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Amphiphilic and mesogenic carbohydrates IX. Perfluoroalkyl substituted monosaccharides: a new group of amphiphilic liquid crystals†

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The thermal properties of twelve 'single-tailed' carbohydrate-based liquid crystal materials which have a perfluoroalkyl chain (n-C_4F_9, n-C_6F_{13}, n-C_8F_{17}) linked to the polar sugar head group are described. All reported amphiphiles, the 6-deoxy-6-*C*-perfluorohexyl-L-altrose **1**, the (5*R*)-xylopentoses **2**, **3** and **4**, the 5,6-dideoxy-6-*C*-perfluoroalkyl-D-glucofuranoses **5** and **6**, the 2,3-*O*-perfluoroalkylidene-D-gulopyranoses **7**, **8** and **9** and the 3,4-*O*-perfluoroalkylidene-D-altropyranoses **10** and **11** form mesophases of the smectic A type. Even a C_4F_9-chain (compounds **2**, **7**, and **10**) is long enough to cause liquid crystalline behaviour.

1. Introduction

A broad variety of *n*-alkyl substituted carbohydrates exhibit thermotropic liquid crystalline properties; for a recent review see [2]. Moreover, the effect on the liquid crystalline properties of amphiphilic D-glucoses and D-mannoses, resulting from replacement of one hydroxy group of their hydrophilic head groups by fluorine, has been examined [1, 2]. However, no indications as to mesogenic properties for perfluoroalkyl substituted carbohydrates are given in the literature so far. For other types of perfluoroalkylated amphiphiles, liquid crystalline behaviour has been reported [3]. Furthermore, it is known that perfluoroalkylated amphiphiles are more effective surfactants than their hydrocarbon counterparts and tend to form ordered supramolecular assemblies much more easily [3–6].

In the known perfluoroalkylated carbohydrates, the perfluoroalkyl chain is attached to the carbohydrate moiety via a hydrocarbon spacer and an ether, ester, amide, amine or phosphate linkage [7, 8]. Carbohydrates of this type are fluorophilic/hydrophilic surfactants and could be used as emulsifiers for artificial oxygen carriers, drug delivery systems or contrast agents based on fluorocarbons [5, 8]. We have investigated the thermotropic behaviour of some new carbohydrate-based perfluoroalkyl amphiphiles representing the first examples of liquid crystals of this type. The perfluoroalkyl chains are linked to the carbohydrate skeleton either with or without a hydrocarbon spacer. The syntheses of the compounds reported here are described in the references [9–12].

2. Experimental

The perfluoroalkylated carbohydrates **1**–**11** were purified by column chromatography and by recrystallization; for details of their analytical characterization see [9–12]. The thermal data for the pure compounds were determined by DSC measurements and polarizing microscopy using a Leitz Laborlux 12 Pol microscope equipped with a Mettler hot stage FP 90 and a Leica WILD MPS 52 for photomicrography. The transition temperatures were determined on the first heating of the substances, because the sugar derivatives underwent changes (decomposition or glycosylation) at temperatures above 120°C. Transition enthalpies were measured by DSC, the thermograms (scan rate 10 K min^{-1}) being obtained using a Perkin-Elmer DSC 2 device. Comparison of the transition temperatures determined by microscopy and DSC showed some slight discrepancies. This is due to the different heating rates and to the fact that the thermally induced reactions of the sugar derivatives may be faster in aluminium DSC pans than on glass slides. The structures, transition temperatures and DSC enthalpies are summarized in tables 1 and 2. All derivatives show typical smectic A fan-shaped textures, some examples of which are shown in the figures 1–3.

3. Results and discussion

The formation of thermotropic mesophases of amphiphiles can be understood as a microphase separation, i.e.

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Table 1. Thermal properties of the equilibrium mixtures of anomeric pyranoses **1**–**4**$_{(P)}$ and furanoses **1**–**4**$_{(F)}$.

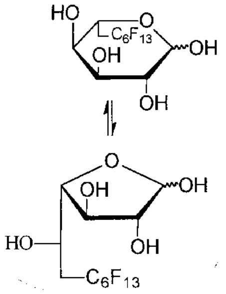
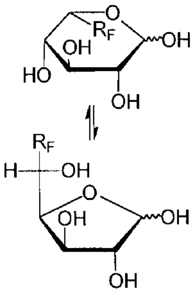
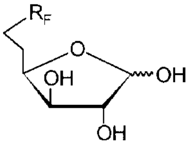
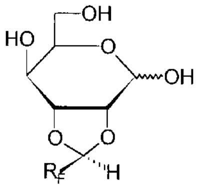
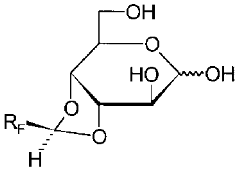
Compound number	Structure	m.p./°C (DSC)	ΔH J g^{-1}	c.p./°C (DSC)	ΔH J g^{-1}
1		136–139 (147–148)	20·7	171–172 (178–181)	
2 ($R_F = C_4F_9$)		148–153 (155–156)	112·3	129–136 (127–142)	
3 ($R_F = C_6F_{13}$)		163–166 (176–177)	105·9	159–168 (186–188)	18·3
4 ($R_F = C_8F_{17}$)		176–177 (178)	78·6	188–192 (194–196)	

Table 2. Thermal properties of compounds **5**–**11**.

Compound number	Structure	m.p./°C (DSC)	ΔH J g^{-1}	c.p./°C (DSC)	ΔH J g^{-1}
5 ($R_F = C_6F_{13}$)		127–129 (133–134)	76·6	147–148 (151–152)	5·9
6 ($R_F = C_8F_{17}$)		136–137 (133–134)	31·9	149–150 (148–149)	
7 ($R_F = C_4F_9$)		86–88 (93–94)	54·2	125–127 (125–126)	7·8
8 ($R_F = C_6F_{13}$)		94·5–95 (95)	55·8	172·5 (171–172)	8·7
9 ($R_F = C_8F_{17}$)		100–101 (104–105)	38·0	194 (191–192)	8·6
10 ($R_F = C_4F_9$)		syrup[a]		89–93 (77–97)	
11 ($R_F = C_6F_{13}$)		syrup[a]		156–159	

[a] Compound did not crystallize.

in terms of a separation of the polar and the non-polar parts of the structures [13, 14]. The 'intramolecular contrast' between the hydrophilic and the hydrophobic parts of an amphiphilic molecule is higher in perfluoroalkyl substituted than in alkyl substituted compounds, i.e. the higher hydrophobicity of the fluorocarbon chain enhances the amphiphilic character of the compounds. Moreover, perfluoroalkyl chains have a greater stiffness than alkyl chains. Because of a large energy difference between the *gauche*- and *trans*-conformations [15], the perfluoroalkyl chains prefer the *trans*-form [15–18] and have an essentially helical conformation. Consequently, the self-organization of the amphiphiles is supported more strongly by perfluoroalkyl than by alkyl chains. Perfluoroalkylated amphiphiles tend to form relatively highly ordered and stabilized aggregates with only a few kinks, though the van der Waals interactions between the chains are lower than those between hydrocarbon chains [5, 6]. Such effects of perfluoroalkyl chains have already been reported for other types of fluorinated surfactants, including the statement that perfluoroalkyl chains stabilize liquid crystalline phases of amphiphiles more than alkyl chains ([5] and papers cited therein). On the other hand, the contribution of the hydrogen-bond network to the lateral stabilization of the mesophases (bilayer type) should not significantly change on replacement of an alkyl for a perfluoroalkyl chain. Merely on OH group located right next to a perfluoroalkyl chain could however have another influence caused by the strong acceptor effect of the fluorine atoms. However, direct comparisons of thermal data for perfluoroalkylated carbohydrates with those of corresponding alkyl derivatives are still not possible, because data for alkyl substituted carbohydrates corresponding to the amphiphiles **1**–**11** are not available in the literature.

3.1. *Perfluoroalkyl substituted amphiphiles with four OH groups*

The 6-deoxy-6-perfluorohexyl-L-altrose **1**, synthesized by radical addition of perfluorohexyl iodide to 6-deoxy-1,2:3,4-di-*O*-isopropylidene-β-L-*arabino*-hex-5-enopyranose and subsequent deprotection [9], consists of a mixture of the α- and β-anomeric pyranoses $\mathbf{1}_{(P)}$ and furanoses $\mathbf{1}_{(F)}$ caused by mutarotation (table 1). By NMR measurements we found a ratio of pyranoses to furanoses of about 1·8 : 1 in solution in acetone-d_6/D_2O [9]. Unfortunately, the corresponding composition of the liquid crystalline state formed over a temperature range of 30 K, could not be determined; for the thermal data of the mixture see table 1.

The homologous L-*ido*-aldoses **2**–**4** are a second example of liquid crystals based on a perfluoroalkyl substituted monosaccharide with four free OH groups. However, while the perfluoroalkyl chain of the L-altroses **1** is attached to the polar head group via a CH_2 unit, the perfluoroalkyl chains of **2**–**4** are connected to the sugar moiety without any spacer. The compounds were synthesized by a sonochemical Barbier-type reaction using the aldehydo sugar 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pento-1,5-dialdofuranose and the corresponding perfluoroalkyl iodide followed by deprotection steps [11]. The L-*ido*-configured compounds **2**–**4** with R_F-chain lengths of four, six, and eight carbon atoms, respectively, consist of mixtures of the corresponding α- and β-anomeric pyranose forms $\mathbf{2}_{(P)}$, $\mathbf{3}_{(P)}$, $\mathbf{4}_{(P)}$, and furanose forms $\mathbf{2}_{(F)}$, $\mathbf{3}_{(F)}$, $\mathbf{4}_{(F)}$, respectively (table 1). The pyranose to furanose ratios were found to be about 1 : 1 in solution in acetone-d6/D_2O (determined by integration of NMR signals). On heating, the L-*ido*-aldoses **2**–**4** form smectic A phases. The short chained derivative **2** is a monotropic mesogen (texture, see figure 1) and **3** and **4** are enantiotropic mesogens; for thermal data see table 1. The clearing point of the monotropic derivative **2** is not very sharp owing to a thermally induced reaction on heating.

3.2. *Perfluoroalkyl substituted amphiphiles with three OH groups*

The preparation of the mesogenic 5,6-dideoxy-6-perfluoroalkyl furanoses **5** and **6** from 3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranose is described in [9]. In both compounds the perfluoroalkyl chain is linked to the polar head group by a CH_2–CH_2 unit. By polarizing optical microscopy a typical SmA fan-shaped texture is to be seen. Figure 2 shows the texture of the perfluorooctyl derivative **6**. The range of the smectic phase is about 20 K for both derivatives **5** and **6**. The transition temperatures of both compounds were confirmed by DSC. Phase transition enthalpies are given only for the perfluorohexyl compound **5** (table 2), since the enthalpy values for the perfluorooctyl derivative **6** are unreliable because of the beginning of thermally induced reaction in the mesophase.

The homologous D-gulopyranoses **7**–**9** and D-altropyranoses **10** and **11** containing a perfluoroalkylidene moiety (table 2) were synthesized via a non-conventional

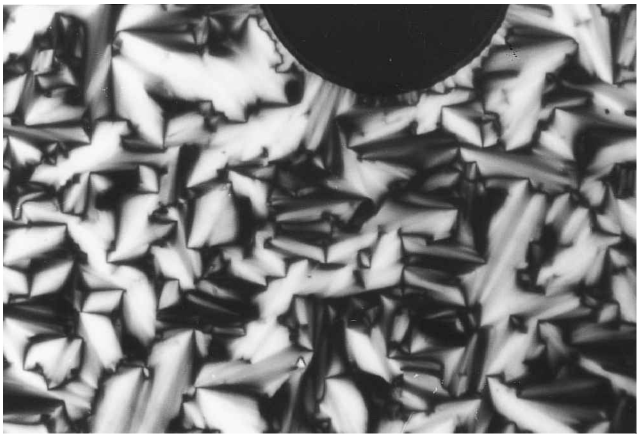


Figure 1. Fan-shaped SmA texture of 5-*C*-perfluorobutyl-substituted L-*ido*-aldose **2**, 125°C, on cooling; 40-fold enhancement.

Figure 2. Fan-shaped SmA texture of 5,6-dideoxy-6-*C*-perfluorooctyl-D-*xylo*-hexanose **6**, 119°C, on cooling; 16-fold enhancement.

acetalation from methyl β-D-galactopyranoside and methyl α-D-mannopyranoside, respectively, with perfluoroaldehydes [10]. Because of the annelated 2,3-acetal (**7**–**9**) or 3,4-acetal (**10**, **11**) ring, the five triols have a fairly rigid head group. Each of the compounds **7**–**11** consists of an anomeric mixture of the corresponding α- and β-pyranose. The amounts of both anomers were found to be about equal in acetone-d6/D_2O solution (determined by integration of NMR signals).

The amphiphilic perfluoroalkyl substituted cyclic acetals **7**–**11**, like the amphiphilic 4,6-*O*-alkylidene-D-glucopyranoses [19, 20], form thermotropic mesophases of the smectic A type with relatively high clearing points; the texture of 2,3-*O*-perfluoroheptylidene-D-gulose (**8**) is shown in figure 3. It is noticeable that even the *gulo*-derivative **7** and the *altro*-derivative **10** with the very short nonafluorobutyl chain form relatively stable mesophases. For the *gulo*-derivatives **7**–**9**, the transition temperatures were determined as effectively by DSC measurements as by polarizing microscopy. Furthermore, the values for the transition enthalpies were determined (table 2). The *altro*-derivatives **10** and **11**, having exceptionally broad mesophase ranges, did not crystallize.

It is known that the miscibility of alkyl and perfluoroalkyl compounds is restricted, because perfluoroalkyl chains are both hydrophobic and lipophobic [5] (for a monograph on mixed surfactant systems see [21]). An important method for confirming the mesophase types of liquid crystals is the contact preparation method using polarizing microscopy. In order to test whether this method could be applied to mixtures of alkyl and perfluoroalkyl substituted liquid crystalline sugars, we performed a miscibility experiment with the perfluoroalkylated carbohydrate **8** and dodecyl α-D-galactopyranoside (m.p. 70·5–72·5°C, c.p. 141°C) [22]. The latter is a typical hydrocarbon tailed amphiphilic carbohydrate with a SmA texture. Both mesophases were totally miscible (figure 4) indicating the generation of normal smectic A phases from perfluoroalkylated carbohydrate derivatives. This result is in agreement with the statement in the literature that the phase behaviour of fluorinated surfactants and hydrocarbon surfactants is similar. Additionally lamellar and hexagonal phases have been observed for perfluorinated surfactants [5].

The melting points of the compounds **2**–**4** are about 70 K higher than the melting points of the *gulo*-acetal-compounds **7**–**9** with the same chain lengths, respectively. This may be mainly due to the additional hydroxyl group. The clearing temperatures occur in about the same range for members of the two different homologous series with a given chain length: C_4 *c.* 125–135°C (**7** and **2**); C_6 *c.* 160–170°C (**8** and **3**); C_8 *c.* 188–194°C

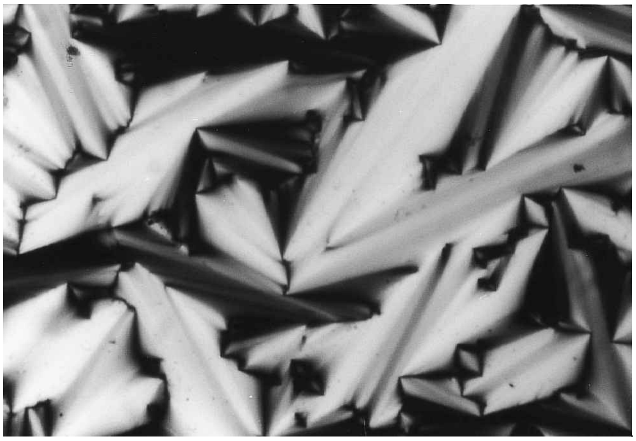


Figure 3. Fan-shaped SmA texture of 2,3-*O*-(perfluoroheptylidene)-D-guloside **8**, 167°C, on cooling; 40-fold enhancement.

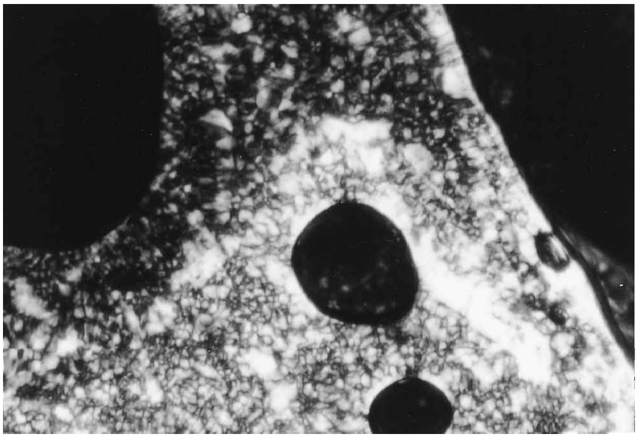


Figure 4. Miscibility of SmA phase of compound **8** (darker, upper texture) with dodecyl α-D-galactopyranoside (brighter, lower texture, with holes), 99°C, on heating; 40-fold enhancement.

(**9** and **4**). Even the clearing temperature range (156–159°C) of the C_6-D-*altro*-derivative **11** is within the range for the other C_6-derivatives **8** and **3** (tables 1 and 2).

4. Conclusions

The supramolecular structural model of smectic mesophases proposed by van Doren and Wingert [23] for 'single tailed' amphiphiles consisting of a hydrophilic head and one lipophilic alkyl chain is basically transferable to perfluoroalkyl substituted sugars. The 'single tailed' mesogens **1**–**11** show relatively high melting and clearing points caused by the influence of the perfluoroalkyl chains. Fluorocarbon chains are not only more hydrophobic but also stiffer than hydrocarbon chains and therefore have less conformational freedom [5]. The CH_2 and CH_2–CH_2 spacers, respectively, between the hydrophilic head group and the fluorocarbon tail within the derivatives **1**, **5** and **6** enhance the flexibility of the chains and may have the effect of lowering the clearing points in comparison with derivatives with the same perfluoroalkyl chain length, but without any spacer.

The successful contact preparation of compound **8** with dodecyl D-galactopyranoside has shown that such experiments can be used to assign the mesophase type of perfluoroalkyl substituted carbohydrate-based amphiphiles. Finally, it is observed that the pyranose/furanose ratio of amphiphilic monosaccharides is influenced by perfluoroalkyl groups in favour of the furanoses.

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