

A New Group of Liquid Crystals Based on Perfluoroalkylated Carbohydrates¹

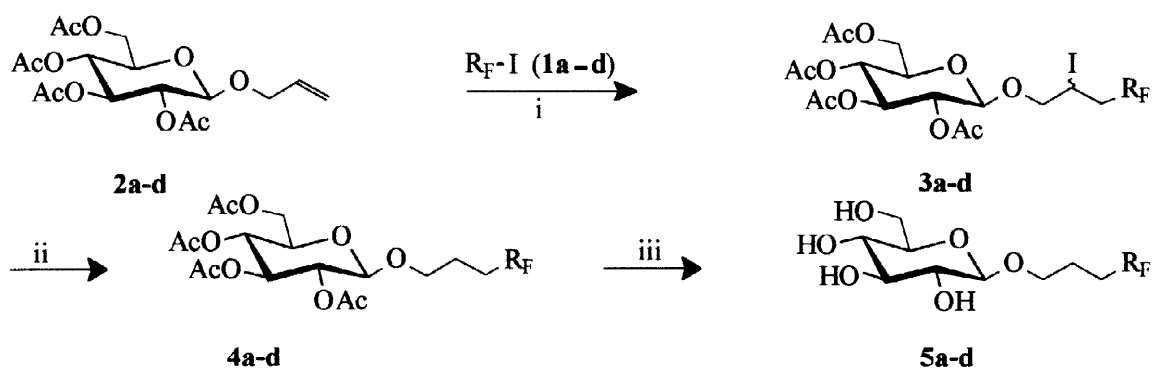
Martin Hein and Ralf Miethchen*

Universität Rostock, Fachbereich Chemie, Buchbinderstrasse 9, D-18051 Rostock, Germany

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Abstract: The mesogenic fluoroalkyl β -D-glucopyranosides **5a-d** (*smectic A*) were generated via a dithionite initiated addition of the homologous 1-iodo-perfluoroalkanes **1a-d** to allyl 2,3,4,6-tetra-O-acetyl- β -D-glucopyranoside (**2**) forming **3a-d** followed by hydrodeiodination to **4a-d** and deacetylation.
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Perfluoroalkylated carbohydrates are useful surfactants and emulsifiers for “water in fluorocarbon” emulsions, respectively^{2,3}. Such amphiphiles should also show interesting thermotropic liquid-crystalline properties, however, only one paper was published so far describing the thermal behaviour of some perfluoroalkyl-substituted monosaccharides⁴. Now, we report the thermal behaviour of some homologous (3-perfluoroalkyl-propyl) β -D-glucopyranosides synthesised as described in the following Scheme:



R_F: **a** = C₄F₉; **b** = C₆F₁₃; **c** = C₈F₁₇; **d** = C₁₀F₂₁

Scheme: *Reagents and conditions:* i = Na₂S₂O₄, NaHCO₃ (MeCN / H₂O), 0–20°C, 1–4 hours; ii = H₂ / Pd / C (MeOH, EtOAc, NaOAc), r.t.; iii = CsF / Al₂O₃ (MeOH), r.t.

* Fax: +49 381 498 1819; e-mail: ralf.miethchen@cks1.rz.uni-rostock.de

The radical addition of perfluoroalkyl iodides to double bonds using sodium dithionite as initiator⁵⁻⁹ is one of the most convenient methods to introduce perfluoroalkyl chains; for other methods of addition see ref. ^{10,11} and papers cited therein. Therefore, the homologous (2-iodo-3-perfluoroalkyl-propyl) 2,3,4,6-tetra-O-acetyl- β -D-glucopyranosides **3a-d** were synthesised from allyl 2,3,4,6-tetra-O-acetyl- β -D-glucopyranoside (**2**) and the perfluoroalkyl iodides **1a-d** in this way. In a typical procedure perfluorohexyl iodide (815 μ l, 3.75 mmol), sodium dithionite (520 mg, 3.0 mmol) and sodium bicarbonate (400 mg, 4.8 mmol) were added to a cooled and stirred solution of the allyl glucoside **2** (580 mg, 1.5 mmol) in 9 ml of an acetonitrile-water mixture (2:1) under inert gas atmosphere. The vigorous stirring of the mixture was continued for 1.5 hours. In the case of the perfluoroalkyl iodides **1c** and **1d**, the reaction time was longer (2-4 hours) and the temperature should be slowly raised from 0°C to room temperature. The crude products of **3a-d** obtained after the work-up procedure¹² were hydrodeiodinated by treatment with H₂ (1 atm., Pd / C) giving the (3-perfluoroalkyl-propyl) 2,3,4,6-tetra-O-acetyl- β -D-glucopyranosides **4a-c** in a yield of 77-86% (related to **2**)¹³. The overall yield of **4d** was significantly lower (26%), probably due to the small solubility of the solid perfluorodecyl iodide in the acetonitrile-water mixture (first step).

The mesogenic fluoroalkyl β -D-glucopyranosides **5a-d**¹⁴ were generated from **4a-d** by deacetylation using a methanolic suspension of alumina supported cesium fluoride (1.53 mmol CsF per gram catalyst)¹⁵ in about quantitative yields¹⁶. After removing of the catalyst by filtration through Celite¹⁷ and evaporation of the solvent, the amphiphiles **5a-d** were purified by column chromatography and their liquid crystalline properties were studied¹⁸; see the Table 1.

Table 1: Thermal properties of the liquid crystals **5a-d** (type: *smectic* A)

compound	melting point (°C) *	ΔH (J/g)	clearing point (°C) *	ΔH (J/g)
5a	145-146 (148)	86	141-142 (140)	3.5
5b	154 (155)	83	184 (180)	2.8
5c	168 (164)	78	208 (204)	2.1
5d	172.5 (174.5)	71	222 (219) dec.	1.6

* DSC values in brackets

It is noticeable that all homologues of **5a-d** strongly tend to form homeotropic layers after melting. Stepped drops and fan like textures, characteristically for *smectic* A phases, were only observe in preparations without cover slide. The amphiphiles **5a-d** show higher melting and clearing points than the fluorine-free alkyl β -D-

glucopyranosides with an equal C-number of their alkyl chain (Figure 1); see also review¹⁹. The increased stability of the liquid crystalline state is probably due to the increased tendency to separate the hydrophilic and fluorophilic part of the molecule (intramolecular contrast), i.e. the higher hydrophobicity of a fluorocarbon chain compared to alkyl chains enhances the amphiphilic character of the compounds. Moreover, perfluoroalkyl chains have a higher stiffness than alkyl chains, prefer strictly the low-energy all-*trans* conformation to *gauche* conformations²⁰⁻²³ and have an essential helical conformation. Consequently, the self-organisation of the amphiphiles is stronger supported by perfluoroalkyl than by alkyl chains; see also ref.⁴.

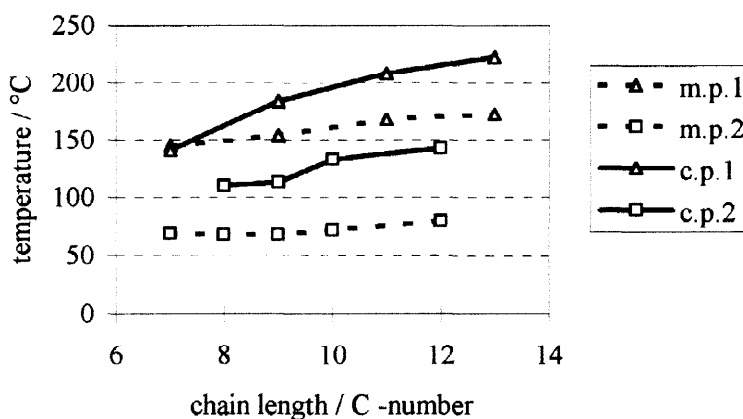


Figure 1: Comparison of the thermal behaviour of the fluoroalkyl β -D-glucopyranosides **5a-d** (m.p.1; c.p.1); and of alkyl β -D-glucopyranosides (m.p.2; c.p.2)^{24,25}.

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12. Subsequently, diethyl ether was added and the mixture was washed with saturated aqueous NaCl solution and water. Then the separated ether phase was dried over Na₂SO₄, filtered and concentrated under reduced pressure (see also ref. ^{6,8}).
13. No excess of 1-iodo-perfluorodecane was used in this case.
14. The structure of the described compounds are supported by their ¹H, ¹³C and ¹⁹F-NMR spectra and by micro analyses, e.g. compound **4a**: ¹H NMR (300.1 MHz, CDCl₃) δ = 5.19 (dd, 1H, J_{3,4} = 9.5 Hz, H-3), 5.06 (dd, 1H, H-4), 4.97 (dd, 1H, J_{2,3} = 9.5 Hz, H-2), 4.49 (d, 1H, J_{1,2} = 7.9 Hz, H-1), 4.23 (dd, 1H, J_{5,6a} = 4.8 Hz, H-6a), 4.12 (dd, 1H, J_{6a,6b} = 12.4 Hz, H-6b), 3.88-3.96 (m, 1H, OCH₂), 3.68 (ddd, 1H, J_{4,5} = 9.9 Hz, J_{5,6b} = 2.5 Hz, H-5), 3.54-3.62 (m, 1H, OCH₂), 2.06, 2.00, 2.00, 1.98 (4 x s, 12H, CH₃), 1.80-2.24 (m, 4H, CH₂-CH₂-R_F). - ¹³C {¹H} NMR (75.5 MHz, CDCl₃) δ = 170.5, 170.2, 169.3, 169.1 (4 x s, CO), 100.8 (s, C-1), 72.6, 71.9, 71.2, 68.4 (4 x s, C-2, C-3, C-4, C-5), 68.2 (s, OCH₂), 61.9 (s, C-6), 27.4 (t, J_{C,F} = 22.3 Hz, CH₂-R_F), 20.2-20.9 (m, 4CH₃ and CH₂-CH₂-CH₂). - ¹⁹F {¹H} NMR (235.3 MHz, CDCl₃) δ = -82.1 to -80.8 (m, CF₃), -115.6 to -113.1 (m, CH₂-CF₂), -124.2 to -124.0 (m, CF₂), -125.9 to -125.6 (m, CF₂).
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16. About 1/15 eq. CsF per acetyl group should be used.
17. To obtain good yields of the deacetylated products **5c** and **5d**, the Celite bed is carefully to rewash with hot methanol.
18. The thermal data of the pure compounds were determined by DSC measurements and polarising microscopy using a Leitz Laborlux 12 Pol microscope equipped with a Mettler hot stage FP 90 and a Leica WILD MPS 52 for photomicrographs. The transition temperatures were determined on the first heating of the substances. Moreover, transition enthalpies were measured by DSC. The thermograms (scan rate 10 K min⁻¹) were obtained using a Perkin-Elmer DSC 2 device.
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