ELSEVIER

Journal of Fluorine Chemistry 85 (1997) 155–161

JOURNAL OF FLUORINE CHEMISTRY

Synthesis of 4-(1H,1H-perfluoroalkoxy)-4′-(6-methacryloyloxy-hexyloxy)-azobenzenes and their liquid crystalline intermediates

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Received 11 January 1997; accepted 18 June 1997

Abstract

The synthesis and characterization of 4-(1H,1H-perfluoroalkoxy)-4′-(6-methacryloyloxy-hexyloxy)-azobenzenes with different lengths of the fluorinated tail group (C_2–C_8) and their liquid crystalline intermediates, starting from 1H,1H-perfluoroalkyl-*p*-nitrophenyl-ethers, is described. The liquid crystalline properties of the compounds were studied by differential scanning calorimetry, polarizing optical microscopy and X-ray diffraction methods. In contrast with their non-fluorinated analogues, all the liquid crystalline products display smectic mesophases caused by the fluorination of the tail group. © 1997 Elsevier Science S.A.

Keywords: Azobenzenes; Fluorinated tails; Smectic mesophases; X-Ray diffraction

1. Introduction

Previously, we have described the synthesis of side-group liquid crystalline polymers (SGLCPs) with 4-trifluoromethoxy-azobenzene units as mesogenic side-groups [1], and have characterized their liquid crystalline properties [2,3]. The strong dependence of the type of mesophase on the length of the spacer group, as well as the enhanced ability to form smectic mesophases due to fluorination, which has also been reported for low-molecular-mass liquid crystals [4], led us to investigate the influence of the length of the fluorinated tail group on the phase behaviour of the resulting polymers. The synthesis was started from *p*-fluoroalkoxy-nitrophenyl ethers, which are not commercially available and had to be synthesized from *p*-nitrophenol and the sulphonic acid esters of the corresponding fluoroalcohols (tosylates, mesylates, triflates). The change in the nature of the leaving group is caused by a strong dependence of the reactivity on the chain length of the fluorinated alcohol under S_N2 conditions. All necessary variations of the synthetic route have been reported previously [5]. In this paper, we present the synthesis of the monomers and their intermediate products and discuss their mesophase behaviour.

2. Experimental details

2.1. General techniques

Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained on a Bruker WP 200 SY (200 MHz) spectrometer; ^{13}C broad-band decoupled NMR spectra were recorded on a Varian Gemini 300 (75 MHz) spectrometer. Internal hexamethyldisilazane (HMDS) was used as reference and the solvent was $CDCl_3$.

Elemental analyses (for F) were carried out according to a standard method.

The thermal behaviour of the products was investigated using a DSC 7 differential scanning calorimeter (Perkin–Elmer). The scanning rate of the heating and cooling runs was 20 K min^{-1}. The maximum of the differential scanning calorimetry (DSC) enthalpic peaks was taken as the phase transition temperature. For phase assignment, the samples were investigated by polarizing optical microscopy (Olympus) combined with a hot stage (Linkham TMHS 600). X-ray diffraction was carried out using a custom-made, temperature-controlled ($\Delta T = \pm 1$ K) chamber with a polaroid flat film camera at a variable distance (100–250 mm) from

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PII S0022-1139(97)00076-6

the sample. Nickel-filtered Cu $K\alpha$ radiation ($\lambda = 0.154$ nm) was focused by a pinhole.

2.2. *Synthesis*

2.2.1. *4-(1H,1H-Perfluoroalkoxy)-anilines (2)*

Method 1 (for **2a–2c**). To 27 mmol of $SnCl_2 \cdot 2H_2O$ and 20 ml of concentrated HCl placed in a flask, 13.5 mmol of the corresponding 1H,1H-perfluoroalkyl-*p*-nitrophenyl-ether (**1**) was slowly added at 100°C. The reaction mixture was stirred for 2 h at 100°C. After cooling to room temperature, 100 ml of water and NaOH were added to reach pH 10. The mixture was extracted with diethyl ether. The ether extracts were washed neutral with brine, dried over $MgSO_4$ and the solvent was distilled off in vacuum. The products can be used without further purification.

Method 2 (for **2c–2g**). A mixture of 20 mmol of **1**, 90 mmol of $SnCl_2 \cdot 2H_2O$ and 100 ml of ethanol was heated for 6 h under reflux. After cooling to room temperature, the mixture was slowly mixed with dilute $NaHCO_3$ to obtain pH 7–8. The rest of the process was identical to method 1.

The yield of the prepared aniline derivatives was not estimated and characterization was not carried out because of the ease of oxidation. The isolated products were immediately used for diazotization. Therefore the estimated yield of the products **3** was calculated over two steps based on the amount of **1** used.

2.2.2. *4-(1H,1H-Perfluoroalkoxy)-4′-hydroxy-azobenzenes (3)*

Method 3 (for **3a–3c**). Compound **2** (13.5 mmol) was dissolved with heating in a mixture of 5 ml of concentrated sulphuric acid and 5 ml of water and, after cooling, diazotized by adding dropwise a solution of 18 mmol of $NaNO_2$ in 5 ml of water at 0–5°C to the acid mixture. Coupling was carried out by slowly adding the clear diazotized solution to a solution of 14.5 mmol of phenol, 25 mmol of NaOH and 140 mmol of Na_2CO_3 in 100 ml of water at 0–5°C. It was sometimes necessary to add extra NaOH to avoid heavy formation of foam. After complete addition, the mixture was stirred for 1 h at 0–5°C. The yellow–orange coloured precipitate was filtered off, dried and recrystallized from *n*-hexane.

Method 4 (for **3d–3g**). Compound **2** (21 mmol) was dissolved with heating in a mixture of 60 ml of glacial acetic acid, 30 ml of concentrated HCl and 30 ml of water. After cooling to 0–5°C, diazotization occurred by adding dropwise a solution of 27 mmol of $NaNO_2$ in 30 ml of water to the acid solution. For coupling, the prepared diazotized solution was added to a stirred solution of 28 mmol of phenol, 75 mmol of NaOH, 95 mmol of Na_2CO_3 and 150 ml of water, and stirred for 1 h at 0–5°C. The yellow–orange to yellow–green coloured precipitate was filtered off, dried and purified by chromatography using a column with silica gel and CH_2Cl_2 as eluent.

Compound **3a**. Yield, 53% (methods 1 and 3). Analysis: calculated for $C_{14}H_{11}F_3N_2O_2$ (296.16): F, 19.24%; found: F, 19.25%. ^1H NMR δ: 7.79 (4H, H-Ar, m, $J = 9.5$ Hz); 6.96 (2H, H-Ar, m, $J = 8.9$ Hz); 6.85 (2H, H-Ar, m, $J = 8.7$ Hz); 4.34 (2H, CH_2, q, $^3J(HF) = 8$ Hz) ppm. ^{13}C NMR δ: 159, 158, 148, 147, 125, 124, 116, 115 (C-Ar); 120 (CF_3, q, $J(CF) = 195$ Hz); 66 (CH_2, q, $^2J(CF) = 36$ Hz) ppm.

Compound **3b**. Yield, 52% (methods 1 and 3). Analysis: calculated for $C_{15}H_{11}F_5N_2O_2$ (346.25): F, 27.43%; found: F, 27.46%. ^1H NMR δ: 7.80 (4H, H-Ar, m, $J = 9.5$ Hz); 6.98 (2H, H-Ar, m, $J = 8.9$ Hz); 6.87 (2H, H-Ar, m, $J = 8.5$ Hz); 4.43 (2H, CH_2, t, $^3J(HF) = 12$ Hz) ppm.

Compound **3c**. Yield, 50% (methods 1 and 3); 80% (methods 2 and 4). Analysis: calculated for $C_{16}H_{11}F_7N_2O_2$ (396.26): F, 33.56%; found: F, 33.38%. ^1H NMR δ: 7.83 (2H, H-Ar, m, $J = 9.1$ Hz); 7.79 (2H, H-Ar, m, $J = 8.9$ Hz); 6.98 (2H, H-Ar, m, $J = 8.9$ Hz); 6.87 (2H, H-Ar, m, $J = 8.9$ Hz); 4.46 (2H, CH_2, t, $^3J(HF) = 13$ Hz) ppm.

Compound **3d**. Yield, 70% (methods 2 and 4). Analysis: calculated for $C_{17}H_{11}F_9N_2O_2$ (446.27): F, 38.31%; found: F, 38.30%. ^1H NMR δ: 7.90 (2H, H-Ar, m, $J = 9$ Hz); 7.85 (2H, H-Ar, m, $J = 9$ Hz); 7.05 (2H, H-Ar, m, $J = 9$ Hz); 6.95 (2H, H-Ar, m, $J = 9$ Hz); 4.55 (2H, CH_2, t, $^3J(HF) = 12.6$ Hz) ppm.

Compound **3e**. Yield, 63% (methods 2 and 4). Analysis: calculated for $C_{18}H_{11}F_{11}N_2O_2$ (496.28): F, 42.11%; found: F, 42.23%. ^1H NMR δ: 7.90 (2H, H-Ar, m, $J = 8.8$ Hz); 7.85 (2H, H-Ar, m, $J = 8.9$ Hz); 7.06 (2H, H-Ar, m, $J = 8.9$ Hz); 6.94 (2H, H-Ar, m, $J = 8.8$ Hz); 4.54 (2H, CH_2, t, $^3J(HF) = 12.8$ Hz) ppm.

Compound **3f**. Yield, 80% (methods 2 and 4). Analysis: calculated for $C_{19}H_{11}F_{13}N_2O_2$ (546.28): F, 45.21%; found: F, 45.24%. ^1H NMR δ: 7.98 (2H, H-Ar, m, $J = 9.1$ Hz); 7.85 (2H, H-Ar, m, $J = 8.8$ Hz); 7.05 (2H, H-Ar, m, $J = 9.1$ Hz); 6.94 (2H, H-Ar, m, $J = 8.8$ Hz); 4.54 (2H, CH_2, t, $^3J(HF) = 12.7$ Hz) ppm.

Compound **3g**. Yield, 73% (methods 2 and 4). Analysis: calculated for $C_{20}H_{11}F_{15}N_2O_2$ (596.29): F, 47.79%; found: F, 46.69%. ^1H NMR δ: 7.90 (2H, H-Ar, m, $J = 9$ Hz); 7.85 (2H, H-Ar, m, $J = 8.8$ Hz); 7.06 (2H, H-Ar, m, $J = 9$ Hz); 6.94 (2H, H-Ar, m, $J = 9$ Hz); 4.51 (2H, CH_2, t, $^3J(HF) = 12.6$ Hz) ppm. ^{13}C NMR δ: 159, 158, 149, 147, 125, 125, 116, 115 (C-Ar); 68 (CH_2, t, $^2J(CF) = 27$ Hz) ppm.

2.2.3. *4-(1H,1H-Perfluoroalkoxy)-4′-(6-bromo-hexyloxy)-azobenzenes (4)*

A mixture of 0.4 mol of 1,6-dibromohexane, 0.2 mol of dry K_2CO_3, 40 mmol of the corresponding product **3** and a trace of KI in 250 ml of dry acetone was stirred vigorously and refluxed for 2–10 h (controlled by thin-layer chromatography). After cooling, the precipitated salt was filtered off and the filtrate was evaporated. The crude product was purified by recrystallization from *n*-hexane.

Compound **4a**. Yield, 73%. Analysis: calculated for $C_{20}H_{22}BrF_3N_2O_2$ (459.30): F, 12.41%; found: F, 12.49%. ^1H NMR δ: 7.82 (4H, H-Ar, m, $J = 9$ Hz); 6.98 (2H, H-Ar, m, $J = 9$ Hz); 6.92 (2H, H-Ar, m, $J = 9$ Hz); 4.36 (2H, CH_2, q, ^3J(HF) = 8 Hz); 3.98 (2H, CH_2-O, t, J = 6.3 Hz); 3.37 (2H, CH_2-Br, t, J = 6.7 Hz); 1.79 (4H, H-spacer, m, br.); 1.47 (4H, H-spacer, m, br.) ppm. ^{13}C NMR δ: 161, 159, 148, 147, 125, 124, 115, 115 (C-Ar); 123 (CF_3, q, ^1J(CF) = 280 Hz); 66 (CH_2, q, ^2J(CF) = 36 Hz); 68, 34, 33, 29, 28, 25 (C-spacer) ppm.

Compound **4b**. Yield, 84%. Analysis: calculated for $C_{21}H_{22}BrF_5N_2O_2$ (509.31): F, 18.65%; found: F, 18.62%. ^1H NMR δ: 7.83 (2H, H-Ar, m, J = 9 Hz); 7.82 (2H, H-Ar, m, J = 9 Hz); 6.98 (2H, H-Ar, m, J = 9 Hz); 6.92 (2H, H-Ar, m, J = 9 Hz); 4.43 (2H, CH_2, t, ^3J(HF) = 12.2 Hz); 3.98 (2H, CH_2-O, t, J = 6.3 Hz); 3.37 (2H, CH_2-Br, t, J = 6.8 Hz); 1.81 (4H, H-spacer, m, br.); 1.47 (4H, H-spacer, m, br.) ppm.

Compound **4c**. Yield, 76%. Analysis: calculated for $C_{22}H_{22}BrF_7N_2O_2$ (559.31): F, 23.78%; found: F, 23.77%. ^1H NMR δ: 7.83 (2H, H-Ar, m, J = 9 Hz); 7.82 (2H, H-Ar, m, J = 9 Hz); 6.99 (2H, H-Ar, m, J = 9 Hz); 6.93 (2H, H-Ar, m, J = 9 Hz); 4.46 (2H, CH_2, t, ^3J(HF) = 12.7 Hz); 3.98 (2H, CH_2-O, t, J = 6.4 Hz); 3.37 (2H, CH_2-Br, t, J = 6.9 Hz); 1.85–1.78 (4H, H-spacer, m, br.); 1.47 (4H, H-spacer, m, br.) ppm.

Compound **4d**. Yield, 93%. Analysis: calculated for $C_{23}H_{22}BrF_9N_2O_2$ (609.32): F, 28.06%; found: F, 28.08%. ^1H NMR δ: 7.90 (2H, H-Ar, m, J = 9 Hz); 7.88 (2H, H-Ar, m, J = 9 Hz); 7.05 (2H, H-Ar, m, J = 9 Hz); 6.99 (2H, H-Ar, m, J = 9 Hz); 4.45 (2H, CH_2, t, ^3J(HF) = 12.7 Hz); 4.04 (2H, CH_2-O, t, J = 6.4 Hz); 3.43 (2H, CH_2-Br, t, J = 6.9 Hz); 1.91–1.84 (4H, H-spacer, m, br.); 1.53 (4H, H-spacer, m, br.) ppm.

Compound **4e**. Yield, 86%. Analysis: calculated for $C_{24}H_{22}BrF_{11}N_2O_2$ (659.33): F, 31.70%; found: F, 29.63%. ^1H NMR δ: 7.89 (4H, H-Ar, m, J = 9 Hz); 7.05 (2H, H-Ar, m, J = 9 Hz); 6.99 (2H, H-Ar, m, J = 9 Hz); 4.54 (2H, CH_2, t, ^3J(HF) = 12.7 Hz); 4.05 (2H, CH_2-O, t, J = 6.4 Hz); 3.44 (2H, CH_2-Br, t, J = 6.7 Hz); 1.91–1.84 (4H, H-spacer, m, br.); 1.54 (4H, H-spacer, m, br.) ppm.

Compound **4f**. Yield, 83%. LC. Analysis: calculated for $C_{25}H_{22}BrF_{13}N_2O_2$ (709.34): F, 34.81%; found: F, 34.69%. ^1H NMR δ: 7.91 (2H, H-Ar, m, J = 9 Hz); 7.89 (2H, H-Ar, m, J = 9 Hz); 7.06 (2H, H-Ar, m, J = 9 Hz); 6.99 (2H, H-Ar, m, J = 9 Hz); 4.54 (2H, CH_2, t, ^3J(HF) = 12.8 Hz); 4.05 (2H, CH_2-O, t, J = 6.4 Hz); 3.44 (2H, CH_2-Br, t, J = 6.8 Hz); 1.91–1.85 (4H, H-spacer, m, br.); 1.54 (4H, H-spacer, m, br.) ppm.

Compound **4g**. Yield, 76%. Analysis: calculated for $C_{26}H_{22}BrF_{15}N_2O_2$ (759.34): F, 37.52%; found: F, 37.54%. ^1H NMR δ: 7.91 (2H, H-Ar, m, J = 9 Hz); 7.89 (2H, H-Ar, m, J = 9 Hz); 7.06 (2H, H-Ar, m, J = 9 Hz); 7.00 (2H, H-Ar, m, J = 9 Hz); 4.54 (2H, CH_2, t, ^3J(HF) = 12.8 Hz); 4.04 (2H, CH_2-O, t, J = 6.4 Hz); 3.44 (2H, CH_2-Br, t, J = 6.8 Hz); 1.91–1.84 (4H, H-spacer, m, br.); 1.54 (4H, H-spacer, m, br.) ppm. ^{13}C NMR δ: 162, 160, 148, 147, 125, 124, 115, 115 (C-Ar); 65 (CH_2, t, ^2J(CF) = 27 Hz); 68, 34, 33, 29, 28, 25 (C-spacer) ppm.

2.2.4. 4-(1H,1H-Perfluoroalkoxy)-4′-(6-methacryloyloxyhexyloxy)-azobenzenes (5)

A mixture of 20 mmol of the corresponding compound **4** and 40 mmol of potassium methacrylate in 100 ml of dried *N,N*-dimethylformamide (DMF) was stirred vigorously and heated for 3–8 h (controlled by thin-layer chromatography) at 60°C (**5a**, **5b**) or 70°C (**5c**–**5g**). The cooled reaction mixture was diluted with water. The precipitate was filtered and dried. The crude product was purified by column chromatography on silica gel using CH_2Cl_2 as eluent and by recrystallization from *n*-hexane.

Compound **5a**. Yield, 82%. Analysis: calculated for $C_{24}H_{27}F_3N_2O_4$ (464.48): F, 12.27%; found: F, 12.31%. ^1H NMR δ: 7.83 (2H, H-Ar, m, J = 9 Hz); 7.81 (2H, H-Ar, m, J = 9 Hz); 6.98 (2H, H-Ar, m, J = 9 Hz); 6.92 (2H, H-Ar, m, J = 9 Hz); 6.04 (1H, s, br.); 5.49 (1H, s, br.); 4.36 (2H, CH_2, q, ^3J(HF) = 8 Hz); 4.10 (2H, $CH_2C{=}O$, t, J = 6.5 Hz); 3.97 (2H, CH_2O, t, J = 6.3 Hz); 1.88 (3H, CH_3, s); 1.78 (2H, H-spacer, m, br.); 1.67 (2H, H-spacer, m, br.); 1.46 (4H, H-spacer, m, br.) ppm. ^{13}C NMR δ: 168 (C=O); 161, 159, 148, 147, 125, 124, 115, 115 (C-Ar); 137, 125 (C=C); 123 (CF_3, q, ^1J(CF) = 270 Hz); 66 (CH_2, q, ^2J(CF) = 36 Hz); 68, 65, 29, 29, 26, 26 (C-spacer); 18 (CH_3) ppm.

Compound **5b**. Yield, 89%. Analysis: calculated for $C_{25}H_{27}F_5N_2O_4$ (514.49): F, 18.46%; found: F, 18.46%. ^1H NMR δ: 7.82 (2H, H-Ar, m, J = 9 Hz); 7.81 (2H, H-Ar, m, J = 9 Hz); 6.97 (2H, H-Ar, m, J = 9 Hz); 6.91 (2H, H-Ar, m, J = 9 Hz); 6.03 (1H, s, br.); 5.47 (1H, s, br.); 4.41 (2H, CH_2, t, ^3J(HF) = 12.2 Hz); 4.09 (2H, $CH_2C{=}O$, t, J = 6.5 Hz); 3.96 (2H, CH_2O, t, J = 6.3 Hz); 1.87 (3H, CH_3, s); 1.77 (2H, H-spacer, m, br.); 1.65 (2H, H-spacer, m, br.); 1.45 (4H, H-spacer, m, br.) ppm.

Compound **5c**. Yield, 85%. Analysis: calculated for $C_{26}H_{27}F_7N_2O_4$ (564.50): F, 23.56%; found: F, 22.96%. ^1H NMR δ: 7.83 (2H, H-Ar, m, J = 9 Hz); 7.81 (2H, H-Ar, m, J = 9 Hz); 6.99 (2H, H-Ar, m, J = 9 Hz); 6.92 (2H, H-Ar, m, J = 9 Hz); 6.04 (1H, s, br.); 5.48 (1H, s, br.); 4.47 (2H, CH_2, t, ^3J(HF) = 12.2 Hz); 4.11 (2H, $CH_2C{=}O$, t, J = 6.7 Hz); 3.98 (2H, CH_2O, t, J = 6.4 Hz); 1.88 (3H, CH_3, s); 1.78 (2H, H-spacer, m, br.); 1.67 (2H, H-spacer, m, br.); 1.45 (4H, H-spacer, m, br.) ppm.

Compound **5d**. Yield, 87%. Analysis: calculated for $C_{27}H_{27}F_9N_2O_4$ (614.50): F, 27.82%; found: F, 27.86%. ^1H NMR δ: 7.88 (4H, H-Ar, m, J = 9 Hz); 7.05 (2H, H-Ar, m, J = 9 Hz); 6.99 (2H, H-Ar, m, J = 9 Hz); 6.10 (1H, s, br.); 5.54 (1H, s, br.); 4.54 (2H, CH_2, t, ^3J(HF) = 12.7 Hz); 4.17 (2H, $CH_2C{=}O$, t, J = 6.7 Hz); 4.04 (2H, CH_2O, t, J = 6.6 Hz); 1.94 (3H, CH_3, s); 1.84 (2H, H-spacer, m, br.); 1.73 (2H, H-spacer, m, br.); 1.54–1.47 (4H, H-spacer, m, br.) ppm.

Compound **5e**. Yield, 79%. Analysis: calculated for $C_{28}H_{27}F_{11}N_2O_4$ (664.51): F, 31.45%; found: F, 31.48%. ^1H NMR δ: 7.88 (4H, H-Ar, m, J = 9 Hz); 7.05 (2H, H-Ar, m, J = 9 Hz); 6.98 (2H, H-Ar, m, J = 9 Hz); 6.10 (1H, s, br.); 5.54 (1H, s, br.); 4.54 (2H, CH_2, t, ^3J(HF) = 12.7 Hz); 4.17 (2H, $CH_2C{=}O$, t, J = 6.7 Hz); 4.04 (2H, CH_2O, t, J = 6.4

Hz); 1.94 (3H, CH_3, s); 1.84 (2H, H-spacer, m, br.); 1.73 (2H, H-spacer, m, br.); 1.54–1.47 (4H, H-spacer, m, br.) ppm.

Compound **5f**. Yield, 90%. Analysis: calculated for $C_{29}H_{27}F_{13}N_2O_4$ (714.52): F, 34.58%; found: F, 34.51%. ^{1}H NMR δ: 7.90 (2H, H-Ar, m, $J=9$ Hz); 7.88 (2H, H-Ar, m, $J=9$ Hz); 7.06 (2H, H-Ar, m, $J=9$ Hz); 6.99 (2H, H-Ar, m, $J=9$ Hz); 6.11 (1H, s, br.); 5.55 (1H, s, br.); 4.55 (2H, CH_2, t, ^3J(HF) = 12.6 Hz); 4.17 (2H, $CH_2C{=}O$, t, $J=6.7$ Hz); 4.05 (2H, CH_2O, t, $J=6.4$ Hz); 1.95 (3H, CH_3, s); 1.84 (2H, H-spacer, m, br.); 1.73 (2H, H-spacer, m, br.); 1.51 (4H, H-spacer, m, br.) ppm.

Compound **5g**. Yield, 87%. Analysis: calculated for $C_{30}H_{27}F_{15}N_2O_4$ (764.52): F, 37.27%; found: F, 37.21%. ^{1}H NMR δ: 7.91 (2H, H-Ar, m, $J=9$ Hz); 7.87 (2H, H-Ar, m, $J=9$ Hz); 7.06 (2H, H-Ar, m, $J=9$ Hz); 6.98 (2H, H-Ar, m, $J=9$ Hz); 6.10 (1H, s, br.); 5.55 (1H, s, br.); 4.54 (2H, CH_2, t, ^3J(HF) = 12.6 Hz); 4.17 (2H, $CH_2C{=}O$, t, $J=6.6$ Hz); 4.05 (2H, CH_2O, t, $J=6.4$ Hz); 1.94 (3H, CH_3, s); 1.84 (2H, H-spacer, m, br.); 1.73 (2H, H-spacer, m, br.); 1.51 (4H, H-spacer, m, br.) ppm. ^{13}C NMR δ: 168 (C=O); 162, 159, 148, 147, 125, 124, 115, 115 (C-Ar); 137, 125 (C=C); 65 (CH_2, t, ^2J(CF) = 27 Hz); 68, 65, 29, 29, 26, 26 (C-spacer); 18 (CH_3) ppm.

3. Results and discussion

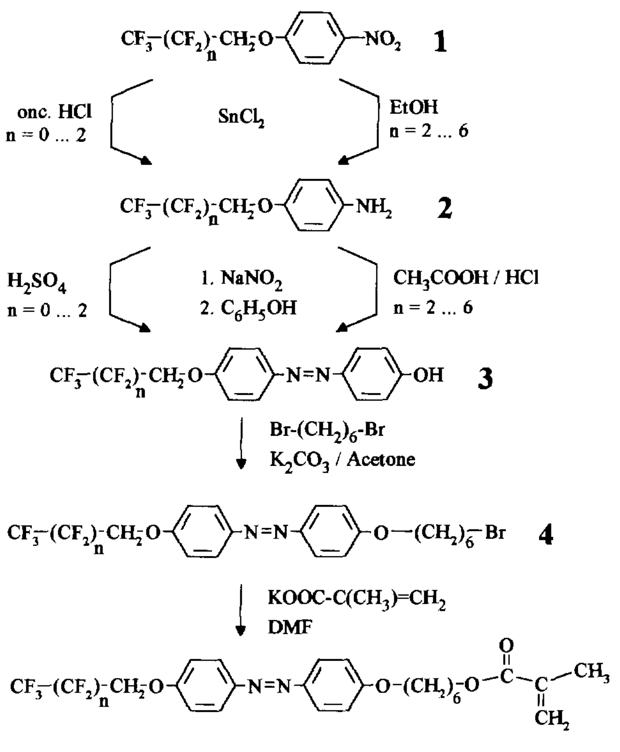
3.1. Synthesis

The methacrylates **5a–5g** and their intermediates were synthesized according to Scheme 1.

The reduction of the 1H,1H-perfluoroalkyl-*p*-nitrophenylethers **1a–1c** with $SnCl_2 \cdot 2H_2O$ in concentrated hydrochloric acid at 100°C to the corresponding anilines **2a–2c** took place according to the literature procedure [6]. However, the yield of the crude products decreased from **2a** (90%) to **2c** (50%), with increasing length of the fluorinated tail group. The synthesis for longer tails failed because of the decreased solubility of the molecules. We obtained a high yield of about 100% for **2c–2g** (crude product) using ethanol as solvent under reflux conditions for 6 h [7].

The conditions for diazotization also had to be changed. Derived from Refs. [8,9], diazotization of **2a–2c** by sodium nitrite in aqueous sulphuric acid at 0–5°C, followed by coupling with phenol at the same temperature, gave the expected substituted azobenzenes **3a–3c** in acceptable yield (50%–53%). The preparation of **3d–3g** was performed in an alternative system of solvents. Instead of sulphuric acid, a mixture of acetic acid and hydrochloric acid was used. The products were obtained in high yield (63%–80%).

The O-alkylation of **3a–3g** in dry acetone under reflux and in the presence of potassium carbonate required a large excess of 1,6-dibromohexane to obtain a convenient yield of **4a–4g** (73%–93%). The time of reaction was very different (2–10 h), but the progress and success of the reaction were controlled by thin-layer chromatography.



5

	a	b	c	d	e	f	g
n	0	1	2	3	4	5	6

Scheme 1.

The reaction of **4a–4g** with the potassium salt of methacrylic acid in DMF at 60°C (**4a**, **4b**) or 70°C (**4c–4g**) led to the corresponding monomers **5a–5g** (82%–90%).

3.2. Liquid crystalline behaviour

Some intermediate products show liquid crystalline (LC) behaviour. In Table 1, it is shown that the azobenzene derivatives **3** with tail groups longer than five carbon atoms form mesophases. This can be understood by taking into consideration their larger length-to-width ratio. The clearing temperatures, estimated from the second DSC heating runs, increase with increasing tail length. This is associated with a broadening of the temperature range of the mesophases, since the crystallization (melting) temperature is not influenced as strongly by the length of the tail group. However, only for **3f** was it possible to obtain a stable fan-like texture in the polarizing microscope, which is formed on cooling from bâtonnets at the clearing temperature. The bâtonnet indicates that a smectic mesophase is formed. On further cooling, this texture remains unchanged at the phase transition to the low-temperature mesophase. For samples **3d**, **3e** and **3g**, crystallization takes place very rapidly.

For **4a–4g**, a detailed phase assignment was achieved. Table 2 indicates that all homologues display mesophase behaviour; **4a** and **4b** show monotropic mesophases (on cool-

Table 1
Phase transition temperatures of compounds **3**

Sample	Temperature (°C) on heating		Temperature (°C) on cooling		
	$T(\mathrm{K}\rightarrow\mathrm{S_{A1}},\mathrm{I})$	$T(\mathrm{S_{A1}}\rightarrow\mathrm{I})$	$T(\mathrm{I}\rightarrow\mathrm{S_{A1}})$	$T(\mathrm{S_{A1}}\rightarrow\mathrm{LC})$	$T(\mathrm{I},\mathrm{S_{A1}},\mathrm{LC}\rightarrow\mathrm{K})$
3a	132	–	–	–	106
3b	138	–	–	–	107
3c	142	–	–	–	120
3d	135	140	120	–	117
3e	143	–	130	–	127
3f	139	147	140	134	125
3g	156	161	154	–	143

Table 2
Phase transition temperatures of compounds **4**

Sample	Temperature (°C) on heating		Temperature (°C) on cooling		
	$T(\mathrm{K}\rightarrow\mathrm{S_{A1}},\mathrm{I})$	$T(\mathrm{S_{A1}}\rightarrow\mathrm{I})$	$T(\mathrm{I}\rightarrow\mathrm{S_{A1}})$	$T(\mathrm{S_{A1}}\rightarrow\mathrm{LC})$	$T(\mathrm{S_{A1}},\mathrm{LC}\rightarrow\mathrm{K})$
4a	102	–	87	69	40
4b	88	–	73	62	58
4c	85	96	89	–	64
4d	80	102	95	–	62
4e	95	120	113	–	80
4f	99	131	126	–	90
4g	106	138	134	–	98

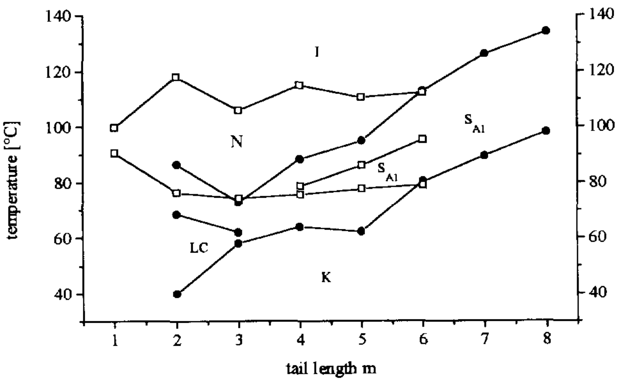


Fig. 1. Phase diagram of compounds **4** and their non-fluorinated analogues (filled circles, fluorinated; open squares, non-fluorinated); transition temperatures observed on cooling.

ing), whereas the higher homologues ($m \geq 4$) show enantiotropic mesophases (on cooling and heating). The phase behaviour of compounds **4** is summarized in Fig. 1, which shows that the temperatures depend on the tail length m. For comparison, the phase behaviour of the non-fluorinated analogues is also given [10].

The phase transition temperatures of the fluorinated compounds **4** increase with increasing tail length and show no significant odd–even effect. For $m \geq 4$, there is only one enantiotropic mesophase and, in all cases, it is possible to observe a fan-like texture (see Fig. 2), which is generated from bâtonnets at the clearing temperature (on cooling). For **4a** and **4b**, the texture remains unchanged at the phase transition to the

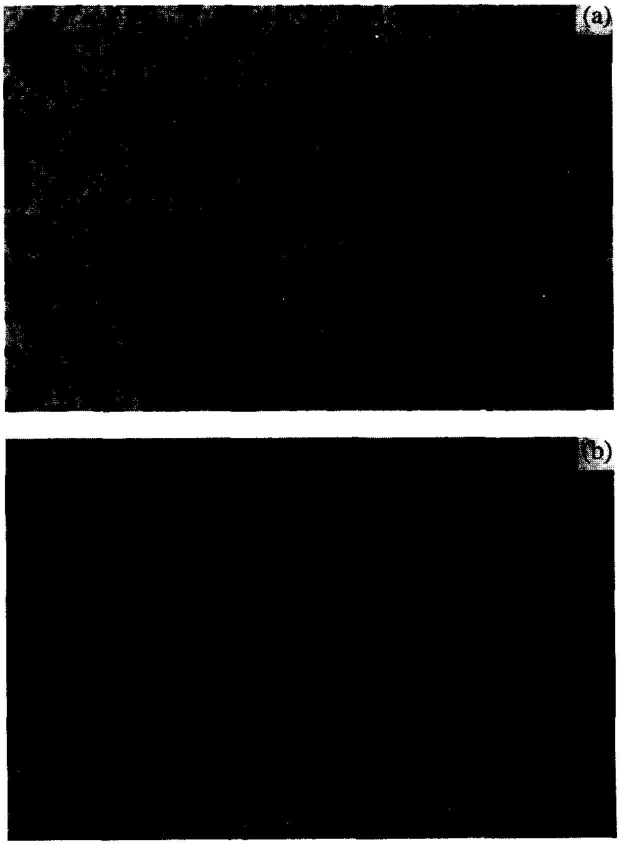


Fig. 2. Fan-like texture: (a) **4c** at 77.5°C generated from bâtonnets; (b) **4c** at 71°C.

Table 3
Layer periodicities and estimated lengths of compounds **4** as a function of the tail length

Sample	Layer periodicities d of smectic phases (nm)	Estimated length l of one molecule (nm)
4c	2.85	2.65
4d	2.98	2.79
4e	3.14	2.92
4f	3.38	3.06
4g	3.59	3.19

Table 4
Phase transition temperatures of monomers **5**

Sample	Temperature (°C) on heating		Temperature (°C) on cooling	
	$T(\text{K}\rightarrow\text{LC,I})$	$T(\text{LC}\rightarrow\text{I})$	$T(\text{I}\rightarrow\text{LC})$	$T(\text{I,LC}\rightarrow\text{K})$
5a	138–140 [a]	–	–	–
5b	118	–	–	102
5c	116	–	–	95
5d	120	–	–	94
5e	115	–	99	96
5f	108	117	113	97
5g	108	126	122	98

[a] Estimated by microscopy.

low-temperature mesophase. From the texture, we conclude that all mesophases are of smectic type. All molecules are arranged in layers.

To determine the type of smectic mesophase, X-ray diffraction measurements on unoriented samples of **4c–4g** were performed. Each X-ray diffraction pattern shows a diffuse halo in the wide-angle region, which demonstrates the liquid-like lateral arrangement of the mesogens. The first-order small-angle reflection is sharp and displays a layer arrangement. The calculated layer periodicities (d) according to this reflection are compared with the lengths of the mesogens (l) estimated by *hyperchem* (see Table 3). All smectic mesophases are of S_A type with nearly total overlap.

In low-molecular-mass liquid crystals, tail fluorination is found to suppress nematic character and enhance the formation of smectic phases [4]. Furthermore, orthogonal smectic phases should be favoured over tilted smectic phases by the incorporation of perfluoroalkoxy tail groups. In agreement with this behaviour, the appearance of S_A phases in the series of compounds **4** in comparison with their non-fluorinated analogues [10] (see Fig. 2) takes place.

For the monomers **5a–5g**, the appearance of mesophases is limited only to longer tail groups ($m \geq 6$). The bulky and polar methacryloyloxy substituent hinders the formation of mesophases. A more ordered crystalline phase seems to be favoured, and only for $m \geq 6$ are mesophases observed (see Table 4). The fan-like textures from the polarizing microscope for **5f** and **5g**, and the calculated layer periodicities from the X-ray diffraction patterns of the mesophases, lead to the conclusion that only S_{A1} phases exist. In comparison with the non-fluorinated analogues with a nematic mesophase for $m = 4$, 5 and 6 and an S_{A1} phase for $m = 6$ [10], the series of fluorinated monomers shows no nematic, but only smectic, phases for $m \geq 6$.

4. Conclusions

The synthesis of methacrylate monomers with the 4′-(1H,1H-perfluoroalkoxy)-azobenzene mesogenic unit and their intermediate products has been described. The phase behaviour of the liquid crystalline products has been studied by different methods. A strong dependence of the phase transitions on the length of the fluorinated tail group is found. As expected, all mesophases are of smectic character. In comparison with other low-molecular-mass liquid crystals and with the non-fluorinated analogues of the prepared molecules, it is found that fluorination suppresses the nematic character and enhances the formation of smectic phases.

Acknowledgements

We gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft.

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