6$H$_4$−CO$^+$, 36.82). Anal. for C$_{29}$H$_{21}$F$_{17}$O$_3$: calc. C 47.04, H 2.86, F 43.62; found C 47.18, H 2.79, F 43.67%. ^{1}H NMR (CDCl$_3$/TMS, 90 MHz) δ_H (ppm): 0.99 (t, 3H, CH$_3$), 1.26–1.84 (m, 4H, CH$_2$CH$_2$), 2.40–2.87 (m, 2H, CH$_2$CF$_2$), 3.97

(t, *J* = 6.0 Hz, 2H, OCH$_2$), 4.60 (t, *J* = 6.0 Hz, 2H, OCH$_2$), 6.82 (d, *J* = 7.5 Hz, 2H, ArH), 7.37–7.56 (m, 4H, ArH), 7.94 (d, *J* = 7.5 Hz, 2H, ArH). ^{19}F NMR (CDCl$_3$/TFA, 56.4 MHz) δ_F (ppm): 3.60 (m, 3F, CF$_3$), 36.10 (m, 2F), 44.70–46.30 (m, 10F), 49.00 (m, 2F). IR (KBr, v_{max}, cm^{-1}) 2937, 2874 (s, C−H), 2217 (s, C≡C), 1715 (vs, C=O), 1599 (s, C$_6$H$_4$), 1203, 1149 (s, C−O−C).

2.2.2. 4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadeca-fluorodecaoxycarbonyl)phenyl 4-(4-n-alkoxy-phenyl)benzoate (*Bn*, *n* = 5–8, 10)

In a typical procedure, under dry N_2, a mixture of compound 4-(4-*n*-hexaoxyphenyl)benzoic acid (119 mg, 0.4 mmol), 4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptade ca-fluorodecaoxycarbonyl)phenol (**5**, 200 mg, 0.34 mmol), DCC (83 mg, 0.4 mmol) and DMAP (5 mg) was added to anhydrous dichloromethane (10 ml). The resulting mixture was stirred at room temperature for 48 h. The precipitate formed was filtered and washed with ether, and the filtrate was washed with water, then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue purified by column chromato-graphy on silica gel using petroleum ether (b.p. 60–90°C)/ethyl acetate (20:1) as eluent. This gave a white solid that was recrystallized from acetone/methanol to yield white flaky crystals of compound **B6**; yield 214 mg (73%). MS (*m/z*): 866 (M$^+$ + 2, 0.40), 281 (*p-n*-C$_6$H$_{13}$O−C$_6$H$_4$−CO$^+$, 100.00), 197 (O−C$_6$H$_4$−C$_6$H$_4$−CO$^+$, 11.49). Anal. for C$_{36}$H$_{29}$F$_{17}$O$_5$: calc. C 50.01, H 3.38, F 37.37; found C 49.91, H 3.66, F 37.56%. ^{1}H NMR (CDCl$_3$/TMS, 300 MHz) δ_H (ppm): 0.89 (3H, t, *J* = 6.55 Hz, CH$_3$), 1.26–1.50 (m, 6H, 3CH$_2$), 1.78–1.87 (m, 2H, CH$_2$), 2.57–2.69 (m, 2H, CH$_2$), 4.02 (t, 2H, *J* = 6.54 Hz, OCH$_2$), 4.65 (t, 2H, *J* = 6.34 Hz, OCH$_2$), 7.01 (d, 2H, *J* = 8.72 Hz, ArH), 7.35 (d, 2H, *J* = 8.75 Hz, ArH), 7.60 (d, 2H, *J* = 8.69 Hz, ArH), 7.71 (d, 2H, *J* = 8.47 Hz, ArH), 8.14 (d, 2H, *J* = 8.66 Hz, ArH), 8.24 (d, 2H, *J* = 8.45 Hz, ArH). ^{19}F NMR (CDCl$_3$/TFA, 282 MHz) δ_F (ppm): 3.8 (t, 3F, *J* = 9.66 Hz, CF$_3$), 36.6 (m, 2F), 44.7 (m, 2F), 45.0 (m, 4F), 45.8 (m, 2F), 46.5 (m, 2F), 49.2 (m, 2F). IR (KBr, v_{max}, cm^{-1}): 2934, 1734 (vs, C=O), 1601 (s, C$_6$H$_4$), 1274, 1202, 1167, 1150 (s, C−O−C), 1080, 888, 834, 769, 712, 690, 662, 504.

2.2.3. 4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadeca-fluorodecaoxycarbonyl)phenyl 4-[(4-n-alkoxy-phenyl)ethynyl]benzoate (*Cn*, *n* = 5, 6, 8, 9)

Members of the homologous series **C*n*** were prepared using a procedure similar to that described for the synthesis of compound **A*n***. The following data are for the compound **C6**. MS (*m/z*): 888 (M$^+$, 0.98). Anal. for C$_{38}$H$_{29}$F$_{17}$O$_5$: calc. C 51.36, H 3.29, F 36.37; found

C 51.17, H 3.40, F 36.22%. ^{1}H NMR (CDCl$_3$/TMS, 300 MHz) δ_H (ppm): 0.89 (3H, t, $J = 6.59$ Hz, CH$_3$), 1.30–1.47 (m, 6H), 1.75–1.82 (m, 2H), 2.57–2.69 (m, 2H), 3.99 (t, 2H, $J = 6.55$ Hz, OCH$_2$), 4.65 (t, 2H, $J = 6.37$ Hz, OCH$_2$), 6.90 (d, 2H, $J = 8.74$ Hz, ArH), 7.33 (d, 2H, $J = 8.67$ Hz, ArH), 7.50 (d, 2H, $J = 8.67$ Hz, ArH), 7.64 (d, 2H, $J = 8.36$ Hz, ArH), 8.13 (d, 2H, $J = 8.85$ Hz, ArH), 8.17 (d, 2H, $J = 8.46$ Hz, ArH). ^{19}F NMR (CDCl$_3$/TFA, 56.4 MHz) δ_F (ppm): 3.8 (t, 3F, $J = 9.66$ Hz, CF$_3$), 36.6 (m, 2F), 44.7 (m, 2F), 45.0 (m, 4F), 45.8 (m, 2F), 46.5 (m, 2F), 49.2 (m, 2F). IR (KBr, ν_{max}, cm^{-1}): 2921, 2219 (s, C≡C), 1734 (vs, C=O), 1601 (s, C$_6$H$_4$), 1496, 1471, 1400, 1264, 1202, 1150 (s, C−O−C), 1100, 1081, 1021, 886, 807, 768, 737, 690, 663, 502.

Other target compounds and intermediates have satisfactory elementary analyses and appropriate ^{1}H and ^{19}F NMR, IR and MS spectral data.

3. Results and discussions

The phase transition behaviours of the target compounds are summarized in the table. Our target is to synthesize mesogens with a broad smectic C phase by introducing highly fluorinated alkyl terminal chains. Therefore, compounds **A***n* were synthesized first. Their transition temperatures are shown in figure 1, which indicates, firstly, that their melting points remain almost the same, but the clearing points are decreased with increasing numbers of methylene units; as a result the mesomorphic range become narrower as the alkyl chain grows from 4 to 16 carbons. From the results for **B***n* and
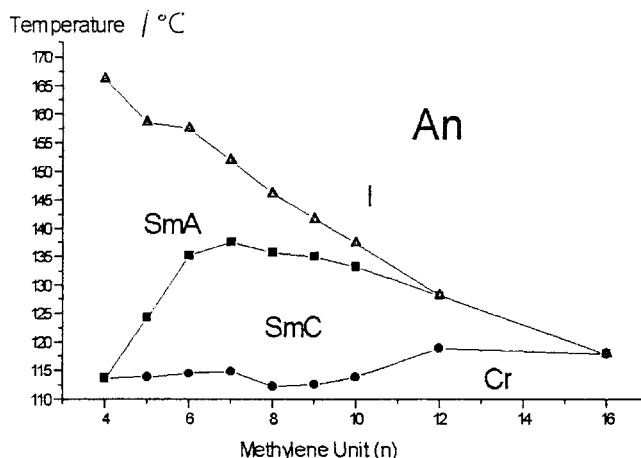

Figure 1. The transition behaviour of compounds **A***n*: dependence of transition temperatures on the length of the alkoxy chain.

C*n* compounds (shown in figures 2 and 3, respectively) we obtain the same rule as for **A***n* compounds. Secondly, **A4** shows only an enantiotropic smectic A phase, while for $n > 4$ enantiotropic smectic A phase and smectic C phases are seen until $n = 12$, when only a smectic C phase is seen. For **A16**, no mesophase exists. Since only one compound, **A12**, possesses the expected single smectic C phase and the temperature range is very short (only 9.1°C). Our work then progressed to the synthesis of mesogens with three aromatic rings as more rigid mesomorphic cores than two aromatic rings, in the expectation of broad smectic C phases.

Table. Phase transition temperatures of the compounds under study: Cr = cryst; SmA = smectic A phase; SmB = smectic B phase; SmC = smectic C phase; I = isotropic liquid; Recr = recrystallization.

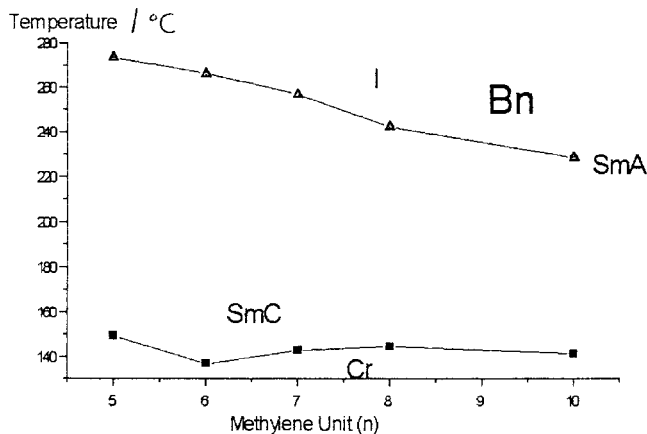| Compound	Transition temperature/°C
A4	Cr 113.6 SmA 166.2 I 163.6 SmA 111.7 SmB 106.6 Recr
A5	Cr 113.9 SmC 124.3 SmA 158.6 I 156.7 SmA 123.1 SmC 106.8 Recr
A6	Cr 114.5 SmC 135.2 SmA 157.5 I 155.3 SmA 132.5 SmC 108.4 Recr
A7	Cr 114.8 SmC 137.5 SmA 151.9 I 149.3 SmA 134.4 SmC 108.2 Recr
A8	Cr 112.2 SmC 135.7 SmA 146.1 I 144.1 SmA 134.2 SmC 106.8 Recr
A9	Cr 112.6 SmC 134.9 SmA 141.6 I 139.6 SmA 133.1 SmC 107.9 Recr
A10	Cr 113.8 SmC 133.1 SmA 137.3 I 135.6 SmA 132.5 SmC 109.5 Recr
A12	Cr 119.0 SmC 128.1 I 125.6 SmC 112.8 Recr
A16	Cr 117.9 I 114.0 Recr
B5	Cr 149.20 SmC 273.69 I 266.74 SmC 115.84 Recr
B6	Cr 136.87 SmC 266.29 I 263.39 SmC 122.73 Recr
B7	Cr 142.76 SmC 256.96 I 254.30 SmC 127.50 Recr
B8	Cr 144.42 SmC 242.46 I 235.99 SmC 130.86 Recr
B10	Cr 141.16 SmC 228.57 SmA 231.51 I 223.31 SmA 221.86 SmC 131.41 Recr
C5	Cr 142.67 SmC 271.56 I 266.51 SmC 121.58 Recr
C6	Cr 133.74 SmC 263.58 I 259.58 SmC 121.48 Recr
C8	Cr 136.18 SmC 228.96 SmA 246.62 I 243.36 SmA 225.56 SmC 125.67 Recr
C9	Cr 135.78 SmC 226.31 SmA 239.83 I 237.03 SmA 222.79 SmC 123.81 Recr

Temperature / °C

Figure 2. The transition behaviour of compounds **B***n*: dependence of transition temperatures on the length of the alkoxy chain.

Temperature / °C

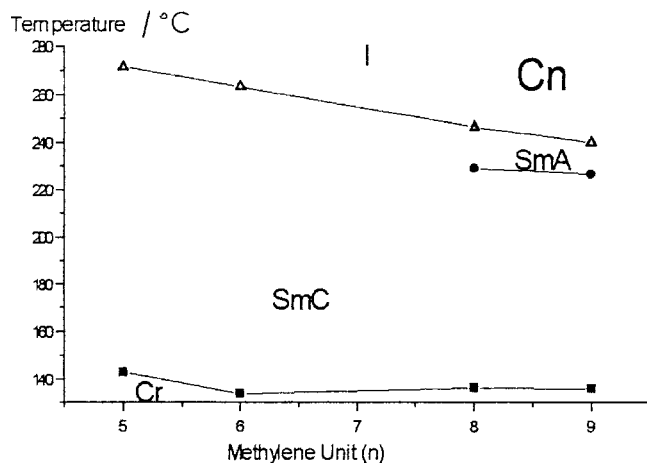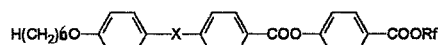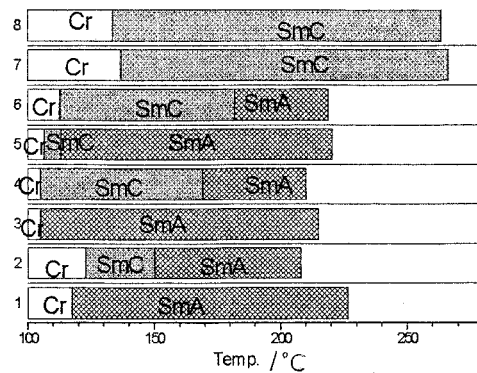
Figure 3. The transition behaviour of compounds **C***n*: dependence of transition temperatures on the length of the alkoxy chain.

X=single bond: 1, 3, 5, 7; triple bond: 2, 4, 6, 8.

Rf=H(CF$_2$)$_2$CH$_2$: 1, 2; H(CF$_2$)$_4$CH$_2$: 3, 4; H(CF$_2$)$_6$CH$_2$: 5, 6; F(CF$_2$)$_8$CH$_2$CH$_2$: 7, 8.

Figure 4. Comparison of mesomorphic properties of selected compounds.

In series **B***n* and **C***n*, broad enantiotropic smectic C phases are present only when the hydrocarbon chains are of intermediate length, but strangely, narrow enantiotropic smectic A phases appear when the length of the hydrocarbon chains increases. This phenomenon is ascribed to the long hydrocarbon chain inducing simple mesophases.

Gray discussed the role of the central group in the simple mesogens A−ph−X−Ph−B, where A and B are suitable terminal substituents, and X is the central group [10]. With minor exceptions, the favourability order for mesomorphic properties has no relationship with A or B, but only with X. The order is: phenyl > [2, 2] dicyclooctoyl > double bond > azoxy > oxy Schiff's base > triple bond > azo > Schiff's base > ester bond > single bond. Thus mesogens containing tolane should have higher

clearing points than those containing biphenyl. From this and previous work [3–5, 11, 12], we selected eight compounds with highly fluorinated alkyl chains and containing tolane or biphenyl, and compared their mesormorphic properties; the result is shown in figure 4, from which we find an abnormal phenomenon. The insertion of a triple bond into the biphenyl group is found to be unfavourable to the formation of smectic phases when two compounds have same phase sequence; the clearing point is $1 > 2$, $3 > 4$, $5 > 6$, $7 > 8$ (n values). This abnormal phenomenon may be ascribed to the highly fluorinated alkyl terminal chains. We also noted that only mesogens with the $C_8F_{17}C_2H_4$ terminal chain have a smectic C phase without a smectic A phase.

In conclusion, all three series of target mesogens exhibit the smectic C phase, as expected, but only three-ring mesogens with intermediate length hydrocarbon terminal chains show only a broad enantiotropic smectic C phase. A triple bond in mesogens with a highly fluorinated alkyl terminal chain is disadvantageous to the formation of the smectic phase.

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