Fluorophobic Effect Generates a Systematic Approach to the Synthesis of the Simplest Class of Rodlike Liquid Crystals Containing a Single Benzene Unit

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4-Substituted *n*-5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorododecan-1-yloxybenzenes, *n*-5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluorododecan-1-yloxybenzenes, and 2-methyl-4-substituted *n*-5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluorododecan-1-yloxybenzenes were synthesized and characterized by a combination of techniques consisting of differential scanning calorimetry (DSC), thermal optical polarized microscopy, and small- and wide-angle X-ray diffraction. Thermotropic s_A and s_C LC phases are exhibited by compounds with NO_2, CN, CO_2CH_3, CH_2OH, CO_2H, and $COCH_3$ substituents in the 4-position of the benzene ring. The thermal stability of the LC phase of these compounds increases with the increase of the length of the perfluorinated segment of their alkoxy group. A ratio of the perhydrogenated $[(CH_2)_m]$/perfluorinated $[F(CF_2)_n]$ segment lengths of $m/n < 1$ favors the formation of LC phases when $n + m = 10$ and 12. Additional substitution in the 2-position of the benzene ring with a methyl group decreases the thermal stability of the LC phase. The s_A phase of these compounds has a bilayered structure in which the perfluorinated segments are interdigitated. These compounds represent the simplest class of rodlike liquid crystals containing a single benzene unit which exhibit classic calamitic phases. The experiments reported in this paper demonstrate a simple and convenient method for the synthesis of liquid crystals containing a single benzene unit via the fluorophobic effect.

Introduction

Perfluorinated alkanes are more rigid and linear and due to their extremely low surface energy are less miscible than the corresponding perhydrogenated alkanes (fluorophobic effect).[1] As a consequence, the repacement of a perhydrogenated alkane with a perfluorinated one in the tail of a rigid rodlike molecular liquid crystal (LC) enhances the thermal stability of its calamitic LC phase.[2] The combination of a suitable length and ratio of perfluorinated and perhydrogenated alkane segments within the same molecule produces a microsegregation at the molecular level, and this process has been shown to be alone responsible for the formation of highly ordered lamellar thermotropic[3,4] and lyotropic mesophases.[5] Recently, we reported a dramatic stabilization of the hexagonal columnar mesophase generated from supramolecular and macromolecular columns via the semifluorination of the alkyl groups of their tapered building blocks.[6] A dramatic enhancement of the ability of tapered groups to self-assemble into

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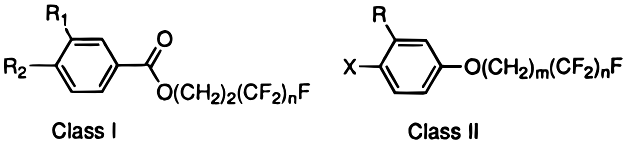
Scheme 1. Thermotropic Rodlike Liquid Crystals Containing a Single Benzene Unit



supramolecular columns which produce hexagonal columnar mesophases via semifluorination was also demonstrated.[7] The stabilization of the hexagonal columnar mesophase generated from fluoroalkylated disklike molecules was reported by Ringsdorf et al.[8] This extremely broad range of capabilities of the fluorophobic effect to induce and stabilize various LC phases prompted us to investigate the potential use of the fluorophobic effect in the design of molecular rodlike liquid crystals which display conventional calamitic mesophases of low order such as nematic (N), smectic A (s_A), and smectic C (s_C).

The synthesis of molecular[9–13] and supramolecular[14,15] rodlike liquid crystals which exhibit conventional calamitic mesophases requires at least two aromatic, cycloaliphatic, or a combination of one aromatic and one cycloaliphatic groups interconnected either directly or through a suitable linking unit. Exceptions are provided by some amphotropic LCs[16] and by some molecular polyene Schiff bases[17a] and supramolecular dienoic[17b] acids. The series of experiments reported in this publication was challenged by a recent publication which reported that some derivatives of 2-(*n*-perfluoroalkyl)ethyl 3- and/or 4-substituted benzoates (Scheme 1, class I) show smectic phases having an orthogonal nature.[2f] The same publication claims that a substituent at position 3 (and not 4 as usually expected) of the benzoate group is indispensable for these compounds to display liquid-crystalline properties. The goal of this publication is to report that a suitable length and ratio between the perfluorinated and perhydrogenated segments of the alkoxy group of a 4-substituted alkoxybenzene (class II, Scheme 1) generates a systematic approach to the synthesis of rodlike liquid crystals containing a single benzene unit. A variety of substituents placed in the 4-position of the benzene ring (i.e., X = NO_2, CN, CO_2CH_3, CH_2OH, $COCH_3$, CO_2H; without and with an additional substituent in position 2) generates class II compounds which exhibit enantiotropic s_A and s_C LC phases. The LC phases of these new compounds were characterized by a combination of differential scanning calorimetry (DSC), thermal optical polarized microscopy, and X-ray diffraction experiments. By contrast to class I compounds,[2f] class II compounds produce calamitic mesophases whose thermal stability is affected by various substituents attached to the benzene ring in the expected way.[9] Therefore, this new class of compounds provides the simplest series of rodlike LCs based on a single benzene unit.

Experimental Section

Materials. 5-Hexen-1-ol (**1**−**6**, 99%), perfluorobutyl iodide (98%), vinylacetic acid (99+%), $LiAlH_4$ (95%), 48% HBr (ACS reagent), tricaprylylmethylammonium chloride (Aliquat 336), 1-bromododecane (**4**−**12/0**) (97%), 4-nitrophenol (**5a**, 98%), 4-cyanophenol (**5b**, 95%), methyl 4-hydroxybenzoate (**5c**, 99%), 4-methoxyphenol (**5d**, 99%), *o*-cresol (**9**, 98%), $AlCl_3$ (98%), and chlorosulfonyl isocyanate (98%, all from Aldrich) were used as received. Perfluorohexyl iodide (99%, Fluka) and perfluorooctyl iodide (99%, Fluka) were used as received. 1,1,2-Trichlorotrifluoroethane (Freon 113, Acros) was used as received. Et_2O (Fisher) was refluxed over sodium ketyl under a N_2 atmosphere and freshly distilled before use. DMF and acetic anhydride (both from Fisher) were used as received.

General Methods. ^{1}H NMR (200 MHz), ^{19}F NMR (188 MHz), and ^{13}C NMR (50 MHz) spectra were recorded on a Varian Gemini 200 spectrometer. ^{19}F NMR spectra for compounds with the same perfluoroalkane chain lengths were identical. The purity of products was determined by a combination of TLC on silica gel plates (Kodak) with fluorescent indicator and HPLC using a Perkin-Elmer Series 10 HPLC equipped with an LC-100 column oven, Nelson Analytical 900 Series integrator data station and a Perkin-Elmer PL gel column of 5×10^2. THF was used as solvent at the oven temperature of 40 °C unless otherwise noted. Detection was by UV absorbance at 254 nm. In some instances, purity was determined by GC using a Hewlett-Packard 5890A gas chromatograph equipped with a Hewlett-Packard 3392A integrator. A packed column consisting of 10% SP2100 on 80/100 Supelcoport stationary phase was used with a head pressure of 40−60 psi. The carrier gas was N_2.

Thermal transitions were measured on a Perkin-Elmer DSC-7. In all cases, the heating and cooling rates were reported as the maxima and minima of their endothermic and exothermic peaks. Zn and In were used as calibration standards. An Olympus BX-40 optical polarized microscope (100× magnification) equipped with a Mettler FP 82 hot stage and a Mettler FP 80 central processor was used to verify thermal transitions and characterize anisotropic textures.

X-ray diffraction experiments were performed using an Image Plate area detector (MAR Research) with a graphite-monochromatized pinhole-collimated beam and a helium tent. Powdered samples were held at constant temperature (±0.1 °C) in a temperature-controlled cell.

Synthesis. The syntheses of $(Ph_3P)_4Pd^0$,[18] 7-octen-1-ol (**1**−**8**),[7] 5-iodo-9,9,10,10,11,11,12,12,12-nonafluorododecan-1-ol (**2**−**8/4**),[7] 9,9,10,10,11,11,12,12,12-nonafluorododecan-1-ol (**3**−**8/4**),[7] *n*-9,9,10,10,11,11,12,12,12-nonafluorododecyl bromide (**4**−**8/4**),[7] 5-iodo-5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluorododecanoic acid (**2**−**4/8**),[7] *n*-5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluorododecan-1-ol (**3**−**4/8**),[7] *n*-5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluorododecyl bromide (**4**−**4/8**),[7]

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methyl 4-(*n*-5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecan-1-yloxy)benzoate (**6c−4/6**),[6b] methyl 4-(*n*-5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-dodecan-1-yloxy)benzoate (**6c−4/8**),[19] 4-(*n*-5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecan-1-yloxy)benzyl alcohol (**7−4/6**),[6b] and 4-(*n*-5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecan-1-yloxy)benzyl alcohol (**7−4/8**)[19] have been described previously.

5-Iodo-7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluorododecan-1-ol (2−6/6). Compound **2−6/6** was synthesized by the palladium(0)-catalyzed radical addition of *n*-perfluorohexyl iodide to **1−6**.[7] A solution of **1** (9.0 g, 90 mmol) and 80 mL of hexanes was cooled to 0 °C under N_2 in a round-bottom flask equipped with a N_2 inlet−outlet. *n*-Perfluorohexyl iodide (40 g, 90 mmol) and $(Ph_3P)_4Pd(0)$ (4.6 g, 4.0 mol %) were added. The heterogeneous orange mixture was allowed to reach room temperature while stirring. After 1 h, the mixture was filtered and the solids were washed with Et_2O. The solvent was distilled and the resultant orange oil (46 g, 93%) was used without further purification. ^1H NMR ($CDCl_3$, δ, ppm, TMS) 1.64 (m, 4H, $(C\mathit{H}_2)_2CH_2CH_2OH$), 1.83 (m, 2H, $C\mathit{H}_2CH_2OH$), 2.87 (m, 2H, $CF_2C\mathit{H}_2$), 3.69 (t, 2H, $C\mathit{H}_2OH$, $J = 6.1$ Hz), 4.34 (m, 1H, $C\mathit{H}I$); ^{19}F NMR ($CDCl_3$, δ, ppm) −81.3 (t, 3F, $C\mathit{F}_3$, $J = 10.2$ Hz), −114.6 (m, 2F, $C\mathit{F}_2CH_2$), −122.3 (t, 2F, $C\mathit{F}_2CF_2CH_2$, $J = 10.3$ Hz), −123.4 (t, 2F, $C\mathit{F}_2CF_2CF_2CH_2$, $J = 4.6$ Hz), −124.2 (t, 2F, $CF_3CF_2C\mathit{F}_2$, $J = 5.1$ Hz), −126.7 (t, 2F, $CF_3C\mathit{F}_2$, $J = 9.2$ Hz).

***n*-7,7,8,8,9,9,10,10,11,12,12,12-Tridecafluorododecan-1-ol (3−6/6).** To a slurry of $LiAlH_4$ (3.29 g, 83.0 mmol) in 200 mL of anhydrous Et_2O was added dropwise a solution of **2−6/6** (45.5 g, 83.3 mmol) in 300 mL of anhydrous Et_2O. After 2 h, the reaction was quenched by successive addition of 3 mL of H_2O, 3 mL of 15% NaOH, and 9 mL of H_2O. The granular solids were filtered and washed with Et_2O. The Et_2O was distilled to yield an orange oil which was purified by vacuum distillation to yield 26.1 g (74.6%) of a clear oil, $bp^{0.8}$ 88−89 °C. Purity (GLC), 99+%; ^1H NMR ($CDCl_3$, δ, ppm, TMS) 1.33−1.66 (m, 8H, $CF_2CH_2(C\mathit{H}_2)_4$), 2.03 (m, 2H, $CF_2C\mathit{H}_2$), 3.66 (t, 2H, $C\mathit{H}_2OH$, $J = 6.5$ Hz); ^{19}F NMR ($CDCl_3$, δ, ppm) −81.3 (t, 3F, $C\mathit{F}_3$, $J = 10.1$ Hz), −114.9 (m, 2F, $C\mathit{F}_2CH_2$), −122.5 (s, 2F, $C\mathit{F}_2CF_2CH_2$), −123.5 (s, 2F, $C\mathit{F}_2CF_2CF_2CH_2$), −124.2 (s, 2F, $CF_3CF_2C\mathit{F}_2$), −126.7 (m, 2F, $CF_3C\mathit{F}_2$); ^{13}C NMR ($CDCl_3$, δ, ppm) 20.1 ($CF_2CH_2\mathit{C}H_2$), 25.5 ($\mathit{C}H_2CH_2CH_2OH$), 28.9 ($CF_2CH_2\mathit{C}H_2$), 30.8 (t, $CF_2\mathit{C}H_2$, $J = 22.5$ Hz), 32.4 ($\mathit{C}H_2CH_2OH$), 62.4 ($\mathit{C}H_2OH$).

***n*-7,7,8,8,9,9,10,10,11,11,12,12,12-Tridecafluorododecyl Bromide (4−6/6).** A mixture of **3−6/6** (25.9 g, 60.0 mmol), Aliquat 336 (1.0 g, 4.0 mol %), and HBr (48%, 21.0 mL, 126 mmol) was heated to 100 °C under stirring.[7] After 8 h, the mixture was cooled to room temperature and extracted with Et_2O. The organic layer was washed three times with H_2O, dried over $MgSO_4$, and filtered. The solvent was evaporated and the product was distilled under vacuum to yield 26.2 g (90.4%) of a clear oil, $bp^{0.4}$ 79−81 °C. Purity (GLC), 95.4%; ^1H NMR ($CDCl_3$, δ, ppm, TMS) 1.39 (m, 6H, $(C\mathit{H}_2)_3CH_2CH_2Br$), 1.71−2.17 (m, 4H, $C\mathit{H}_2CH_2Br$, $CF_2C\mathit{H}_2$), 3.42 (t, 2H, $C\mathit{H}_2Br$, $J = 6.6$ Hz); ^{13}C NMR ($CDCl_3$, δ, ppm) 20.7 ($CF_2CH_2\mathit{C}H_2$), 28.5 ($\mathit{C}H_2CH_2CH_2Br$), 28.9 ($CF_2CH_2\mathit{C}H_2$), 31.0 (t, $CF_2\mathit{C}H_2$, $J = 22.5$ Hz), 33.2 ($\mathit{C}H_2CH_2Br$), 33.8 ($\mathit{C}H_2Br$).

General Procedure for the Synthesis of 4-Substituted Perfluoroalkylalkyloxybenzenes. 4-(*n*-5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluorododecan-1-yloxy)nitrobenzene (6a−4/8). Compound **5a** (0.14 g, 0.10 mmol) was dissolved in 10 mL of DMF containing K_2CO_3 (0.41 g, 0.30 mmol). The mixture was heated to 65 °C and stirred vigorously in a N_2 atmosphere. **4−4/8** (0.55 g, 0.10 mmol) was added, and the reaction was checked periodically by ^1H NMR. After 2.5 h, the mixture was cooled to room temperature, poured into 200 mL of ice-water, and acidified with 10% HCl. The product was collected by vacuum filtration and recrystallized from cold MeOH to obtain 0.43 g (70%) of white flakes. TLC (5:1 hexanes:ethyl acetate) $R_f = 0.44$. ^1H NMR ($CDCl_3$, TMS, δ, ppm) 1.91 (m, 4H, $CF_2CH_2(C\mathit{H}_2)_2$), 2.17 (m, 2H, $CF_2C\mathit{H}_2$), 4.10 (t, 2H, $C\mathit{H}_2OAr$, $J = 5.7$ Hz), 6.98 (d, 2H, ortho to O, $J = 9.3$ Hz), 8.19 (d, 2H, ortho to NO_2, $J = 9.3$ Hz); ^{19}F NMR ($CDCl_3$, δ, ppm) −81.3 (t, 3F, $C\mathit{F}_3$, $J = 10.0$ Hz), −115.0 (m, 2F, $C\mathit{F}_2CH_2$), −122.4 (m, 6F, $(C\mathit{F}_2)_3CF_2CH_2$), −123.3 (m, 2F, $CF_3CF_2CF_2C\mathit{F}_2$), −124.1 (m, 6F, $CF_3CF_2C\mathit{F}_2$), −126.7 (m, 6F, $CF_3C\mathit{F}_2$); ^{13}C NMR ($CDCl_3$, δ, ppm) 17.2 ($CF_2CH_2\mathit{C}H_2$), 28.4 ($\mathit{C}H_2CH_2OAr$), 30.6 (t, $CF_2\mathit{C}H_2$, $J = 22.1$ Hz), 68.0 ($\mathit{C}H_2OAr$), 114.4 (ortho to O), 125.8 (ortho to NO_2), 141.7 (ipso to NO_2), 163.9 (ipso to O).

4-(*n*-Dodecan-1-yloxy)benzonitrile (6b−12/0). Recrystallization from cold MeOH yielded 2.1 g (73%) of a white powder. TLC (5:1 hexanes:ethyl acetate) $R_f = 0.68$. ^1H NMR ($CDCl_3$, TMS, δ, ppm) 0.88 (t, 3H, $C\mathit{H}_3$, $J = 6.2$ Hz), 1.26 (br s, 18H, $CH_3(C\mathit{H}_2)_9$), 1.80 (m, 2H, $C\mathit{H}_2CH_2OAr$), 3.99 (t, 2H, $C\mathit{H}_2OAr$, $J = 6.5$ Hz), 6.95 (d, 2H, ortho to O, $J = 9.0$ Hz), 7.55 (d, 2H, ortho to CN, $J = 9.0$ Hz); ^{13}C NMR ($CDCl_3$, δ, ppm) 13.9 ($\mathit{C}H_3$), 22.5 ($CH_3\mathit{C}H_2$), 25.7 ($\mathit{C}H_2CH_2CH_2O$), 28.8, 29.1, 29.4 ($CH_3CH_2CH_2(\mathit{C}H_2)_6$ and $\mathit{C}H_2CH_2O$), 31.7 ($CH_3CH_2\mathit{C}H_2$), 68.2 ($\mathit{C}H_2OAr$), 103.4 (ipso to CN), 115.0 (ortho to O), 118.9 ($\mathit{C}N$), 133.6 (ortho to CN), 162.2 (ipso to O).

4-(*n*-9,9,10,10,11,11,12,12,12-Nonafluorododecan-1-yloxy)benzonitrile (6b−8/4). Recrystallization from cold MeOH yielded 69 mg (70%) of a white solid. TLC (5:1 hexanes:ethyl acetate) $R_f = 0.82$. ^1H NMR ($CDCl_3$, TMS, δ, ppm) 1.39−1.61 (m, 10H, $CF_2CH_2(C\mathit{H}_2)_5$), 1.81 (m, 2H, $C\mathit{H}_2CH_2OAr$), 2.05 (m, 2H, $CF_2C\mathit{H}_2$), 4.00 (t, 2H, $C\mathit{H}_2OAr$, $J = 6.4$ Hz), 6.91 (d, 2H, ortho to O, $J = 6.8$ Hz), 7.56 (d, 2H, ortho to CN, $J = 6.9$ Hz); ^{19}F NMR ($CDCl_3$, δ, ppm) −81.7 (m, 3F, $C\mathit{F}_3$), −115.3 (m, 2F, $C\mathit{F}_2CH_2$), −125.1 (m, 2F, $C\mathit{F}_2CF_2CH_2$), −126.7 (m, 2F, $CF_3C\mathit{F}_2$); ^{13}C NMR ($CDCl_3$, δ, ppm) 20.1 ($CF_2CH_2\mathit{C}H_2$), 25.9 ($\mathit{C}H_2CH_2CH_2OAr$), 29.0 ($CF_2CH_2(\mathit{C}H_2)_3$ and $\mathit{C}H_2CH_2OAr$), 30.8 (t, $CF_2\mathit{C}H_2$, $J = 22.1$ Hz), 68.3 ($\mathit{C}H_2OAr$), 115.2 (ortho to O), 133.9 (ortho to CN), 162.3 (ipso to O).

4-(*n*-7,7,8,8,9,9,10,10,11,11,12,12,12-Tridecafluorododecan-1-yloxy)benzonitrile (6b−6/6). Recrystallization from cold MeOH yielded 0.78 g (77%) of white flakes. TLC (5:1 hexanes:ethyl acetate) $R_f = 0.39$. ^1H NMR ($CDCl_3$, TMS, δ, ppm) 1.46−1.56 (m, 6H, $CF_2CH_2(C\mathit{H}_2)_3$), 1.81 (m, 2H, $C\mathit{H}_2CH_2OAr$), 2.18 (m, 2H, $CF_2C\mathit{H}_2$), 4.01 (t, 2H, $C\mathit{H}_2OAr$, $J = 6.3$ Hz), 6.96 (d, 2H, ortho to O, $J = 6.9$ Hz), 7.61 (d, 2H, ortho to CN, $J = 6.8$ Hz); ^{13}C NMR ($CDCl_3$, δ, ppm) 20.1 ($CF_2CH_2\mathit{C}H_2$), 25.7 ($\mathit{C}H_2CH_2CH_2OAr$), 28.8 ($CF_2CH_2\mathit{C}H_2$ and $\mathit{C}H_2CH_2OAr$), 30.8 (t, $CF_2\mathit{C}H_2$, $J = 22.1$ Hz), 68.1 ($\mathit{C}H_2OAr$), 104.0 (ipso to CN), 115.2 (ortho to O), 118.9 ($\mathit{C}N$), 133.9 (ortho to CN) 162.3 (ipso to O).

4-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluorododecan-1-yloxy)benzonitrile (6b−4/8). Recrystallization from cold MeOH yielded 0.41 g (69%) as white flakes. TLC (5:1 hexanes:ethyl acetate) $R_f = 0.26$. ^1H NMR ($CDCl_3$, TMS, δ, ppm) 1.89 (m, 4H, $CF_2CH_2(C\mathit{H}_2)_2$), 2.18 (m, 2H, $CF_2C\mathit{H}_2$), 4.05 (t, 2H, $C\mathit{H}_2OAr$, $J = 5.5$ Hz), 6.96 (d, 2H, ortho to O, $J = 8.8$ Hz), 7.57 (d, 2H, ortho to CN, $J = 8.8$ Hz); ^{13}C NMR ($CDCl_3$, δ, ppm) 17.1 ($CF_2CH_2\mathit{C}H_2$), 28.4 ($\mathit{C}H_2CH_2OAr$), 30.5 (t, $CF_2\mathit{C}H_2$, $J = 22.4$ Hz), 67.6 ($\mathit{C}H_2OAr$), 104.1 (ipso to CN), 115.1 (ortho to O), 119.1 ($\mathit{C}N$), 133.9 (ortho to CN), 162.1 (ipso to O).

4-Fluoro-(12,12,12,11,11,10,10,9,9,8,8,7,7,6,6,5,5-Heptadecafluorododecan-1-yloxy)benzene (6d−4/8). Recrystallization from cold MeOH yielded 0.36 g (62%) of a white powder. TLC (5:1 hexanes:ethyl acetate) $R_f = 0.64$. ^1H NMR ($CDCl_3$, TMS, δ, ppm) 1.87 (m, 4H, $CF_2CH_2(C\mathit{H}_2)_2$), 2.16 (m, 2H, $CF_2C\mathit{H}_2$), 3.96 (t, 2H, $C\mathit{H}_2OAr$, $J = 5.6$ Hz), 6.86 (dd, 2H, ortho to O, $J_{H-H} = 6.92$ Hz, $J_{H-F} = 4.4$ Hz), 6.98 (dd, 2H, ortho to O, $J_{H-H} = 8.2$ Hz, $J_{H-F} = 5.7$ Hz); ^{19}F NMR ($CDCl_3$, δ, ppm) −81.3 (t, 3F, $C\mathit{F}_3$, $J = 10.0$ Hz), −115.0 (m, 2F, $C\mathit{F}_2CH_2$), −122.4 (m, 6F, $(C\mathit{F}_2)_3CF_2CH_2$), −123.3 (m, 2F, $CF_3CF_2CF_2C\mathit{F}_2$), −124.1 (m, 6F, $CF_3CF_2C\mathit{F}_2$), −124.4 (s, 1F, $Ar\mathit{F}$), −126.7 (m, 6F, $CF_3C\mathit{F}_2$); ^{13}C NMR ($CDCl_3$, δ, ppm) 18.5 ($CF_2CH_2\mathit{C}H_2$), 28.4 ($\mathit{C}H_2CH_2OAr$), 30.5 (t, $CF_2\mathit{C}H_2$, $J = 22.4$ Hz), 67.6 ($\mathit{C}H_2OAr$), 115.1, 116.0 (ortho to O, F), 155.1, 159.8 (ipso to O, F).

4-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluorododecan-1-yloxy)methoxybenzene (6d−4/8). Recrystallization from cold MeOH yielded 0.40 g (67%) of a white powder. TLC (5:1 hexanes:ethyl acetate) $R_f = 0.64$. ^1H NMR ($CDCl_3$, TMS, δ, ppm) 1.86 (m, 4H, $CF_2CH_2(C\mathit{H}_2)_2$), 2.16 (m,

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[19] Percec, V.; Johansson, G.; Ungar, G.; Zhou, J. P. *J. Am. Chem. Soc.*, in press.

2H, CF_2CH_2), 3.77 (s, 3H, OCH_3), 3.95 (t, 2H, CH_2OAr, $J =$ 5.6 Hz), 6.84 (s, 4H, ortho to O); ^{13}C NMR ($CDCl_3$, δ, ppm) 17.3 ($CF_2CH_2CH_2$), 28.9 (CH_2CH_2OAr), 30.7 (t, CF_2CH_2, $J =$ 22.6 Hz), 55.6 (OCH_3), 67.9 (CH_2OAr), 114.7, 115.5 (ortho to O), 153.1, 154.1 (ipso to O).

4-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluorododecan-1-yloxy)benzoic Acid (8−4/8). To **6c−4/8** (3.0 g, 4.8 mmol) in 30 mL of 95% EtOH was added 3 mL of 10 N aqueous KOH solution, and the reaction was heated to reflux. After 2 h, the mixture was cooled to room temperature and dissolved by addition of THF. The solution was acidified with concentrated HCl, concentrated on a rotary evaporator, and poured into water. After filtration, the resultant white solid was recrystallized from cold acetone to yield 2.65 g (94%) of white needles with limited solubility in $CDCl_3$ and THF. TLC (5:1 hexanes:ethyl acetate) $R_f = 0.11$. ^1H NMR ($CDCl_3$, TMS, δ, ppm) 1.90 (m, 4H, $CF_2CH_2(CH_2)_2$), 2.17 (m, 2H, CF_2CH_2), 4.09 (t, 2H, CH_2OAr, $J =$ 5.6 Hz), 6.92 (d, 2H, ortho to O, $J =$ 8.8), 8.03 (d, 2H, ortho to CO_2, $J =$ 8.8Hz).

4-Hydroxy-3-methylacetophenone (10). Compound **10** was synthesized in two steps by acylation of **9** with acetic anhydride followed by a Fries rearrangement to **10**.[20] To a solution of **9** (10.8 g, 0.100 mmol) in a mixture of 50 mL of 3 N NaOH and 200 g of crushed ice was added acetic anhydride (15 mL, 0.16 mol). The solution was allowed to warm to room temperature. After acidification with concentrated HCl, the product was extracted two times with Et_2O, washed twice with H_2O, and dried over $MgSO_4$. The solvent was removed on a rotary evaporator, and the product was purified by vacuum distillation to yield 11.1 g (74%) of the acetate as a clear oil. To a solution of the acetate (11.1 g, 73.9 mmol) in 45 mL of nitrobenzene was added $AlCl_3$ (11.1 g, 83.0 mmol) portionwise. The reaction was periodically cooled with a MeOH−dry ice bath during addition. After complete addition, the reaction mixture was stirred at room temperature for 20 h after which time it was quenched by pouring into a mixture of ice and 10% HCl. The product was extracted with CH_2Cl_2, washed with H_2O, and dried over $MgSO_4$. The solvent was removed by distillation, and the product recrystallized from a mixture of hexanes and ethyl acetate to yield 7.70 g (70%) of a crystalline material, mp 104−105 °C, lit.[21] mp 104 °C. ^1H NMR ($CDCl_3$, TMS, δ, ppm) 2.29 (s, 3H, $ArCH_3$), 2.56 (s, 3H, CH_3CO), 5.9 (br s, 1H, OH), 6.85 (d, 2H, ortho to O, $J =$ 8.3 Hz), 7.77 (d, 2H, ortho to CO, $J =$ 8.4 Hz), 7.79 (s, 1H, ortho to CH_3); ^{13}C NMR ($CDCl_3$, δ, ppm) 15.7 ($ArCH_3$), 36.0 (CH_3CO), 114.9 (ortho to OH), 124.8 (ipso to CH_3), 129.7 (para to CH_3), 129.8 (ipso to $COCH_3$), 132.0 (ortho to CH_3), 160.0 (ipso to OH), 199.3 ($COCH_3$).

4-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluorododecan-1-yloxy)-3-methylacetophenone (11−4/8). Compound **11−4/8** was synthesized according to the general procedure described for the synthesis of **6a−4/8**. Recrystallization from cold MeOH yielded 2.5 g (70%) of a white powder. TLC (5:1 hexanes:ethyl acetate) $R_f = 0.28$; ^1H NMR ($CDCl_3$, TMS, δ, ppm) 1.92 (m, 4H, $CF_2CH_2(CH_2)_2$), 2.17 (m, 2H, CF_2CH_2), 2.25 (s, 3H, $ArCH_3$), 2.55 (s, 3H, $ArCOCH_3$), 4.08 (t, 2H, CH_2OAr, $J =$ 5.4 Hz), 6.84 (d, 2H, ortho to O, $J =$ 8.5 Hz), 7.79−8.83 (overlapped peaks, 2H, ortho to CO); ^{13}C NMR ($CDCl_3$, δ, ppm) 16.1 ($ArCH_3$), 17.3 ($CF_2CH_2CH_2$), 26.2 ($COCH_3$), 28.6 (CH_2CH_2OAr), 30.7 (t, CF_2CH_2, $J =$ 22.6 Hz), 67.4 (CH_2OAr), 109.9 (ortho to O), 124.0 (ipso to CH_3), 128.4 (para to CH_3), 130.2 (ipso to $COCH_3$), 131.0 (ortho to CH_3), 133.9 (ortho to CN), 162.1 (ipso to O).

4-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluorododecan-1-yloxy)-3-methylbenzoic Acid (12−4/8). Oxidation of **11−4/8** was carried out in two steps by first preparing the 1-phenacylpyridinium iodide followed by hydrolysis with ethanolic NaOH.[22] To a solution of **11−4/8** (1.64 g, 2.48 mmol) in 16 mL of pyridine was added I_2 (0.63 g, 2.48 mmol). The mixture was heated at 100 °C for 5 h, after which time conversion was determined to be 85% by ^1H NMR analysis. After 16 h, additional I_2 (0.5 g, excess) was added, and stirring was continued for 6 h. The reaction was cooled to room temperature, poured into H_2O, and filtered. The crude product was dried on the filter. The pyridinium iodide was dissolved in 20 mL of 50% aqueous EtOH to which NaOH (1.5 g, excess) was added. The mixture was heated at reflux for 1.5 h and subsequently cooled to room temperature. After acidification with 10% HCl, the precipitate was collected by vacuum filtration. After recrystallization from cold MeOH, 0.88 g (57%) of a light yellow powder was obtained. TLC (5:1 hexanes:ethyl acetate) $R_f = 0.28$; ^1H NMR ($CDCl_3$, TMS, δ, ppm) 1.93 (m, 4H, $CF_2CH_2(CH_2)_2$), 2.25 (overlapped peaks, 5H, CH_3 and CF_2CH_2), 4.09 (t, 2H, CH_2OAr, $J =$ 5.6 Hz), 6.86 (d, 2H, ortho to O, $J =$ 8.5 Hz), 7.91 (s, 1H, ortho to CH_3), 7.93 (d, 1H, ortho to CO_2H, $J =$ 8.4 Hz).

4-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluorododecan-1-yloxy)-3-methylbenzonitrile (13−4/8). Compound **12−4/8** was converted to **13−4/8** with chlorosulfonyl isocyanate in the presence of catalytic DMF.[23] Compound **12−4/8** (0.50 g, 0.80 mmol) was suspended in 5 mL of CH_2Cl_2. Freon 113 (6 mL) was added until a homogeneous solution was obtained. Chlorosulfonyl isocyanate (0.10 mL, excess) was added and the mixture was heated at reflux for 1 h. The reaction vessel was immersed in an ice-water bath, and several drops of DMF was added. The reaction mixture was stirred for an additional 15 min and then poured into ice-water. The organic layer was separated and washed three times with water, dried over $MgSO_4$, and filtered. The solvent was removed on a rotary evaporator, and the resultant solid was purified by flash column chromatography (SiO_2, CH_2Cl_2) to yield 0.22 g (47%) of a white powder. TLC (5:1 hexanes:ethyl acetate) $R_f = 0.42$; ^1H NMR ($CDCl_3$, TMS, δ, ppm) 1.91 (m, 4H, $CF_2CH_2(CH_2)_2$), 2.22 (overlapped peaks, 5H, CH_3 and CF_2CH_2), 4.06 (t, 2H, CH_2OAr, $J =$ 5.4 Hz), 6.85 (d, 2H, ortho to O, $J =$ 8.4 Hz), 7.43 (s, 1H, ortho to CH_3), 7.46 (d, 1H, ortho to CN, $J =$ 8.4 Hz); ^{13}C NMR ($CDCl_3$, δ, ppm) 15.8 ($ArCH_3$), 17.3 ($CF_2CH_2CH_2$), 28.5 (CH_2CH_2OAr), 30.6 (t, CF_2CH_2, $J =$ 22.2 Hz), 67.5 (CH_2OAr), 103.6 (ipso to CN), 110.8 (ortho to O), 119.4 (CN), 124.0 (ipso to CH_3), 128.2 (para to CH_3), 131.9 (ortho to CH_3), 134.0 (ortho to CN), 160.3 (ipso to O).

Results and Discussion

Synthesis. A systematic approach to the synthesis of rodlike liquid crystals based on a single alkoxybenzene unit relies on the ability to prepare semifluorinated alkyl bromides with varying ratios (m/n) of their perhydrogenated [$(CH_2)_m$] to perfluorinated [$F(CF_2)_n$] segments. The overall chain length ($m + n$) should be controllable as well.

Scheme 2 outlines our preferred synthesis of semifluorinated alkyl bromides, **4-*m*/*n*** ($m + n = 12$; $m =$ number of perhydrogenated methylenic units; $n =$ number of perfluorinated methylenic units). This general synthetic procedure can be adapted to a variety of commercially available or synthetically accessible[7] α-alken-ω-ols and perfluoroalkyl iodides to produce semifluorinated alkyl bromides of variable chain lengths. Compound **2−8/4** was obtained by the mild, $(Ph_3P)_4Pd^0$-catalyzed radical addition[24] of *n*-perfluorobutyl iodide to 7-octen-1-ol (**1−8**). The synthesis of **1−8** was reported in detail elsewhere.[7] We prefer this method over the conventional one which uses radical initiators such as peroxides or azo compounds,[25] since our procedure requires lower temperatures and shorter reaction times,

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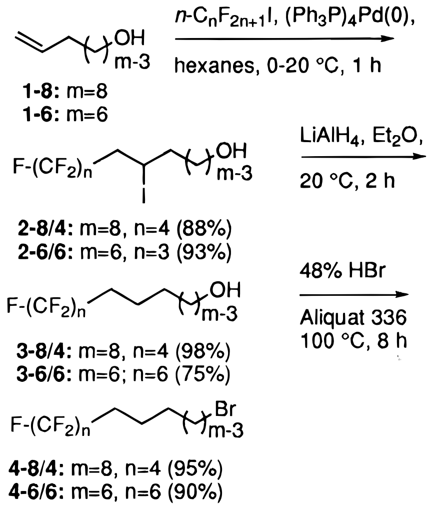
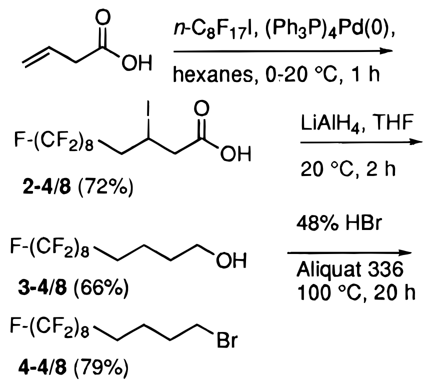
Scheme 2. Synthesis of 4-*m*/*n*



Scheme 3. Synthesis of 4−4/8



tolerates many functional groups, and is generally more selective. Similarly, from commercially available 5-hexen-1-ol (**1−6**) and *n*-perfluorohexyl iodide, **2−6/6** was obtained in 93% yield. The reduction of the iodo group of **2-*m*/*n*** with LiAlH$_4$ afforded the semifluorinated alcohols, **3-*m*/*n***, in 98% and 75% yields. Bromination of **3-*m*/*n*** with 48% HBr and Aliquat 336 as a phase-transfer catalyst (PTC)[26] gave **4−8/4** and **4−6/6** in 95% and 90% yields, respectively.

Scheme 3 outlines the synthesis of **4−4/8**. The low cost and high purity of the commercially available vinylacetic acid make this synthetic procedure very suitable for these investigations compared to the more expensive and less synthetically accessible α-alken-ω-ols required for $m > 4$. Compound **2−4/8** was obtained in 72% yield by the (Ph$_3$P)$_4$Pd^0-catalyzed radical addition of *n*-perfluorooctyl iodide to vinylacetic acid. One-pot reduction of the iodo and carboxylic acid groups of **2−4/8** with LiAlH$_4$ afforded **3−4/8** in 66% yield. Finally, PTC-catalyzed bromination of **3−4/8** gave **4−4/8** in 79% yield.

Scheme 4 outlines the general method for the synthesis of 4-substituted *n*-perfluoroalkoxybenzenes with varying alkyl chain length ($m + n = 10$ or 12) and degree of perfluorination (m/n) in their alkoxy tail. Alkylation of various 4-substituted phenols by the semifluorinated alkyl bromides was accomplished in good-to-excellent yield in DMF with K$_2$CO$_3$ as base. Typical reaction times and temperatures were 2−4 h at 65 °C. Benzyl alcohols, **7−4/6** and **7−4/8**, were obtained in 89% and 75% yield by LiAlH$_4$ reduction of the corresponding methyl esters (**6c−4/6**, **6c−4/8**). Compound **8−4/8** was obtained by basic hydrolysis of the methyl ester group of **6c−4/8** in ethanolic KOH.

To investigate the effect of lateral substitution of the benzene ring on the mesomorphic behavior of this class of liquid crystals, the 3-methylated benzonitrile, **13−4/8**, was synthesized (Scheme 5). Esterification of **9** with (Ac)$_2$O followed by Fries rearrangement under kinetically controlled conditions[20] gave **10** in 52% overall yield. Alkylation of **10** with **4−4/8** in DMF in the presence of K$_2$CO$_3$ afforded the ketone **11−4/8** in 70% yield. Selective oxidation of **11−4/8** to the carboxylic acid **12−4/8** was accomplished in two steps.[22] First **11−4/8** was transformed into its 1-phenacylpyridinium iodide with I$_2$/pyridine followed by hydrolysis in 50% ethanolic NaOH. After acidification, **12−4/8** was obtained in 57% overall yield. Other methods such as KMnO$_4$ or haloform oxidation were not suitable for this reaction due to the lability of the 3-methyl substituent. In the final step, conversion of **12−4/8** to the benzonitrile **13−4/8** was accomplished in 48% yield by in situ formation of the *N*-chlorosulfonylbenzamide from chlorosulfonyl isocyanate and **12−4/8** followed by DMF-catalyzed elimination of SO$_3$ and HCl.[23]

Thermal and Optical Characterization. The phase behavior of the series of 4-substituted alkoxybenzenes was determined by a combination of DSC, thermal optical polarized microscopy, and for selected samples X-ray diffraction experiments to be discussed in the following subsection. The temperature transitions and the corresponding enthalpy changes from the second heating and first cooling DSC scans are reported in Table 1. Since the first heating scans were identical with the second heating scans, they are not reported unless otherwise noted. Second heating and first cooling DSC scans for all liquid-crystalline compounds are shown in Figure 1a,b, respectively.

Compound **12F8PhNO$_2$** (X = NO$_2$) displays a monotropic s$_A$ mesophase. The crystalline melting endotherm is observed at 73 °C on heating. On cooling, the s$_A$ mesophase appears at 69 °C followed by crystallization at 44 °C. Replacement of the NO$_2$ substituent with a CN group has little effect on the phase behavior. Compound **12F8PhCN** (X = CN) melts at 72 °C into a s$_A$ mesophase which is observable only over a very narrow temperature range of 1 °C during the second heating scan. On cooling from the isotropic melt, the s$_A$ mesophase forms at 70 °C.

Characterization of **12F8PhNO$_2$** and **12F8PhCN** by thermal optical polarized microscopy provides some very important information. Samples were prepared by sandwiching the powdered material between untreated glass slides. On cooling from the isotropic melt, a transient flash of birefringence was observed at the isotropic−s$_A$ transition accompanied by a very rapid homeotropic alignment. The birefringent domains induced by mechanical shearing relaxed almost instantaneously back to the homeotropic state when the strain was removed. Upon further cooling to the s$_A$−crystalline transition temperature, the growth of spherulites was observed. The rapid and complete homeotropic alignment of **12F8PhNO$_2$** and **12F8PhCN** most probably arises from a strong incompatibility between the

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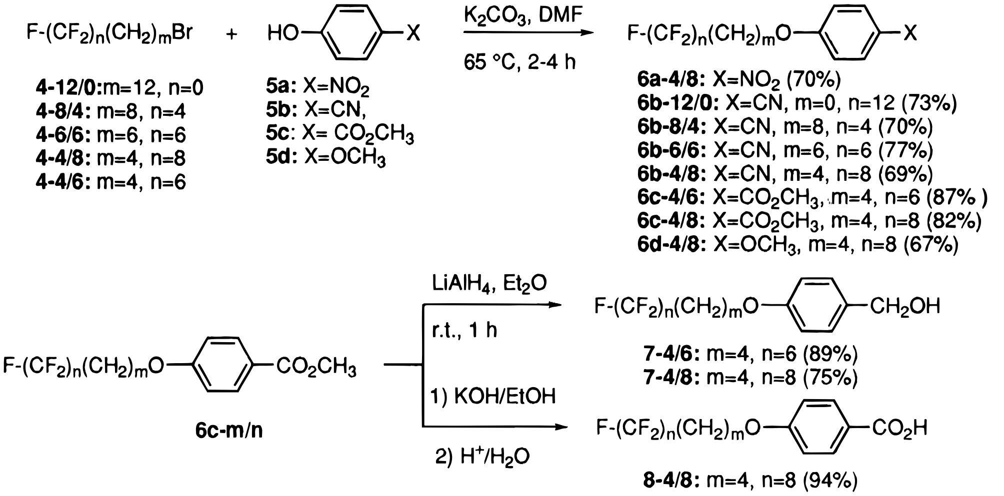
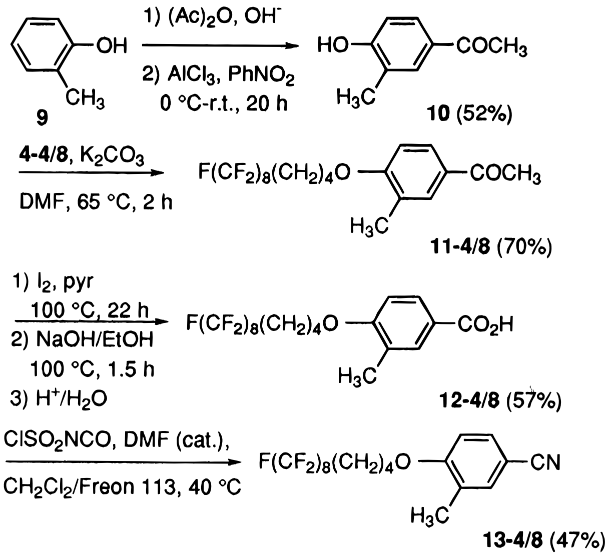
Scheme 4. Synthesis of Perfluoroalkylated Liquid Crystals 6-*m*/*n*, 7-*m*/*n*, and 8-*m*/*n*



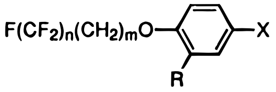
Scheme 5. Synthesis of Liquid Crystals, 11-*m*/*n*, 12-*m*/*n*, and 13-*m*/*n*



high energy surface of the untreated glass substrate and the low-energy interface of the perfluoroalkane segments of the liquid-crystalline material. A sample of **12F8PhNO$_2$** was sandwiched between polyimide-coated glass slides and slowly cooled from the isotropic melt. Figure 2 shows the characteristic focal–conic texture observed for the s$_A$ phase of **12F8PhNO$_2$** at 67 °C. A similar texture is displayed in Figure 3 for the s$_A$ phase of **12F8PhCN** observed at 66 °C between polyimide-treated glass slides. Some homeotropic alignment remains as evidenced by the presence of discontinuous, optically isotropic domains within the sample.

Compounds **10F6PhCO$_2$CH$_3$** and **12F8PhCO$_2$CH$_3$** (X = CO$_2$CH$_3$) display enantiotropic s$_A$ mesophases with clearing temperatures of 58 and 81 °C, respectively. The higher isotropization temperature of **12F8PhCO$_2$CH$_3$** with respect to **10F6PhCO$_2$CH$_3$** can be attributed to its increased perfluoroalkyl chain length.[2b,c,e,f,h] Conventional liquid crystals derived from mesogenic units which contain at least two aromatic units connected by a suitable linking group typically exhibit transition

Table 1. Thermal Characterization of Perfluoroalkylated Liquid Crystals



entry	name	*m*	*n*	R	X	yield (%)	phase transitions (°C) and corresponding enthalpy changes (in parentheses, kcal/mol)[a]	
3a–4/8	12F8PhNO$_2$	4	8	H	NO$_2$	70	k 73 (9.22) i	i 69 (0.63) s$_A$ 44 (7.49) k
3b–12/0	12PhCN	12	0	H	CN	73	k 42–44 i	
3b–8/4	12F4PhCN	8	4	H	CN	70	k 46 (9.53) i	i 30 (9.10) k
3b–6/6	12F6PhCN	6	6	H	CN	77	k 70 (10.2) i	i 55 (10.1) k
3b–4/8	12F8PhCN	4	8	H	CN	69	k 72 (9.35)[b] s$_A$ 73 (–) i	i 70 (0.79) s$_A$ 52 (7.63) k
3c–4/6	10F6PhCO$_2$CH$_3$	4	6	H	CO$_2$CH$_3$	87	–k 29 (0.58) k 54 (7.15) s$_A$ 58 (1.54) i[c] k$_1$ 44 (2.17) –k 45 k$_2$ 54 (6.54) s$_A$ 58 (1.43) i	i 53 (1.50) s$_A$ 17 (5.11) k
3c–4/8	12F8PhCO$_2$CH$_3$	4	8	H	CO$_2$CH$_3$	82	k 69 (6.35) s$_A$ 81 (1.45) i	i 75 (1.48) s$_A$ 52 (5.71) k
3d–4/8	12F8PhOCH$_3$	4	8	H	OCH$_3$	67	k 67 (6.43) i	i 52 (6.27) k
4–4/6	10F6PhCH$_2$OH	6	4	H	CH$_2$OH	89	k 62 (5.33) i	i 55 (0.16) s$_A$ 51 (4.86) k
4–4/8	12F8PhCH$_2$OH	4	8	H	CH$_2$OH	75	k 91 (6.70) i	i 88 (0.20) s$_A$ 81 (6.18) k
5–4/8	12F8PhCO$_2$H	4	8	H	CO$_2$H	94	k 165 (0.36) s 178 (3.36) s$_C$ 190 (–) s$_A$ 193 (2.83)[b] i	i 189 (2.15) s$_A$ 184 (0.11) s$_C$ 173 (3.31) s 152 (0.11) k
8–4/8	12F8Ph(Me)COCH$_3$	4	8	Me	COCH$_3$	70	k 61 (7.27) i k 51 (7.39) i	i 46 (0.53) s$_A$
9–4/8	12F8Ph(Me)CO$_2$H	4	8	Me	CO$_2$H	57	k 129 (4.39) s$_C$, s$_A$ 152 (1.25) i	i 147 (1.25) s$_A$, s$_C$ 116 (4.45) k
10–4/8	12F8Ph(Me)CN	4	8	Me	CN	47	k 53 (7.56) i[c] k 53 (7.69)[b] s$_A$ 55 (–) i	i 50 (0.90) s$_A$ 29 (6.03) k

[a] Data are from the first cooling and second heating scans unless otherwise noted. [b] Sum of overlapped transition enthalpies. [c] Data obtained during the first heating scan.

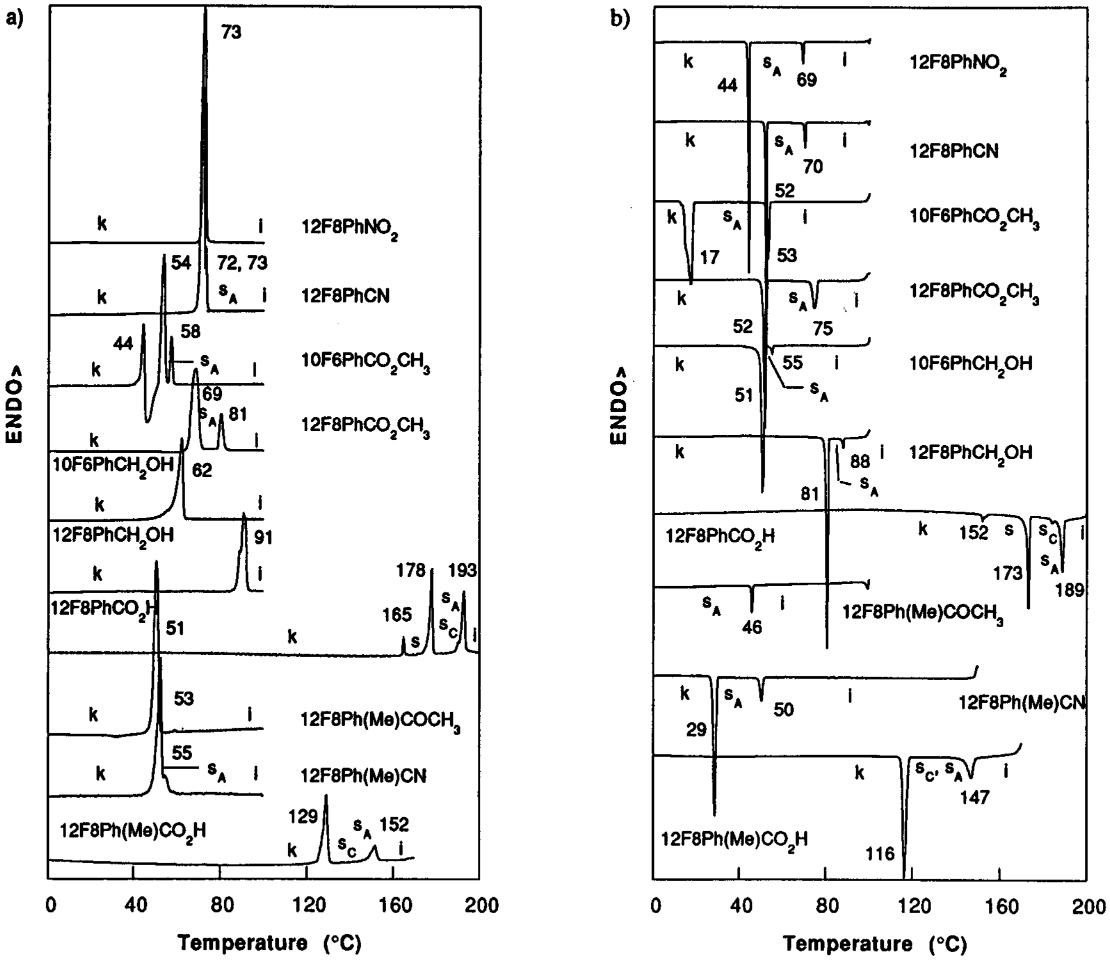


Figure 1. DSC traces (10 °C min^{-1}) of perfluoroalkylated liquid crystals recorded during the (a) second heating scan and (b) cooling scan.

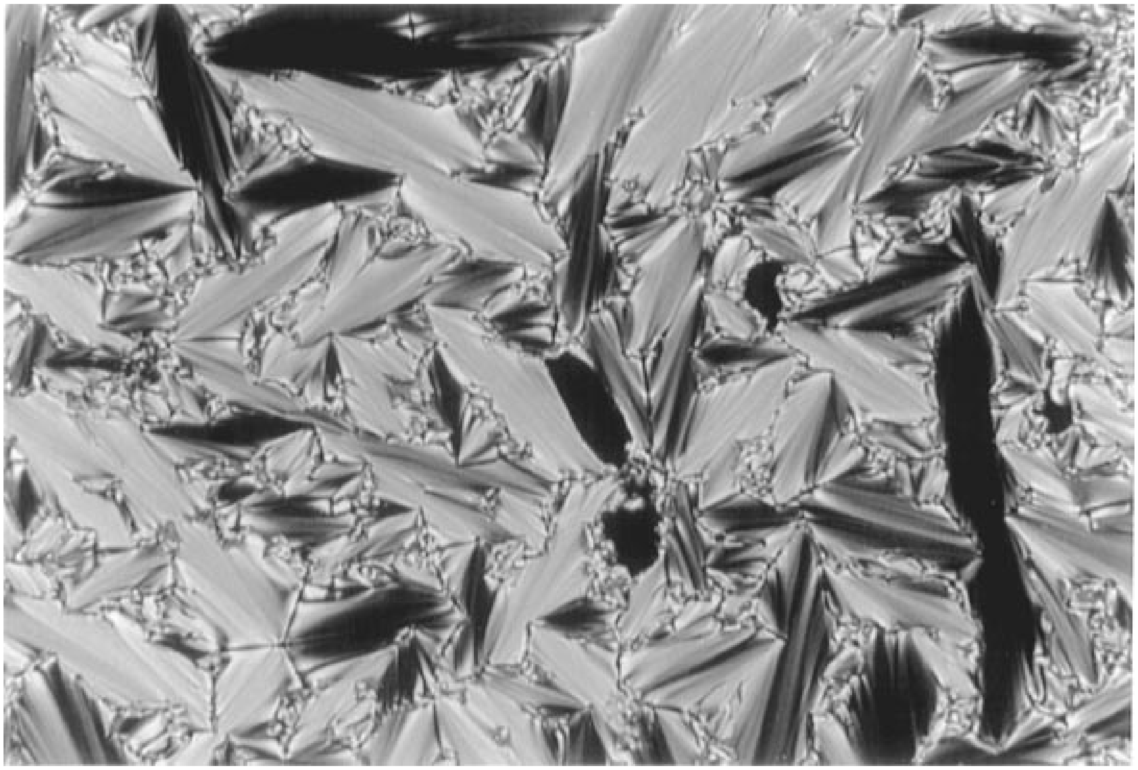


Figure 2. Focal-conic fan texture of the s$_A$ phase of **12F8PhNO$_2$** observed on cooling (10 °C min^{-1}) to 67 °C from the isotropic state; sample sandwiched between polyimide-coated glass slides.

temperatures which first increase in an odd–even manner as a function of the number of alkyl groups and then decrease until a plateau is reached. Replacement of the perhydrogenated alkyl chain with a perfluori-

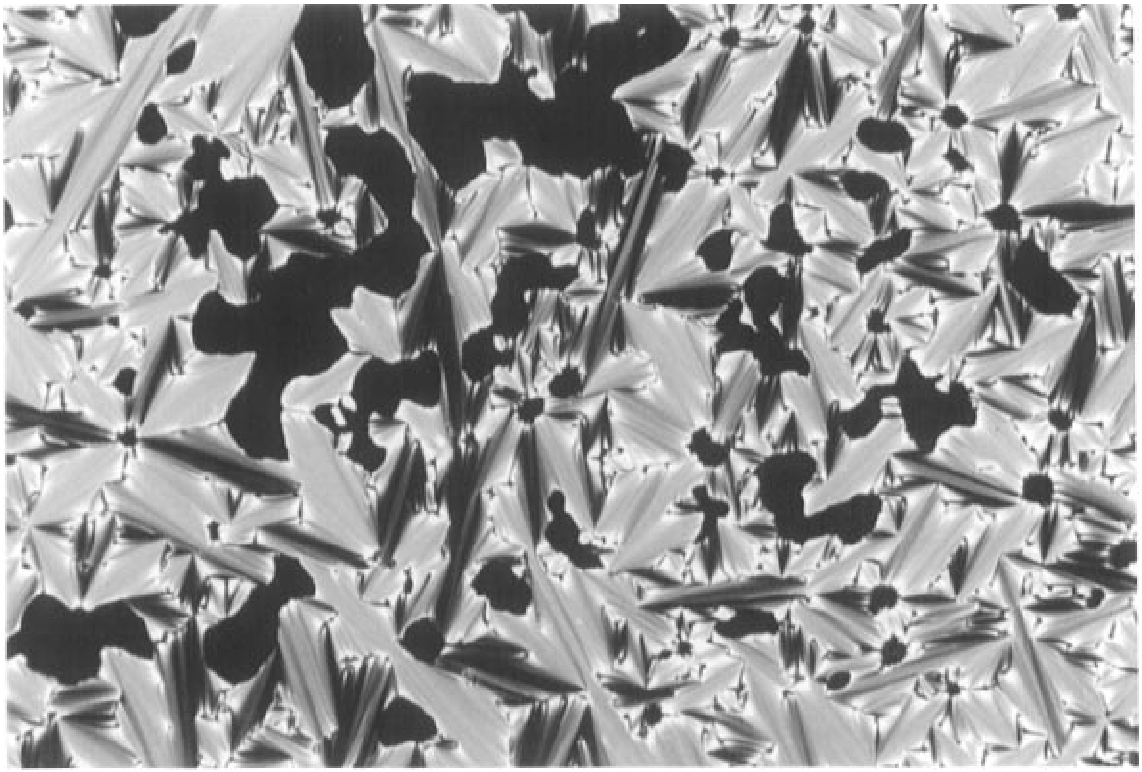


Figure 3. Focal-conic fan texture of the s_A phase of **12F8PhCN** observed on cooling (10 °C min^{-1}) to 66 °C from the isotropic state; sample sandwiched between polyimide-coated glass slides.

nated one results in a smectic–isotropic transition whose temperature increases dramatically and linearly with increasing the perfluoroalkyl chain length.[2c] On the basis of this result, the large increase in the isotropization temperature of **12F8PhCO$_2$CH$_3$** vs **10F6-PhCO$_2$CH$_3$** can be attributed predominantly to the increased length of the perfluoroalkyl segment, *n*, and to a lesser extent to the overall increase in the chain length, $m + n$. Optical micrographs of the focal conic textures of the s_A mesophase of **10F6PhCO$_2$CH$_3$** and **12F8PhCO$_2$CH$_3$** obtained on polyimide-treated glass slides are shown in Figures 4 and 5, respectively. Replacement of the methyl ester group of **12F8-PhCO$_2$CH$_3$** with a methoxy group as exemplified by **12F8PhOCH$_3$** (X = OCH$_3$) results in the complete loss of the liquid-crystalline phase.

Compounds **10F6PhCH$_2$OH** and **12F8PhCH$_2$OH** display a monotropic s_A mesophase. The isotropic–s_A transition temperature of the latter ($n = 8$) is 33 °C higher than the former ($n = 6$). However, in both cases the transition enthalpy is small ($\Delta H \approx 0.2$ kcal/mol). Attempts to obtain a nonhomeotropic alignment on treated and untreated glass slides were unsuccessful. The textures observed on polyimide treated glass slides were characterized by large, continuous homeotropic domains enclosing small, discontinuous, birefringent domains.

Compound **12F8PhCO$_2$H** is distinctive among the liquid crystals discussed so far. DSC analysis (Figure 1, Table 1) shows four transitions on both heating and cooling scans. On the basis of DSC, thermal optical polarized microscopy and X-ray diffraction analyses, the following phase sequence was assigned. **12F8PhCO$_2$H** is crystalline and melts at 165 °C into an as-yet undetermined high-order smectic mesophase. Such mesophases (e.g., s_B, s_E, s_H, s_K) are characterized by three-dimensional long-range order within the layer but weaker interlayer order.[11,12] Above 178 °C, a s_C mesophase is observed which undergoes a s_C–s_A transition at 190 °C. The s_A mesophase exists over a very narrow temperature range, and isotropization occurs at 193 °C. All of the transitions are observed on cooling with a low degree of supercooling (≤6 °C) with the exception of the smectic–crystalline transition which is supercooled by 13 °C. Examination of the enthalpies of transition provide support for the phase sequence. Low enthalpies of transition ($\Delta H < 0.4$ kcal/mol) are observed for the s_A–s_C and the smectic–crystalline transitions. This behavior is expected for transitions in which a small change in molecular order occurs. The anisotropic textures exhibited by **12F8PhCO$_2$H** on polyimide-treated glass slides are shown in Figure 6. Figure 6a shows the paramorphotic s_C texture obtained at 183 °C on cooling from the s_A mesophase. On further cooling to the s_C–smectic transition (Figure 6b), the texture undergoes a dramatic change from the focal conic texture to a mosaic texture characteristic of a higher ordered smectic phase. Figure 6c shows the appearance of the banded morphology within the mosaic texture observed on cooling **12F8PhCO$_2$H** below its crystallization temperature. **12F8PhCO$_2$H** displays the highest isotropization temperature and the broadest mesophase range of all of the examples presented in this series. Hydrogen-bonded dimers of *p*-alkoxy-substituted benzoic acids are a class of liquid crystals which form highly stable liquid-crystalline phases even in the absence of perfluoroalkylation.[10a]

The synthetic methodology outlined in this series of experiments has enabled us to evaluate the effect of the ratio, *m*/*n*, of the perhydrogenated to the perfluorinated segment length on the phase behavior. Inspection of the transition temperatures of **12FnPhCN** ($n = 0$, 4, 6,

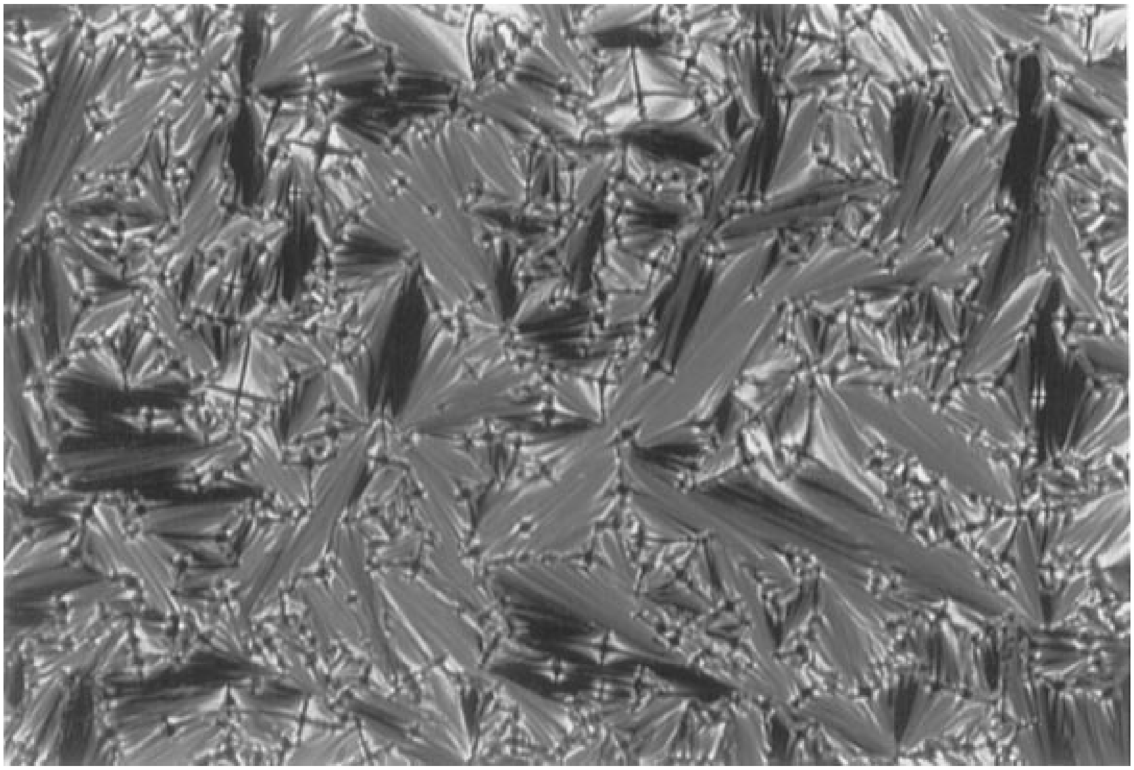


Figure 4. Focal-conic fan texture of the s_A phase of **$10F6PhCO_2CH_3$** observed on cooling (10 °C min^{-1}) to 50 °C from the isotropic state; sample sandwiched between polyimide-coated glass slides.

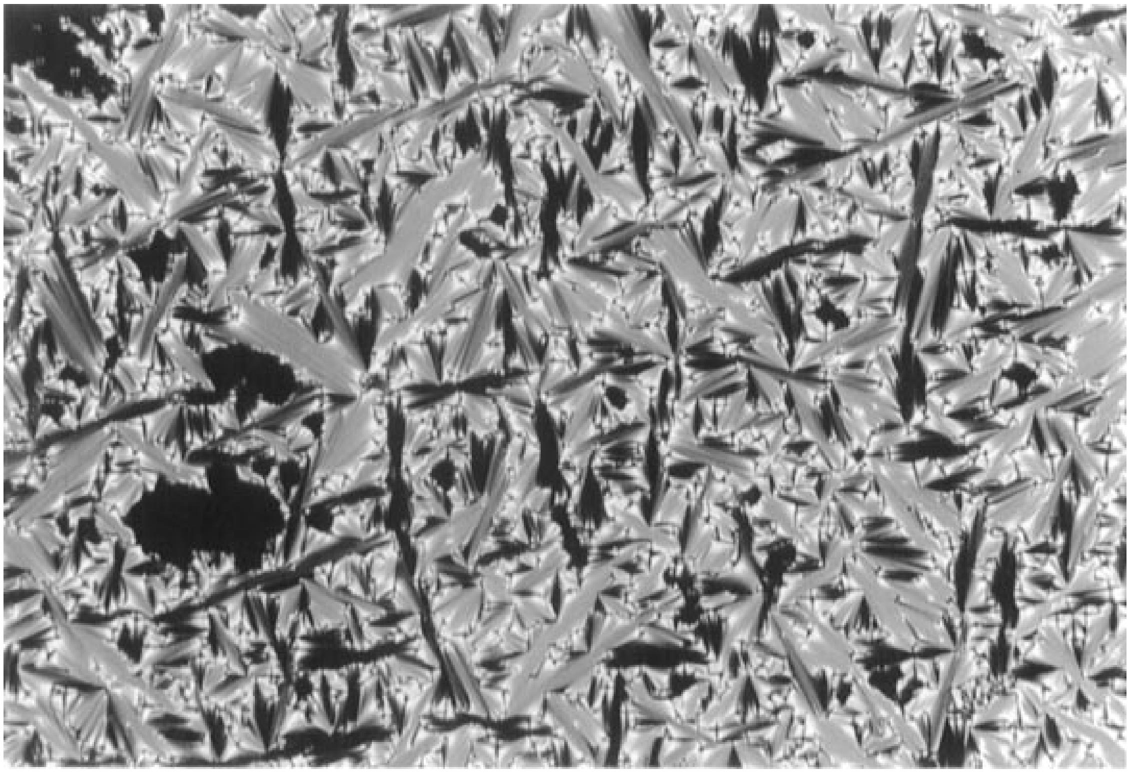


Figure 5. Focal-conic fan texture of the s_A phase of **$12F8PhCO_2CH_3$** observed on cooling (10 °C min^{-1}) to 50 °C from the isotropic state; sample sandwiched between polyimide-coated glass slides.

8) from Table 1 shows that as m/n decreases, a discontinuous increase of the melting temperature is observed. For $m \geq 1$, no mesomorphism is observed, while for the case of $m/n < 1$, a monotropic s_A mesophase is displayed. On the basis of the results of the present investigation and literature data[2f] perfluoroalkylalkoxy tails with $m/n < 1$ are most suitable for the generation of liquid-crystalline phases from mesogens containing a single benzene unit.

It was hoped that the introduction of a lateral methyl substituent on the benzene ring would facilitate the formation of a nematic mesophase by disrupting the lateral packing of the mesogenic units. **12F8Ph(Me)-$COCH_3$** and **$12F8Ph(Me)CO_2H$** are intermediates for

Figure 6. Textures observed on cooling **$12F8PhCO_2H$** from the isotropic state (10 °C min^{-1}); (a) the paramorphotic focal-conic fan texture of the s_C phase observed on cooling (10 °C min^{-1}) to 183 °C from the s_A phase; (b) the mosaic texture of the higher order smectic phase observed on cooling to 170 °C; (c) the banded mosaic texture observed on cooling to 148 °C. Sample sandwiched between polyimide-coated glass slides.

the preparation of **12F8Ph(Me)CN**. **$12F8Ph(Me)COCH_3$** and **12F8Ph(Me)CN** display a monotropic s_A mesophase with isotropic$-s_A$ transition temperatures of 46 and 50 °C, respectively. Comparison of **12F8PhCN** and **12F8Ph(Me)CN** shows that lateral substitution lowers as expected the isotropic$-s_A$ phase transition temperature by 20 °C. Characteristic focal conic textures were observed for the s_A mesophase of samples prepared on polyimide-treated glass slides.

DSC analysis of **$12F8Ph(Me)CO_2H$** (Figure 1, Table 1) shows that lateral substitution lowers the isotropization temperature of **$12F8PhCO_2H$** by 41 °C. The somewhat broad transition observed on isotropization is most probably due to an overlap of the s_C-s_A and s_A-isotropic phase transitions. The anisotropic texture displayed by **$12F8Ph(Me)CO_2H$** at 143 °C upon cooling from the isotropic melt is shown in Figure 7. The schlieren texture is indicative of a nematic or s_C mesophase. The schlieren texture of a s_C phase is indicated by the absence of $s = \pm{}^1\!/_2$ disclinations. Furthermore, the schlieren s_C texture is paramorphotic and generally observed on cooling a homeotropically aligned s_A mesophase.[11] In the case of **$12F8Ph(Me)CO_2H$**, the schlieren texture is observed on both untreated and polyimide-treated glass slides indicating that it forms on cooling from a homeotropically aligned s_A mesophase with a very narrow temperature range. A comparison of the phase transition temperatures of **$12F8Ph(Me)CO_2H$** and **$12F8PhCO_2H$** clearly shows the destabilization of the LC phase via lateral substitution.

X-ray Diffraction Analysis. Small- and wide-angle X-ray diffraction analyses on selected 4-substituted alkoxybenzenes from this series were carried out in order to verify the phase assignment and to provide information on the possible molecular packing arrangements within the liquid-crystalline phase. Powder diffraction patterns were obtained from samples that had been slowly cooled from the isotropic melt into their liquid-crystalline mesophase. All results are summarized in Table 2.

All compounds with the exception of **$12F8PhCH_2OH$** and **$10F6PhCH_2OH$** exhibit three reflections in their smectic phase with reciprocal *d* spacings in the ratio of 1:2:3. The smallest angle reflection represents the layer thickness and is indexed as d_{001}. At wide angles, a diffuse halo is observed at 5−6 Å corresponding to the distance between the disordered perfluoroalkyl chains.[3a,b] The molecular lengths from molecular models are summarized in Table 2 as well. For the case of **$12F8PhCO_2H$**, the molecular length is reported for a dimer in which H-bonding between the carboxylic acid moieties is assumed.

The ratio of the layer spacing, *d*, to the molecular length, *l*, is reported in Table 2. The values range between 1.3 and 1.7 for all of the compounds except **$12F8PhCO_2H$**. A value of $d/l > 1$ implies a bilayer structure for the s_A mesophase. Bilayer packing arrangements for the s_A mesophase of conventional liquid crystals such as 4-alkyl-4′-cyanobiphenyl which contains a highly polar CN group are well-known.[11] In these arrangements, slightly interdigitated head-to-head pairing of the dipoles leads to d/l ratios of ~1.4:1. **12F8Ph(Me)CN** has a significantly larger ratio of 1.68:1. Furthermore, **$12F8PhCO_2CH_3$** and **$12F8PhCH_2OH$** which contain nonpolar groups on the benzene ring pack into a bilayer arrangement as well. To account for the larger d/l ratios and the bilayer arrangement of nonpolar mesogenic groups, the packing arrangement for **$12F8PhCO_2CH_3$** shown in Figure 8 is proposed. The incompatibility of the perfluorinated and perhydrogenated/aromatic segments leads to a microphase segregated bilayer arrangement. Maximum overlap of the perfluorinated segments results in relatively high d/l ratios. Polar substituents are not required for this bilayer packing arrangement. In fact, the presence of highly polar substituents such as CN or NO_2 in which the dipole is directed parallel to the molecular long axis should result in a bilayer arrangement analogous to that

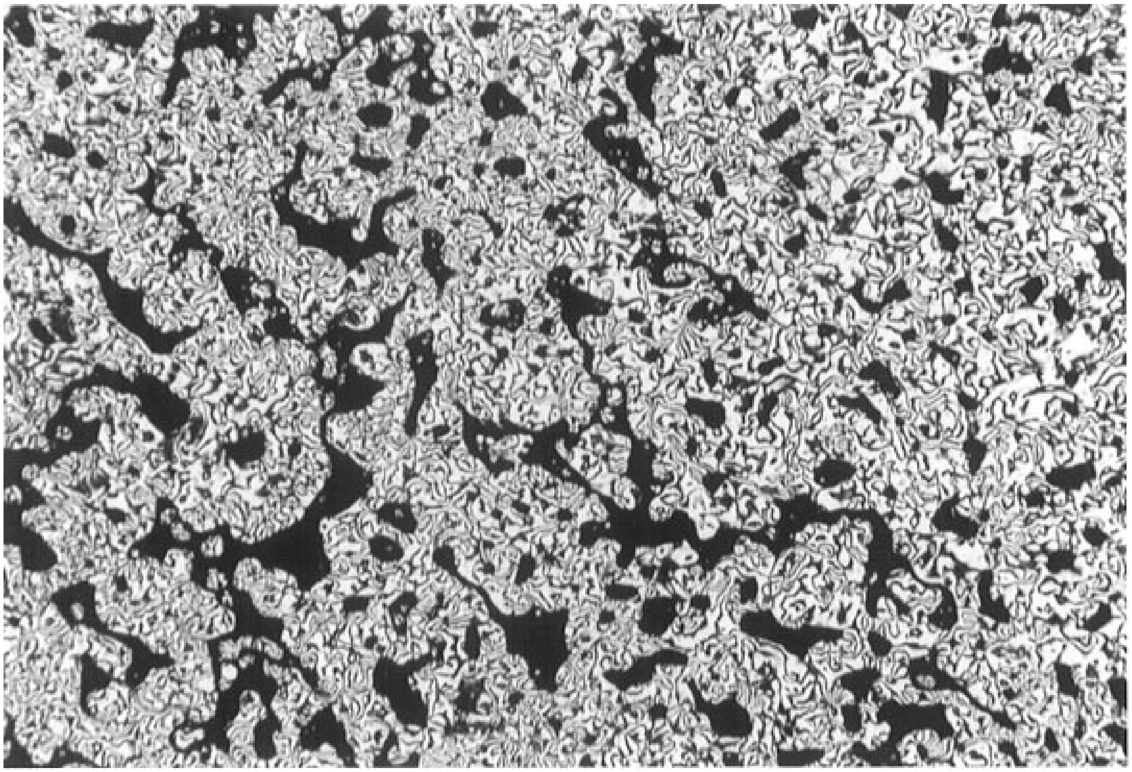


Figure 7. Schlieren texture of the s_C phase of **12F8Ph(Me)CO$_2$H** observed on cooling (10 °C min^{-1}) to 140 °C from the homeotropic s_A phase; sample sandwiched between polyimide-coated glass slides.

Table 2. X-ray Diffraction Analysis of Selected Fluoroalkylated Liquid Crystals

entry	name	*T* (°C)	d_{001} (Å)	d_{002} (Å)	d_{003} (Å)	layer (Å)	molecular length (Å)	ratio[a] *d*/*l*	phase
3c−4/6	**10F6PhCO$_2$CH$_3$**	50	28.2	14.1	9.38	28.2	22.1	1.28	bimolecular s_A
3c−4/8	**12F8PhCO$_2$CH$_3$**	75	33.3	16.5	11.0	33.1	24.6	1.35	bimolecular s_A
4−4/6	**10F6PhCH$_2$OH**	54−52[b]	32.9			32.9	20.8	1.58	bimolecular s_A
4−4/8	**12F8PhCH$_2$OH**	90−87	36.9			36.9	23.0	1.60	bimolecular s_A
5−4/8	**12F8PhCO$_2$H**	181	36.3	18.0	11.9	36.0	43.7[c]	0.82	dimeric s_C
5−4/8	**12F8PhCO$_2$H**	170				30.2	43.7	0.69	crystal H or K
8−4/8	**12F8Ph(Me)CO$_2$H**	138	35.8	17.6	11.7	35.5	43.7[c]	0.81	dimeric s_C
10−4/8	**12F8Ph(Me)CN**	50−45	36.3	17.9		36.1	22.6	1.60	bimolecular s_A
10−4/8	**12F8Ph(Me)CN**	33−29	38.1	19.0	12.6	38.0	22.6	1.68	bimolecular s_A

[a] Ratio of the layer spacing, *d*, to the molecular length, *l*. [b] Obtained during slow cooling at a constant rate. [c] Molecular length of the hydrogen-bonded dimer.

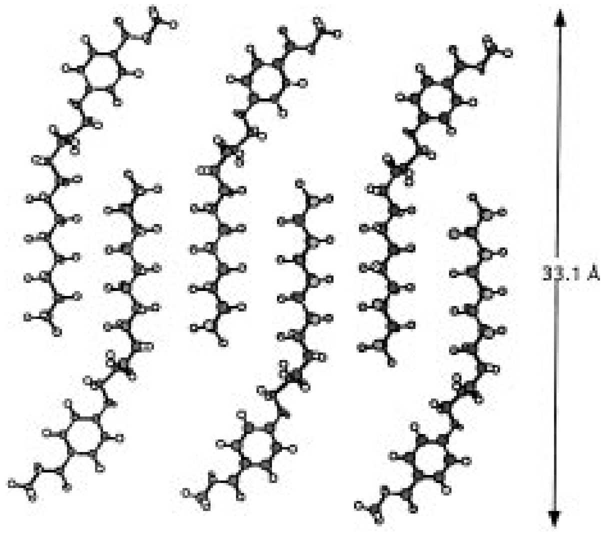


Figure 8. Proposed molecular arrangement of **12F8-PhCO$_2$CH$_3$** within the s_A layer.

in Figure 8 in which the polar groups are concentrated at the interface of the layers. To minimize repulsive interactions, partial interdigitation of the polar groups would be required, resulting in frustration of the layered packing arrangement. The proposed arrangement can explain the increased thermodynamic stability of the s_A phase of **12F8PhCO$_2$CH$_3$** relative to **12F8PhCN** and **12F8PhNO$_2$**.

12F8PhCO$_2$H and **12F8Ph(CH$_3$)CO$_2$H** were analyzed by X-ray diffraction in their s_C mesophase. For the former, three reflections were observed with a layer spacing of 36.0 Å. Accounting for temperature differences, the same layer spacing was observed for **12F8Ph(CH$_3$)CO$_2$H**. The *d*/*l* ratios for the H-bonded dimers are 0.82 and 0.81, respectively. Therefore, a tilt angle of 34.5° from the layer normal can be calculated. Analysis of **12F8PhCO$_2$H** at 170 °C which is in the higher order smectic mesophase showed a decrease in the layer thickness with increasing tilt angle.

Conclusions

A rational, versatile, and systematic approach to the synthesis of rodlike liquid crystals containing a single benzene unit has been described. The key structural element is the incorporation of an alkyl tail consisting of a perfluorinated/perhydrogenated block sequence of controlled length and ratio between the two components. The immiscibility of fluorocarbon and hydrocarbon segments along with the increased rigidity of the fluorocarbon segment is the basis of the fluorophobic effect. By increasing the overall rigidity of the mesogenic unit as well as promoting microphase segregation, perfluorination of the alkyl tail serves to facilitate the formation of enantiotropic s_A and s_C mesophases in this series of 4-substituted alkoxybenzenes. The ability to form lamellar liquid crystals requires a perhydrogenated/perfluorinated segment (m/n) ratio less than unity. Increasing the length ($m + n$) and amount of perfluorination of the alkoxy tail stabilizes the liquid-crystalline phases. Contrary to a previous report,[2f] lateral substitution on the benzene ring is not necessary to achieve mesomorphism and has a deleterious effect on the thermodynamic stability of the lamellar mesophases in this system. For these reasons, we consider these compounds to be the simplest class of rodlike liquid crystals. Many opportunities exist for the fine tuning of the structural parameters such as alkyl tail length, degree of perfluorination and the polarity, and functionality of the aromatic substituents. Such investigations can help to further elucidate the structural parameters required for stabilization of liquid-crystalline phases. The orientational dynamics of these materials seem to be quite rapid as observed by the instantaneous homeotropic realignment after shearing.

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