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Amphipilic and mesogenic carbohydrates XII. New thermotropic mesogens based on perfluoroalkyl-substituted carbohydrates†

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In continuing studies of amphiphilic and mesogenic carbohydrates, the mesomorphic properties of a new group of perfluoroalkylated amphiphilic mesogens are discussed. Smectic A phases dominate the mesomorphic behaviour of the new materials, but one compound exhibits a columnar mesophase and three others have SmA–SmC* transitions. The synthesis of these materials has already been reported and involved dithionite-mediated *O*- and *S*-perfluoroalkylations with 1-iodoperfluoroalkanes.

1. Introduction

Perfluoroalkylated amphiphiles are more effective surfactants than their hydrocarbon counterparts [2–5]; carbohydrate-based compounds of this type are suitable as emulsifiers for artificial oxygen carriers, drug delivery systems or contrast agents [4, 6]. Recently, the thermomesomorphic properties of some 'single tailed' perfluoroalkyl-substituted sugar amphiphiles were described [1, 7]. These compounds form, like 'single tailed' alkylated sugar amphiphiles, only SmA phases [8]. However, their mesophases seem to be more favoured than those of the alkyl derivatives, because of the increased intramolecular contrast within the molecules and because of the greater stiffness of perfluoroalkyl chains compared with alkyl chains. One of the consequences is that carbohydrate-based amphiphiles can show liquid crystalline properties even when their hydrophobic molecular segment is simply a perfluorobutyl chain [7].

In this paper the mesomorphic properties of a new group of perfluoroalkylated amphiphilic and non-amphiphilic mesogens are discussed; the strategy of their syntheses, the evidence for their structures and the NMR data for the compounds and their precursors are reported in separate papers [9, 10].

2. Experimental

The perfluoroalkylated carbohydrates **1–16** were purified by column chromatography and by recrystallization. The thermal data for the pure compounds were determined by DSC measurements and polarizing optical microscopy using a Leitz Laborlux 12 Pol microscope equipped with a Mettler hot stage FP 90 and a Leica WILD MPS 52 for photomicrographs. Transition enthalpies were also measured by DSC. The thermograms (scan rate 5 and 10 K min^{-1}, respectively) were obtained using a Perkin-Elmer DSC 2. The structures and transition temperatures are summarized in tables 1 and 2.

2.1. *Synthesis of the amphiphilic sugars with a highly fluorinated hydrophobic chain*

Dithionite-mediated perfluoroalkylations with 1-iodoperfluoroalkanes are facile procedures to introduce highly fluorinated chains into sugar molecules. Thus, the amphiphilic (3-perfluoroalkyl-propyl) β-D-glucopyranosides **1–4** were prepared via *C*-perfluoroalkylation of allyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside [1, 9]. The 'single tailed' (3-perfluorooctyl-propyl) derivative **3** was the starting material for the introduction of a hydrocarbon chain in addition to the fluorinated alkyl chain. Compound **3** was acylated with dodecanoyl chloride in the presence of pyridine giving the (3-perfluorooctyl-propyl)-6-*O*-dodecanoyl β-D-glucopyranoside **5** [9]. The

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†For part XI see ref. [1]

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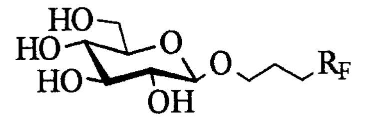
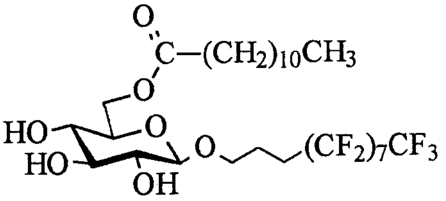
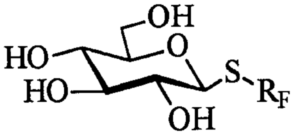
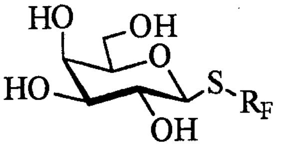
Table 1. Thermal properties of the amphiphilic mesogens **1–9** (for the syntheses of the compounds see [9]).

Compound	Structure	m.p./°C	Mesophase	c.p./°C
1		145–146	SmA	141–142[b]
	$R_F = C_4F_9$			
2	$R_F = C_6F_{13}$	154	SmA	184
3	$R_F = C_8F_{17}$	168	SmA	208
4	$R_F = C_{10}F_{21}$	172.5	SmA	222 (decomp.)
5		73–74	columnar[a]	146–147
6		120	SmA	181–183[c]
	$R_F = C_6F_{13}$			
7	$R_F = C_8F_{17}$	123–124	SmA	186–188[c]
8				
	$R_F = C_6F_{13}$			
9	$R_F = C_8F_{17}$	121–122	SmA	156–158[c]

[a] Formation of an unknown metastable phase below 58°C, figure 1.

[b] Monotropic transition.

[c] Decomposition is observed above 135–140°C.

amphiphilic mesogens **6–9** were obtained by dithionite-mediated *S*-perfluoroalkylations of 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose and 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galatopyranose followed by deacetylation [9]. It is noteworthy that the D-galactose derivatives **8** and **9** tend to form gels when they are recrystallized from ethyl acetate–toluene mixtures.

2.2. *Synthesis of the non-amphiphilic fluoroalkylated sugars*

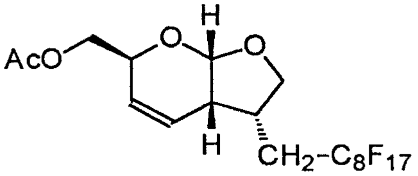
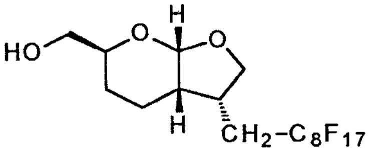
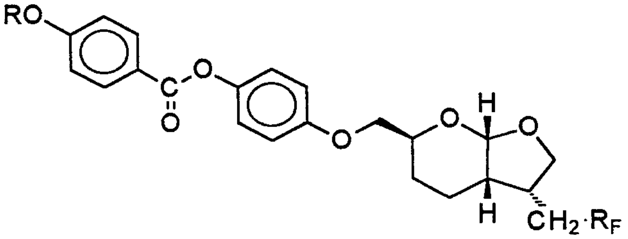
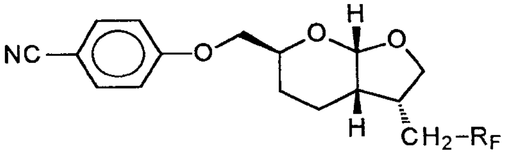
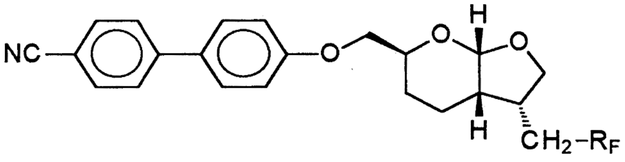
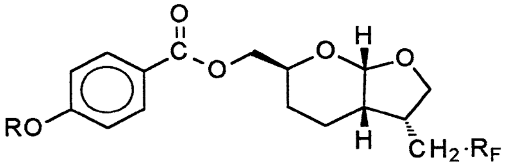
The perfluoroalkyl-substituted chiral 'building blocks' **10** and **11** were prepared from allyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside and 1-iodo-perfluorooctane via a dithionite-mediated radical reaction as the key step [10]. Two of the three new stereogenic centres formed in this '*Domino*-reaction' [12] are totally controlled. Compound **11** was coupled, severally, with 4-cyano-phenol, 4-cyano-4′-hydroxybiphenyl, and 4-(4-heptyloxybenzoyloxy)phenol, in the presence of diethyl azodicarboxylate (DEAD) and triphenylphosphine ('Mitsunobu-conditions' [13]) yielding the mesogens **13–15** [10]. Furthermore, the 4-heptyloxybenzoyl derivative **16** was synthesized from **11** by esterification. Finally, the C_4F_9-substituted derivative **12** was synthesized using the same procedures reported for the C_8F_{17} derivative **13** [11].

3. Results and discussion

3.1. *Thermal properties of polyfluoroalkyl-substituted amphiphilic mesogens 1–9*

The 'single tailed' amphiphilic *O*- (**1–4**) [1, 9], and *S*-glycosides (**6–9**) [9] presented in table 1 form smectic mesophases with typical SmA fan-shaped textures. It is noteworthy that the (3-perfluoroalkyl-propyl) β-D-glucopyranosides **1–4** show a strong tendency to form homeotropic layers after melting. Stepped drops and fan-like

Table 2. Thermal properties of the mesogens **10–15** and the non-mesogenic derivative **16** determined by polarizing microscopy (for the syntheses of the compounds see [10, 11]).

Compound	Structure	m.p./°C	Mesophase	c.p./°C
10		72–73 (73)[a]	SmA	56 (55)[a,f]
11		106–107 (106)[a]	SmA[b]	116–117 (115)[a]
12	 $R = n\text{-}C_7H_{15}$; $R_F = n\text{-}C_4F_9$	135 (134)[a]	SmC*/SmA 172 (170)[a,c]	174–175 (174)[a]
13	$R = n\text{-}C_7H_{15}$; $R_F = n\text{-}C_8F_{17}$	155–156[d] (155)[a]	SmC*/SmA 205–206	216–217 (decomp.)
14	 $R_F = n\text{-}C_8F_{17}$	128–129 (128)[a]	SmA	170–171
15	 $R_F = n\text{-}C_8F_{17}$	133–134 (133)[a]	SmA[e]	> 260 (decomp.)
16	 $R = n\text{-}C_7H_{15}$; $R_F = n\text{-}C_8F_{17}$	104–105	—	—

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[a] DSC values.

[b] A metastable higher ordered phase was observed below 99°C.

[c] Figure 3.

[d] A metastable crystal modification was observed between 147 and 143°C (DSC values).

[e] SmA (layer thickness: 48.5 ± 0.5 Å). Furthermore, a metastable smectic C* phase was observed below 120–121°C (layer thickness at 115°C, 47.5 ± 0.5 Å).

[f] Monotropic transition.

textures, characteristically for smectic A phases, were observed only in preparations without a cover slide. The compounds **1–4** show higher melting and clearing points than the fluorine-free alkyl β-D-glucopyranosides with the same number of C-atoms in the alkyl chain [1]. This effect seems to be connected with the greater stiffness (less conformational freedom) of fluorocarbon chains compared with hydrocarbon chains [4].

Whereas in **1–4** the flexibility of the hydrophobic chain is still slightly enhanced by a trimethylene spacer, the thioglycosides **6–9** do not contain a hydrocarbon spacer, i.e. the perfluoroalkyl chain is directly linked to the hydrophilic sugar moiety. The mesophases of the compounds **6–9** are not chemically stable up to their clearing points. Above temperatures of 135°C reactions are observed (probably thermal glycosylations). In spite of these reactions, a mesophase remains. Thus, the clearing temperatures given in table 1 are not the transition temperatures of the pure compounds **6–9** but those of any resulting mixtures.

The amphiphilic (3-perfluorooctyl-propyl) 6-*O*-dodecanoyl-β-D-glucopyranoside (**5**) shows very interesting thermal behaviour. On heating, only one columnar mesophase is observed (m.p. 73–74°C; c.p. 146–147°C). However, when this phase is cooled below the melting temperature, it transforms into a second, still unknown phase at about 57°C—see table 1. The textures of these two mesophases are depicted in figure 1.

Compound **5** contains a hydrocarbon chain besides the perfluoroalkyl chain. The miscibility of lipophilic and fluorophilic moieties depends on temperature. Thus, a segregation of two different hydrophobic segments would be conceivable at lower temperatures and in the crystalline state. However, the crystals of **5** were not suitable for X-ray analysis.

3.2. *Thermal properties of non-amphiphilic derivatives*

Calamitic, non-amphiphilic chiral mesogens containing deoxygenated carbohydrate moieties show promise of giving cholesteric or smectic C* phases. Some models of this type of liquid crystal were described, e.g., in [14, 15]. Perfluoroalkyl substituted, non-amphiphilic mesogens based on carbohydrates should meet the requirements for the formation of chiral mesophases.

The C_8F_{17} substituted hexahydrofuro[2,3-b]pyrans **10** and **11** [10] used as precursors for the synthesis of the non-amphiphilic mesogens **13–15** are already liquid crystalline, forming SmA phases. The thickness of the SmA layers of **11** is 32.7 Å (X-ray measurement). On heating and cooling, compound **11** shows a strong tendency to homeotropy in the mesophase. Moreover, a metastable (monotropic), high ordered mesophase was observed on cooling, but an exact assignment of the mesophase type is difficult (probably SmB). A cubic phase may be excluded, because birefringence always remains both on shearing the sample and on cooling samples that show a richly textured SmA phase.

The compounds **12**, **13** and **15** show polymorphism (formation of SmC* and SmA phases), whereas the cyanophenyl derivative **14** forms exclusively a SmA

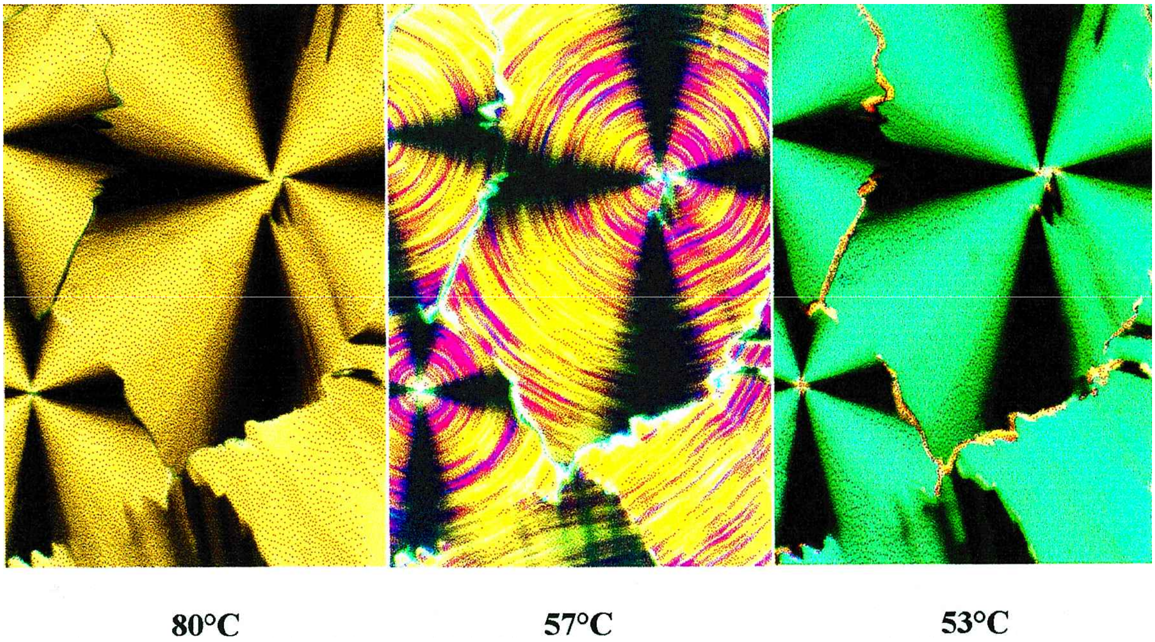


Figure 1. Textures of compound **5** (Leitz Laborlux 12 Pol microscope equipped with a Mettler hot stage FP 90 and a Leica WILD MPS 52 for photomicrographs); thermal data see table 1. Left to right: columnar phase, transition to unknown phase and unknown phase.

phase; thermal data are in table 2. The thermogram of compound **12** is shown in figure 2. Thus, a smectic C* phase is observed above the melting points of **12** (134°C) and **13** (155°C). On further heating, a smectic A phase is formed (**12**: 170°C; **13**: 205–206°C); see table 2. The photomicrographs of figure 3 show the typical striated fan-shaped texture of the SmC* phase caused by the helical structure and the 'normal', fan-shaped texture of the SmA phase of **12**. These pictures were taken near to the transition temperature SmA → SmC*. Furthermore, it was found by X-ray measurements that the thickness of the SmC* layers is dependent on temperature, a further indication of the existence of a SmC* phase. Finally, it is noteworthy that the texture of the corresponding C_8F_{17} derivative **13** shows a broken fan-shaped texture with only a few striated regions.

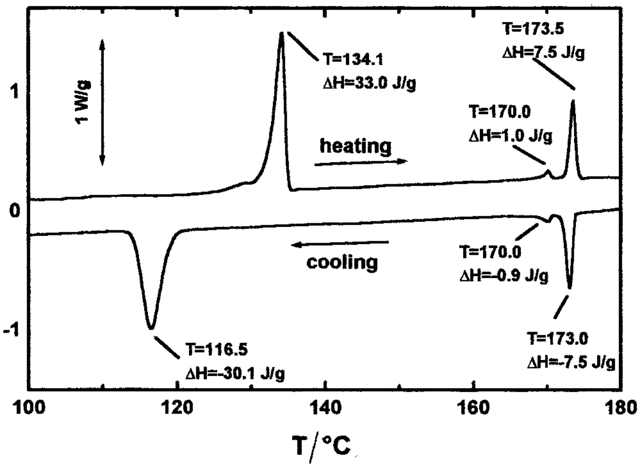


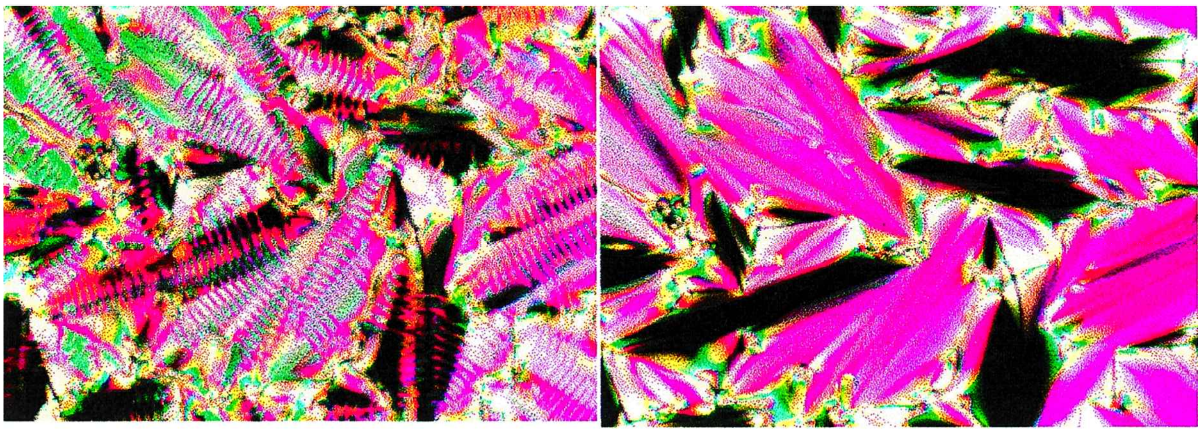
Figure 2. Thermogram of compound **12** (heating rate 5°C min^{-1}).

In the case of the cyanobiphenyl derivative **15**, the smectic C* phase is monotropic, i.e. it is only observed on supercooling of the melt. The assignment of the metastable phase was difficult, because of the considerable predilection of **15** for crystallization. The sample of **15** was heated to 140°C and subsequently cooled. The SmA → SmC* phase transformation was observed at about 120°C, detected by formation of transverse-banded lines within the texture. However, after rapid heating of the sample above the clearing point and subsequent cooling, the SmA → SmC* transformation point was significantly lowered, but a nice fan-shaped texture of the SmA phase was observed *en route*. The thickness of the SmA layers was 48.5 ± 0.5 Å determined by X-ray measurements. We estimate the molecular length of compound **15** to be about 30 Å using molecular structure models, i.e. always two calamitic molecules of **15** arranged in line are required to explain the measured thickness of the layer.

A qualitative miscibility experiment of **12** with the nematic compound 1,4-di-(4-heptyloxybenzoyloxy)benzene not only induced a cholesteric phase, but also a blue phase could be observed. Compound **16** (m.p. 104–105°C) is not liquid crystalline, probably due to the unfavourable three dimensional structure of the molecules.

4. Final remarks

It is known that the miscibility of alkyl and perfluoroalkyl compounds is restricted because perfluoroalkyl chains are both hydrophobic and lipophobic [4]; for a monograph on mixed surfactant systems see [16]. Additionally lamellar and hexagonal phases have been observed for perfluorinated surfactants [4] (and papers cited therein).



(SmC* phase at 168°C) (SmA phase at 172°C)

Figure 3. Polymorphism of compound **12** (Leitz Laborlux 12 Pol microscope equipped with a Mettler hot stage FP 90 and a Leica WILD MPS 52 for photomicrographs); thermal data see table 2.

The thermal properties of the perfluoroalkyl substituted non-amphiphilic mesogens **10–15** confirm the observation of Liu and Nohira [17] that the stability of smectic phases increases with increasing fluorination.

The authors thank Dr Siegmar Diele, Prof. Dr Wolfgang Weissflog (Institut für Physikalische Chemie der Martin-Luther-Universitaet Halle-Wittenberg) and Dr Volkmar Vill (Institut für Organische Chemie der Universitaet Hamburg) for the measurements of the thickness of layers by X-ray analysis and for fruitful discussions.

References

[1] Hein, M., and Miethchen, R., 1998, *Tetrahedron Lett.*, **39,** 6679.
[2] Riess, J. G., 1994, *Colloids Surfaces A, Physicochemical and Engineering Aspects*, **84,** 33.
[3] Kokelenberg, H., and Pollet, R., 1985, *Tenside, Detergents*, **22,** 1.
[4] Kissa, E., 1994, *Fluorinated Surfactants. Synthesis, Properties, Applications* (New York: M. Dekker).
[5] Riess, J. G., 1995, *J. Liposome Res.*, **5,** 413.
[6] Riess, J. G., and Greiner, J., 1993, in *Carbohydrates as Organic Raw Materials II*, edited by G. Descotes, (Weinheim: VCH), pp. 209–259.
[7] Zur, C., Miller, A. O., and Miethchen, R., 1998, *Liq. Cryst.*, **24,** 695.
[8] Review: Prade, H., Miethchen, R., and Vill, V., 1995, *J. prakt. Chem.*, **337,** 427.
[9] Hein, M., Miethchen, R., and Schwaebisch, D., 1999, *J. Fluorine Chem.*, **98,** 55.
[10] Hein, M., and Miethchen, R., 1999, *Eur. J. org. Chem.*, 2429.
[11] Hein, M., 1999, PhD thesis, University of Rostock, Germany.
[12] Tietze, L. F., 1996, *Chem. Rev.*, **96,** 115.
[13] Review: Hughes, D. L., 1992, *The Mitsunobu Reaction* in *Organic Reactions*, Vol. 42 (New York: J. Wiley & Sons), pp. 335–656.
[14] Pudlo, P., Thiem, J., and Vill, V., 1990, *Chem. Ber.*, **123,** 1129; Vill, V., and Tunder, H. W., 1995, *Liebigs Ann. Chem.*, 1055.
[15] Smits, E., Engberts, J. B. F. N., Kellogg, R. M., and van Doren, H. A., 1995, *Mol. Cryst. liq. Cryst.*, **260,** 185.
[16] Ogino, K., and Abe, M., (editors), 1993, *Mixed Surfactant Systems*, Surfactant Science Series, Vol. 46 (New York: M. Dekker).
[17] Liu, H., and Nohira, H., 1997, *Liq. Cryst.*, **22,** 217.