ELSEVIER

www.elsevier.nl/locate/carres

Carbohydrate Research 327 (2000) 169–183

CARBOHYDRATE RESEARCH

Review

Liquid crystals based on fluorinated carbohydrates

Ralf Miethchen *, Martin Hein

Department of Organic Chemistry, University of Rostock, Buchbinderstraße 9, D-18051 Rostock, Germany

Received 20 April 1999

Abstract

Fluorine introduced in the hydrophilic or the hydrophobic region of amphiphiles influences the thermomesomorphy of amphiphilic and monophilic fluorosugars in a very specific manner. This paper is the first review about chiral mesogens based on fluorinated carbohydrates. It covers the literature published so far. Analytical objectives are given to: (i) Effects of fluorine atoms on the H-bonding network of the hydrophilic region of sugar amphiphiles; (ii) Effects of perfluoroalkyl chains compared to alkyl chains; (iii) Polymorphism, e.g., also formation of smectic S_C^* phases.

Keywords: Carbohydrates; Amphiphiles; Deoxyfluoro sugars; Mesogens; Liquid crystals; Polyfluoroalkylated sugars

Contents

* Corresponding author. Tel.: +49-381-4981764; fax: +49-381-4981819.
E-mail address: ralf.miethchen@chemie.uni-rostock.de (R. Miethchen).

0008-6215/00/$ - see front matter © 2000 Elsevier Science Ltd. All rights reserved.
PII: S0008-6215(99)00317-1

1. Introduction

In the last 2 decades, much attention has been devoted to the liquid–crystalline properties of carbohydrate derivatives (for reviews, see [1–5]). Thermotropic mesophases of sugar amphiphiles are induced by 'intramolecular incompatibility'. In other words, the liquid–crystalline state can be described in terms of a micro phase-separation. Because hydrophobic and hydrophilic moieties are not mixed randomly, both alkyl (or F-alkyl) chains packing (van der Waals interactions) and head groups packing (hydrogen-bonded networks) could contribute to the stability of such mesophases (for simplified models see Ref. [3,6,7]). Recently, Goodby and co-workers [3] developed the concept that amphiphilic mesophases (smectic type) are basically held together by strong interactions of the hydroxyl groups, while the aliphatic chains almost act as a solvent between the layers of the head groups.

The spontaneous self-organisation of molecules forming supramolecular structures does not lead to a rigid state, but more or less fluid systems arise. These systems can often evolve into other aggregation forms (polymorphism). The phase transitions are believed to proceed in a stepwise process that begins with a (partial) breakdown of the three-dimensional network of hydrogen bonds between the carbohydrate moieties (cr–lc). The mesophase is mainly stabilised by the remaining hydrogen bonding within the hydrophilic region of carbohydrate residues, and additionally by van der Waals attractions (see also Ref. [3]). These interactions are no longer sufficiently strong at the clearing point (lc–iso).

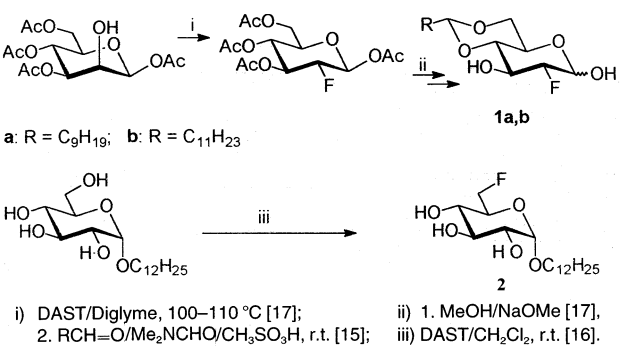
There is obviously a close relationship between the number of lipophilic moieties in the molecules and the type of phase that is formed. Two types of thermotropic liquid–crystalline phases, smectic and columnar, are observed in the class of amphiphilic carbohydrate-based mesogens.

As it has often been proved for numerous 'single tailed' carbohydrate-based amphiphiles, all of them form smectic mesophases [1]. Based on X-ray powder patterns, it was concluded that the smectic phase must have a bilayer structure [6,8–10]. The model postulates an arrangement in which the molecules are ordered tail-to-tail with partially overlapping alkyl chains with sugar groups sandwiched between aliphatic lamellae [3].

2. Smectic mesogens based on fluorinated carbohydrates

2.1. General discussion

All amphiphiles based on carbohydrates that are linked to only one hydrophobic chain such as an alkyl or polyfluoroalkyl chain form smectic mesophases on heating. The better the fit of the carbohydrate moiety with the three-dimensional hydrogen-bonded network, the greater is the stabilising effect on mesophases, i.e., the number of free OH-groups as well as their arrangement (e.g., equatorial or axial) is important. Therefore, replacement of an hydroxyl group by a fluorine atom always leads to a significant destabilisation of the corresponding mesophases formed by an amphiphilic sugar. Whereas hydroxyl groups contribute to the cooperative networks as hydrogen donors and acceptors, C–F groups act exclusively as weak acceptors [9,11]. The existence of a C–F···H–O-bridge was proved in crystalline 2-deoxy-2-fluoro-β-D-mannopyranosyl fluoride [12]. Moreover, enzymatic investigations with glycogen phosphorylase on deoxy- and deoxyfluoro-derivatives of D-glucose confirmed that a C-linked F-atom of a D-glucose moiety is a hydrogen-bond acceptor. Significant differences in enzyme activities were not observed when the OH-group, which was replaced by fluorine, did exclusively participate as a H-bond acceptor. In contrast



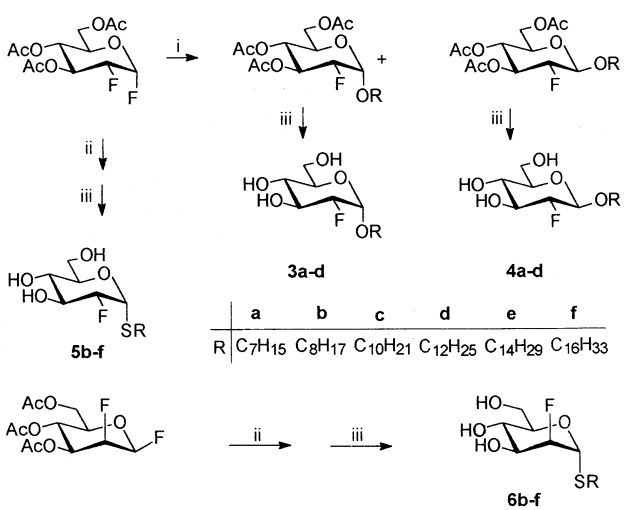
Scheme 1.

significant differences were found when this OH-group was a H-bond donor [12].

If fluorine is introduced into the hydrophobic part of an amphiphilic carbohydrate, e.g., in the form of polyfluoroalkyl chains, the intramolecular contrast within the amphiphile is significantly increased. However, fluorocarbon chains are not only more hydrophobic, but are also more rigid than hydrocarbon chains because of a large energy difference between the gauche and trans conformations. Thus, fluorinated chains prefer the trans form with less conformational freedom and an essential helical conformation [13,14]. Thus, replacement of an alkyl chain by a highly fluorinated chain generally leads to a significant stabilisation of the corresponding mesophases formed by an amphiphilic sugar.

2.2. Synthesis of the amphiphilic sugars fluorinated at the hydrophilic head

The first examples of fluorinated carbohydrate-based mesogens described in the literature are the 4,6-*O*-alkylidene-2-deoxy-2-fluoro-D-glucopyranoses **1a** and **1b** [15]. The introduction of the fluorine atom was achieved by the treatment of 1,3,4,6-tetra-*O*-acetyl-D-mannopyranose with diethylaminosulfur trifluoride (DAST) in dichloromethane at room temperature. The same agent was also used for the preparation of dodecyl 6-deoxy-6-fluoro-α-D-glucopyranoside (**2**, Scheme 1) [16].



Scheme 2.

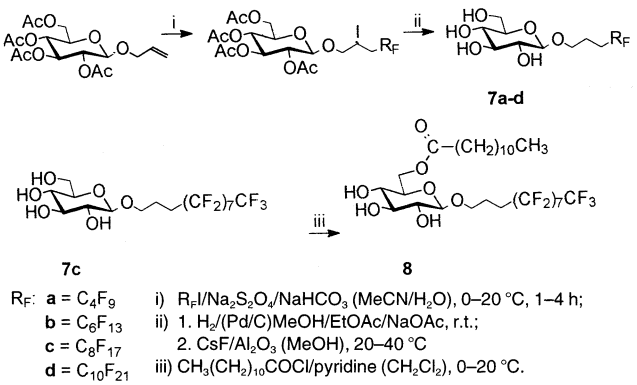
The liquid crystalline alkyl 2-deoxy-2-fluoro-α-D-glucopyranoside (**3a**–**d**) [17], alkyl 2-deoxy-2-fluoro-β-D-glucopyranoside (**4a**–**d**) [17], alkyl 2-deoxy-2-fluoro-1-thio-α-D-glucopyranoside (**5b**–**f**) [18], and alkyl 2-deoxy-2-fluoro-1-thio-α-D-mannopyranoside derivatives (**6b**–**f**) [18] were synthesised as shown in Scheme 2; for some amphiphilic glycosyl fluorides see Ref. [16]. Starting from 3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-α-D-glucopyranosyl fluoride, obtained by treatment of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-fluoro-β-D-glucopyranose [19] with $HF/MeNO_2$ [17] or starting from 3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-β-D-mannopyranosyl fluoride, the homologous alkyl 2-deoxy-2-fluoro-D-glucopyranosides, (α anomers **3a**–**d** and β anomers **4a**–**d**) [17], as well as the alkyl 2-deoxy-2-fluoro-1-thio-α-D-glucopyranosides (**5b**–**f**) [18] and alkyl 2-deoxy-2-fluoro-1-thio-α-D-mannopyranosides (**6b**–**f**) [18], were accessible (Scheme 2). Because the starting material is rather unreactive, the O-glycosylation processes catalysed by $TiF_4/AgClO_4$ required long reaction times (24 h). The alkyl 2-deoxy-2-fluoro-D-glucopyranosides were formed in a ratio of α:β 4:1 with yields of 65–78%.

For the S-glycosylation of alkanethiols with 3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-α-D-glucopyranosyl fluoride, the catalyst $BF_3{\cdot}Et_2O$ was more effective than $TiF_4/AgClO_4$. Because the anomeric mixtures of the alkyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-1-thio-D-glucosides (44–62% yield, ratio α:β between 1.7:1 and 3:1) were difficult to separate, only the α anomers obtained in pure form were deacetylated giving **5b**–**f** [18]. The analogous alkyl 2-deoxy-2-fluoro-1-thio-α-D-mannopyranosides (**6b**–**f**) were prepared in the same way via S-glycosylation of the corresponding alkanethiols with 3,4,6-tri-*O*-acetyl-2-deoxy-2-fluoro-β-D-mannopyranosyl fluoride [20] in the presence of $BF_3{\cdot}Et_2O$ [18].

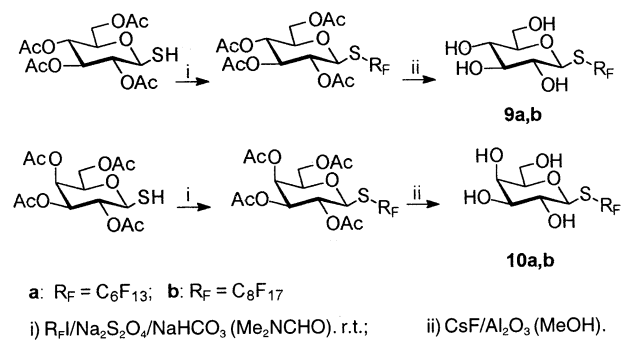
2.3. Synthesis of amphiphilic sugars fluorinated in the hydrophobic chain

The radical addition of 1-iodoperfluoroalkanes to double bonds using sodium

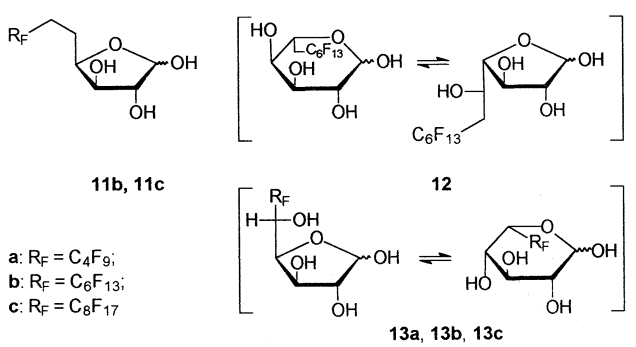
dithionite as initiator [21–28] is one of the most convenient methods to introduce perfluoroalkyl chains; for other methods of addition see Refs. [20,29] and papers cited therein. Thus, the homologous (3-perfluoroalkylpropyl) β-D-glucopyranosides (**7a–d**) were synthesised from allyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside and 1-iodoperfluoroalkanes via the iodo derivatives according to Scheme 3. The 'single-tailed' amphiphile **7c** was selected as model for introducing a second hydrophobic chain by acylation, generating compound **8** (Scheme 3).



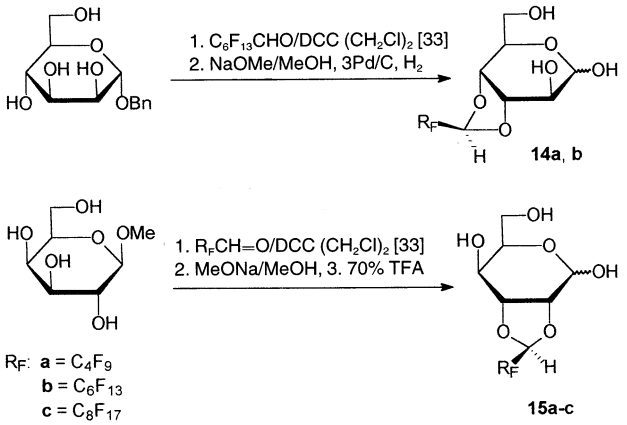
Scheme 3.



Scheme 4.



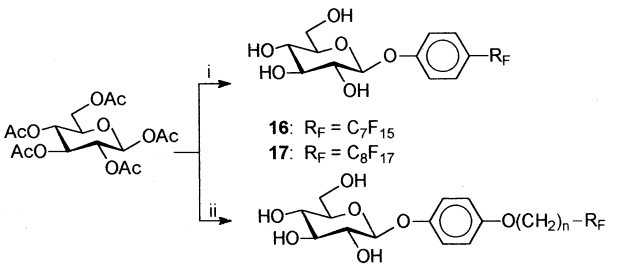
Scheme 5.



Scheme 6.

Dithionite-mediated S-perfluoroalkylations of 1-thio-sugars are easy procedures as well [27]. Thus, treatment 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-galactopyranose, respectively, with 1-iodoperfluoroalkanes, gave in the presence of sodium dithionite and sodium hydrogen carbonate, the corresponding perfluoroalkyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glycopyranosides in good to moderate yields (Scheme 4). It is noticeable that these reactions also proceed when sodium dithionite is absent. However, the reactions run much slower and less selective. Thiolates, which are formed from the thiols when sodium hydrogen carbonate was added as acid scavenger, probably resulted in perfluoroalkylations as described in Ref. [30]. The mesogens **9b**,**c** and **10b**,**c** were obtained from the acetyl derivatives by treatment with a methanolic suspension of alumina-supported cesium fluoride [27].

The preparation of further fluorinated 'single-tailed' mesogens is described in Schemes 5–7. Thus, the trihydroxy derivatives **11b**,**c** were obtained via a dithionite-mediated radical perfluoroalkylation of 3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranose [31], the tetrahydroxy derivative **12** via a dithionite-mediated radical perfluoroalkylation of 6-deoxy-1,2:3,4-di-*O*-isopropylidene-β-L-*arabino*-hex-5-enopyranose [31] and the tetrahydroxy derivatives **13a–c** via a nucleophilic perfluoroalkylation of 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pento-

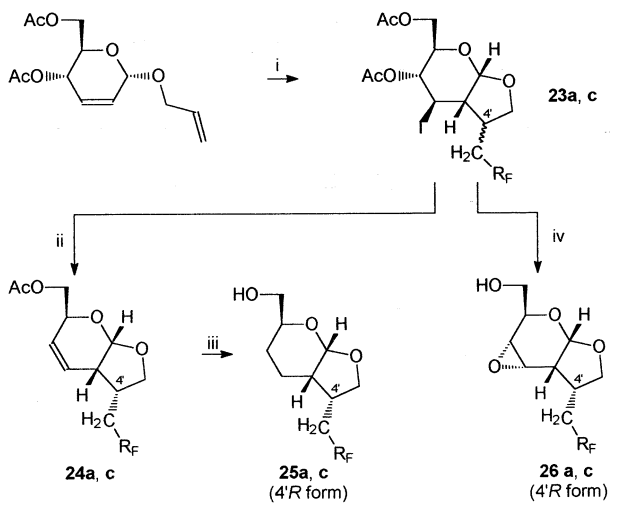


16: $R_F = C_7F_{15}$
17: $R_F = C_8F_{17}$

18: n = 4, $R_F = C_4F_9$; **19**: n = 5, $R_F = C_4F_9$;
20: n = 6, $R_F = C_4F_9$; **21**: n = 4, $R_F = C_6F_{13}$
22: n = 5, $R_F = C_6F_{13}$.

i) 1. R_F-C_6H_4OH, BF_3, Et_2O, r.t.; 2. Me_3N, H_2O, MeOH
ii) 1. R_F-$(CH_2)_n$-OC_6H_4OH, BF_3, Et_2O, r.t.; 2. Me_3N, H_2O, MeOH

Scheme 7.



a: $R_F = C_4F_9$; **c**: $R_F = C_8F_{17}$
i) $R_FI/Na_2S_2O_4/NaHCO_3$, 0 °C; ii) Zn/Cu/Me_2NCHO, 115 °C;
iii) 1. CsF/Al_2O_3/MeOH, r.t., 2. H_2/Pd/C/EtOAc/MeOH;
iv) KO'Bu/MeOH, 20–40 °C, 30 min.

Scheme 8.

dialdo-1,4-furanose [32] (Scheme 5). However, the selectivity of these syntheses is only moderate.

The 3,4-*O*-perfluoroalkylidene-D-altrose derivatives **14a**,**b** and the homologous 2,3-*O*-perfluoroalkylidene-D-gulose derivatives **15a**–**c** were prepared from benzyl α-D-mannoside and methyl β-D-galactoside, respectively, according to Scheme 6 [33]. The key step of the syntheses is a non-conventional acetalation using perfluoroaldehydes and DCC. This reaction step includes an epimerisation at C-3.

More recently, a French group [34] described the synthesis of two homologous series of 4-perfluoroalkylphenyl β-D-glucopyranosides (**16**, **17**) and 4-polyfluoroalkyloxyphenyl β-D-glucopyranosides (**18**–**22**) by a BF_3-catalysed glycosylation of fluoroalkylsubstituted phenols with penta-*O*-acetyl-β-D-glucopyranose. β-D-Glucosides were obtained exclusively (Scheme 7).

2.4. Synthesis of non-amphiphilic sugars fluorinated in the hydrophobic chain

The chiral perfluoroalkyl substituted hexahydrofuro[2,3-*b*]pyran derivatives **23a** and **23c** were prepared from allyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside and 1-iodoperfluoroalkanes via a dithionate-mediated radical 'domino-reaction' [28]. Only one pair of diastereomers, the (4′-*R*)-form and the (4′-*S*)-form of these compounds (4–5:1), was obtained in the first step, i.e., two of the three new stereogenic centres were totally controlled (Scheme 8).

After a reductive elimination with Zn/Cu, the corresponding major diastereomers of **24a** and **24c** (4′-R form), respectively, could be separated by column chromatographic purification [28]. These products were converted into the tetrahydro-α-D-*erythro*-hexopyranoso[1,2-*b*]furans (**25a**, **25c**) according to Scheme 8. Moreover, the intermediates **23a** and **23c** were converted into the epoxides **26a** and **26c** by treatment with methanolic potassium *tert*-butoxide [45] (Scheme 8).

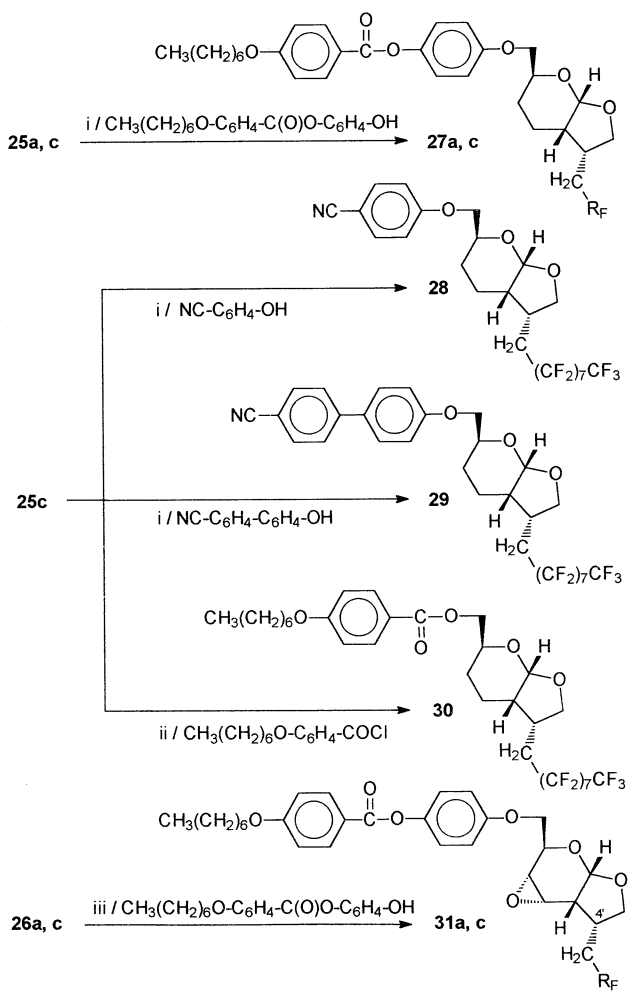
The compounds **25a**,**c** and **26a**,**c** are convenient building blocks to prepare the monophilic chiral mesogens **27a**,**c**, **28**, **29**, and **31a**,**c** by Mitsunobu etherification [28]. In the case of **31a**,**c**, the procedure was modified, and the reagent diisopropyl azodicarboxylate (DIAD) also gave better yields (85–87%) too than its diethylester analogue (DEAD; see Section 6). Moreover, the 4-heptyloxybenzoyl derivative **30** was synthesised by esterification (Scheme 9). However, this compound is not liquid crystalline.

3. Thermal properties of amphiphilic derivatives

3.1. Monofluorinated mesogens

The amphiphiles **1a**,**b** [15], **2** [16] **3a**–**d** [17], **4a**–**d** [17], **5b**–**f** [18], and **6b**–**f** [18], (Table 1,

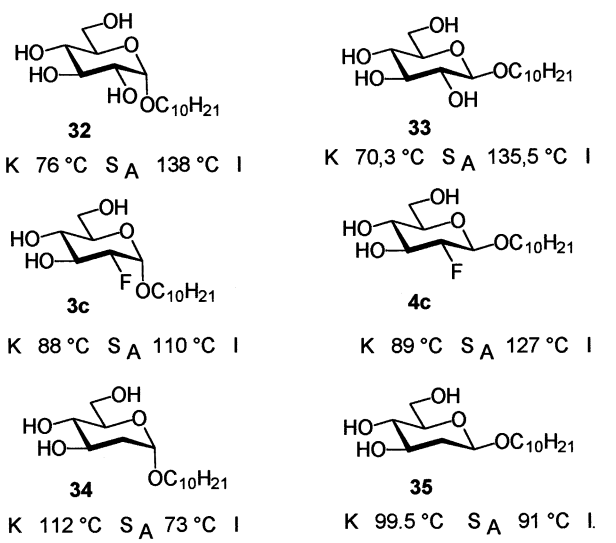
Schemes 1 and 2), which are monofluorinated within the hydrophilic head region, show only narrow-ranged mesophases compared to the analogous fluorine-free OH compounds because replacement of a C–OH bond by C–F reduces the hydrogen bonding between the head groups of the carbohydrate mesogens. The type of mesophase formed is smectic A (S_A). The significant changes of thermal properties caused by substitution of an OH-group by fluorine and hydrogen, respectively, are representatively expressed by the examples in Scheme 10. The two anomeric decyl D-*arabino*-hexopyranosides (**34**, **35**) show, compared with the corresponding C-2 OH (**32**, **33**) and C-2 F (**3c**, **4c**) derivatives, the lowest clearing temperatures, because the methylene



Scheme 9.

Table 1
Thermal behaviour of amphiphilic, monofluorinated mesogens

	Mp (°C)	Phase	Cp (°C)	Ref.
1a	54–57	S_A	72–74	[15]
1b	60–75	S_A	80–90	[15]
2	52.5	S_A	44.5	[16]
3a	52	S_A	64	[17]
3b	78.5	S_A	83	[17]
3c	88	S_A	110	[17]
3d	91	S_A	114	[17]
4a	81	S_A	74	[17]
4b	85	S_A	103.5	[17]
4c	89	S_A	127	[17]
4d	90	S_A	129	[17]
5b	101.5	S_A	109	[18]
5c	103.5	S_A	124.5	[18]
5d	107–108	S_A	132	[18]
5e	111–113	S_A	136.5	[18]
5f	112–115	S_A	136	[18]
6b	67.2	S_A	47.5	[18]
6c	72.6	S_A	77.7	[18]
6d	82.5	S_A	90.9	[18]
6e	91.3	S_A	98.1	[18]
6f	95.4	S_A	99.5	[18]



Scheme 10.

moiety is not able to participate in the polar network in any way [1,17,35].

Dodecyl 6-deoxy-6-fluoro-α-D-glucopyranoside (**2**) forms a monotropic smectic phase [19]. It is noticeable that, in contrast, dodecyl 6-deoxy-6-fluoro-α-D-galactopyranoside [19] and some 6-deoxy sugars (alkyl L-fucopyranosides) [36] are not liquid crystals. In contact with water, compound **2** shows lyotropic

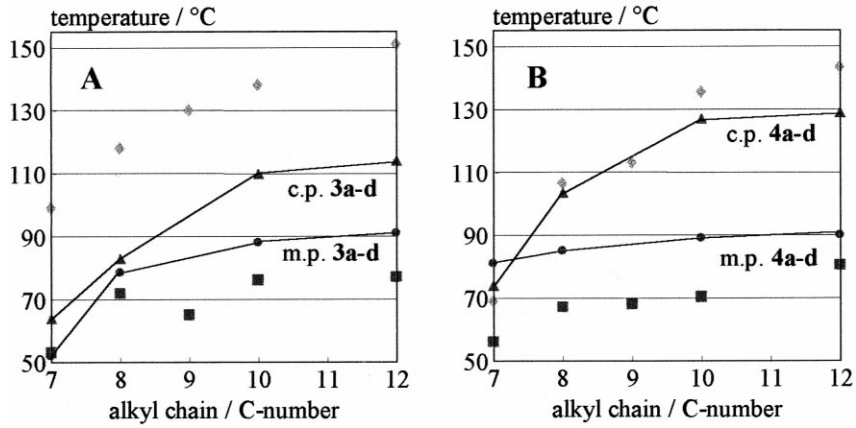


Fig. 1. (A) Thermal behaviour of alkyl 2-deoxy-2-fluoro-α-D-glucopyranosides (**3a**–**d**) (● = mp, ▲ = cp) [17] and alkyl α-D-glucopyranosides [35] (■ = mp, ◇ = cp); (B) thermal behaviour of alkyl 2-deoxy-2-fluoro-β-D-glucopyranosides (**4a**–**d**) (● = mp, ▲ = cp) [17] and alkyl β-D-glucopyranosides [35] (■ = mp, ◇ = cp).

properties. The 4,6-*O*-alkylidene-2-deoxy-2-fluoro-D-glucopyranoses (**1a**, **1b**) form thermotropic (smectic A) and lyotropic liquid crystalline phases as well. Broad two-phase temperature ranges without sharp phase transitions are observed in the case of the enantiotopically thermotropic phases. At first, the compounds melt to a non-structured marbled mesophase that soon becomes homeotropically orientated on further heating. Domains of the mesophase and of the isotropic phase coexist in the relatively broad two-phase clearing ranges. During cooling down, typical bâtonnets form preferably in the periphery. The lower homologous 4,6-*O*-hexylidene and 4,6-*O*-heptylidene derivatives of **1a**,**b**, likewise show in contact with water lyotropic behaviour, but they are not thermotropic liquid crystals [15].

In Figs. 1 and 2, the thermal properties of the 2-deoxy-2-fluoro glucosides **3a**–**d**, **4a**–**d**, and **5b**–**f** are compared among themselves and with the corresponding fluorine-free glucosides. As expected, homologous alkyl 2-deoxy-2-fluoro-α-D-glucopyranosides (**3a**–**d**) [17] form less-stable mesophases (lower clearing temperatures) than alkyl α-D-glucopyranosides [35] (Fig. 1). On the other hand, the mesophases of **3a**–**d** [17] are less stable as compared to those of the corresponding alkyl 2-deoxy-2-fluoro-β-D-glucopyranosides (**4a**–**d**) as well as the corresponding alkyl 2-deoxy-2-fluoro-1-thio-α-D-glucopyranosides (**5b**–**f**) [18] (Scheme 10, Figs. 1 and 2). The latter result correlates with former observations that S-glucosides show higher clearing temperatures than the corresponding O-glucosides [1]. Re-

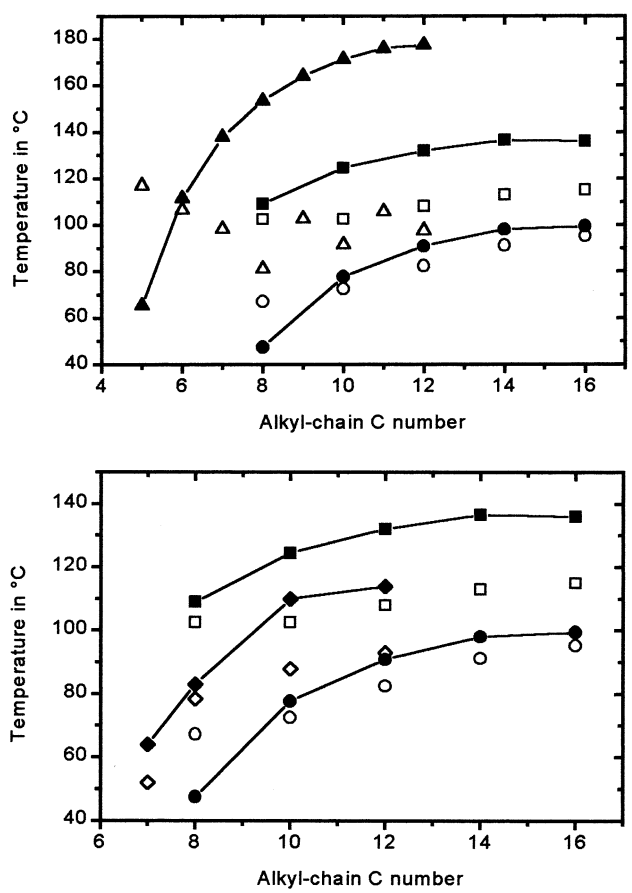


Fig. 2. Thermotropic behaviour of the △/▲ alkyl 1-thio-α-D-glucopyranosides [1]; ◇/◆ alkyl 2-deoxy-2-fluoro-α-D-glucopyranosides (**3a**–**d**) [17]; □/■ alkyl 2-deoxy-2-fluoro-1-thio-α-D-glucopyranosides (**5b**–**f**) [18]; ○/● alkyl 2-deoxy-2-fluoro-1-thio-α-D-mannopyranosides (**6b**–**f**) [18].

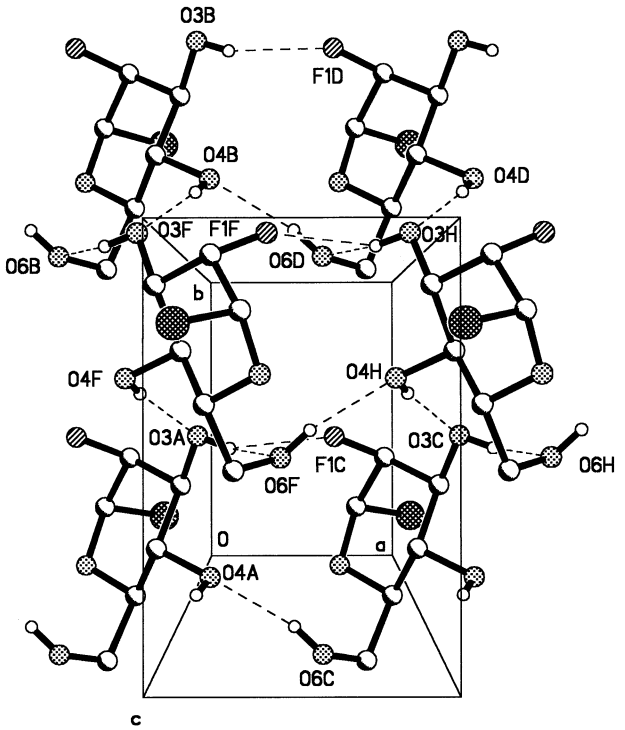


Fig. 3. Molecular arrangement of the polar head groups of **6b** (view down the *c*-axis, alkyl chains at S omitted).

cently, Goodby and co-workers [3] draw the general conclusion that the efficiency of the linking group in the formation of thermotropic phases follows the order –SR > OCOR > –OR.

A comparison of the homologous series, alkyl 2-fluoro-2-deoxy-1-thio-α-D-glucopyranosides (**5b**–**f**) and alkyl 1-thio-α-D-glucopyranosides, shows similar melting temperatures, but significantly decreased clearing temperatures for **5b**–**f**. This result indicates that the functional group in the 2-position is incorporated into the two-dimensional polar 'head-to-head' cooperative network within one and the same layer, but not (or hardly) between different layers of the smectic phase [18]. The decreasing of the clearing temperature is due to the weakness of the cooperative polar network, because fluorine acts as only a weak hydrogen-bond acceptor.

The alkyl 2-deoxy-2-fluoro-1-thio-α-D-mannopyranosides (**6b**–**f**) show lower melting and clearing temperatures than the corresponding alkyl 2-deoxy-2-fluoro-1-thio-α-D-glucopyranosides (**5b**–**f**), and the octyl derivative **6b** is even a monotropic mesogen [18]. This indicates that the axially arranged fluorine atom in the 2-position of the *manno*-derivatives allows only a weaker cooperation in the polar network as compared to the equatorial arranged one in **5b**–**f**.

The crystal structure of octyl 2-deoxy-2-fluoro-1-thio-α-D-mannopyranoside **6b** was determined by an X-ray measurement (orthorhombic, space group $P2_12_12_1$; Figs. 3 and 4). The hydrophilic and lipophilic partial structures of the molecule form, as expected, strictly separated regions within the crystal lattice. While there are two intramolecular hydrogen bonds within the molecule, the polar layers are packed via an intermolecular network of hydrogen bonds and short contacts,

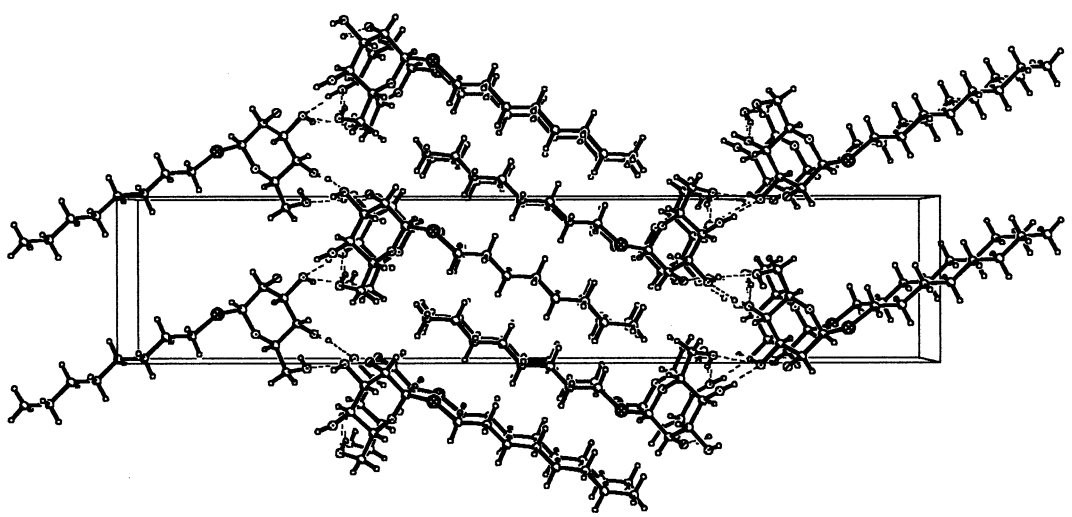


Fig. 4. Crystallographic arrangement of compound **6b** in the unit cell (view parallel to *a*-axis).

Table 2
Thermal behaviour of amphiphilic, perfluoroalkyl-substituted mesogens

	Mp (°C)	Phase	Cp (°C)	Ref.
7a	145–146	S_A	141–142	[27,37]
7b	154	S_A	184	[27,37]
7c	168	S_A	208	[27,37]
7d	172–173	S_A	222 (dec)	[27,37]
8	73–74	X [a]	146–147	[27,37]
9b	120	S_A	181–182 [b]	[27,37]
9c	123–124	S_A	186–188 [b]	[27,37]
10b	59–60	S_A	163–164 [b]	[27,37]
10c	121–122	S_A	156–158 [b]	[27,37]
11b	133–134	S_A	151–152	[31,38]
11c	133–134	S_A	148–149	[31,38]
12	147–148	S_A	178–181	[31,38]
13a	155–156	S_A	127–142	[32,38]
13b	176–177	S_A	186–188	[32,38]
13c	178	S_A	194–196	[32,38]
14a	syrup	S_A	89–93	[33,38]
14b	syrup	S_A	156–159	[33,38]
15a	93–94	S_A	125–126	[33,38]
15b	95	S_A	171–172	[33,38]
15c	104–105	S_A	191–192	[33,38]

[a] Columnar mesophase. Moreover, formation of an unknown metastable phase below 58 °C, Fig. 6.
[b] Decomposition is observed above 135–140 °C.

Table 3
Thermal data of amphiphilic, perfluoroalkyl-substituted mesogens

	Mp (°C)	Phase	Cp (°C)	Ref.
16	165.5	S_A	202.7	[34]
17	168.7; 175.0	S_A	218.8	[34]
18	82.2	S_A	254.8	[34]
19	86.3	S_A	251.7	[34]
20	93.4	S_A	238.2	[34]
21	102.8	S_A	263.1	[34]
22	63.5; 91.8	S_A	264.3	[34]

respectively. In the *a*-direction, the 3-OH-group of each pyranose moiety is the H-donor to the F-atom in the neighbouring molecule, while the 6-OH is donor for the O-4 of the same neighbouring molecule. In the *b*-direction, symmetry conditions result in a head-to-head linkage of two stacks of molecules via two hydrogen-bonding motifs. One consists of 4-OH as donor and O-3 in the neighbouring molecule as acceptor. The other includes the same 3-OH group as donor towards the O-6 in the starting molecule, resulting in an eight-membered ring motif consisting of the sequence O-4···F–H-4···F–O-3···A–H-3···A–O-6···F–C-6···F–C-5···F–C-4···F. So, the hydrogen of the 3-OH group is in a short contact to both a fluorine and an oxygen; the length of the C2–F bond is 139.3 pm.

From the arrangement of the molecules of **6b** in the crystal lattice, it can be easily understood why liquid–crystalline phases are formed after melting. Obviously, there are domains with non-polar alkyl chains and parts with polar head groups facing each other. The nearest alkyl chains have distances of about 4.1 Å. The arrangement of the molecules within the smectic mesophase of **6b** is probably similar. This result correlates with an earlier report about the detection of a C–F···H–O-bond within crystalline 2-deoxy-2-fluoro-β-D-mannoyranosyl fluoride [12].

3.2. Polyfluorinated mesogens

The smectic mesophases of polyfluoroalkyl substituted carbohydrates are more stable then those of alkyl substituted carbohydrates (Tables 2 and 3). It is remarkable that even a perfluorobutyl chain linked to a carbohydrate moiety may be sufficient to result in liquid crystalline behaviour (compounds **13a**, **14a**, **15a**). Alkylene spacers between the hydrophilic head group and the fluorocarbon tail enhance the flexibility of the chains. That may have the effect of lowering the clearing points in comparison to derivatives with the same perfluoroalkyl chain length, but without any spacer. When an alkyl (or other lipophilic moiety) and a polyfluoroalkyl chain is introduced in the same sugar moiety, segregation of the lipophilic and fluorophilic chains is to be expected at definite temperatures which serves to induce polymorphism.

All the 'single-tailed' amphiphiles that are perfluorinated in any position of the molecule, i.e., the O- (**7a**–**d**) [26,27,37], and *S*-glycosides (**9b**,**c**, **10b**,**c**) [27,37], the 5,6-dideoxy-6-*C*-D-xylo-hexoses (**11b**,**c**) [31,38], 6-deoxy-6-perfluorohexyl-L-altrose (**12**) [31,38], the L-ido-aldohexoses (**13a**–**c**) [32,38], the perfluoroalkylidene D-altroses (**14a**,**b**) [33,38], the perfluoroalkylidene D-guloses (**15a**–**c**)

Table 4
Thermal behaviour of the non-amphiphilic, perfluoroalkyl-substituted mesogens

	Mp (°C)	Mesophase	Cp (°C)	Ref.
24c	73	S_A	55	[28,37]
25c	106	S_A [a]	115	[28,37]
26a	syrup	smectic at rt		[45]
26c	114–115 [b]	S_B (?) → S_A (122)	142	[45]
27a	134	S_C^* → S_A (170)	174	[28,37] [c]
27c	155 [d]	S_C^* → S_A (205–206)	216–217 (dec)	[28,37]
28	128	S_A; layer thickness: 48.5 ± 0.5 Å [e]	170–171	[28,37]
29	133	S_A	>260 (dec)	[28,37]
30	104–105			[28]
31a	147–148	S_C^* → S_A (157)	164–165	[45]
31c	155–156	S_C^* → S_A (191)	209–210	[45]

[a] A metastable higher ordered phase was observed below 99 °C.
[b] Crystal polymorphism: 80 °C (4.7 J g^{-1}) and 84 °C (4.2 J g^{-1}).
[c] Texture see Fig. 7.
[d] A metastable crystal modification was observed between 147 and 143 °C.
[e] A metastable smectic C* phase was observed below 120–121 °C (layer thickness: at 115 °C: 47.5 ± 0.5 Å).

[33,38], and the hexahydrofuro[2,3-*b*]pyran derivative (**24c**) [28,37] form smectic A phases with typical S_A fan-shaped textures. The short-chained nonafluorobutyl derivative **13a** is certainly a monotropic mesogen. Because of an annelated ring, the five bicyclic triols **14a**,**b** and **15a**–**c** and the bicyclic monohydroxy derivatives **25c** and **26a**,**c** have a fairly rigid head group. This probably contributes to a stabilisation of the corresponding mesophases. The syrupy epoxide **26a** is already liquid crystalline at room temperature (probably smectic). The crystalline homologous **26c** shows an interesting polymorphism. On heating, crystal transitions are observed before the compound melts at 114–115 °C forming a highly viscose mesophase (S_B phase?) with volume contraction. This phase transforms into a smectic A phase at 122 °C and into an isotropic melt at 142 °C (Table 4). The S_A-phase strongly tends to form a homeotropic arrangement.

It is noteworthy that the (3-perfluoroalkylpropyl) β-D-glucopyranosides (**7a**–**d**) also tend to form homeotropic layers after melting. Stepped drops and fan-like textures, which are characteristic for smectic A phases, were observed only in preparations without a cover slide. Compounds **7a**–**d** show higher melting and clearing points than the fluorine-free alkyl β-D-glucopyranosides with an equal C-number in their alkyl chain (Fig. 5) [26,27,37].

The mesophases of the thioglycosides **9b**,**c** and **10b**,**c** are not chemically stable up to the clearing points [27,37]. 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 2 are not the transition temperatures of the pure compounds **9b**,**c** and **10b**,**c**, but those of any mixtures. The *altro*-derivatives **14a**,**b**, having exceptionally broad mesophase ranges, did not crystallise.

Enantiotropic smectic A mesophases were also found in the case of the homologous series **16**, **17** and **18**–**22** (Scheme 7, Table 3). On cooling from the isotropic phase, bâtonnets and focal-conic areas, all fan like, were observed. Some homologues of the series **18**–

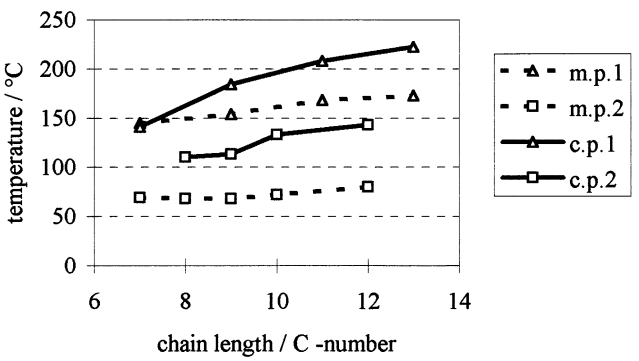


Fig. 5. Comparison of the thermal behaviour of the fluoroalkyl β-D-glucopyranosides **7a**–**d** (m.p.1; c.p.1) [37]; and of alkyl β-D-glucopyranosides (m.p.2; c.p.2) [8,10].

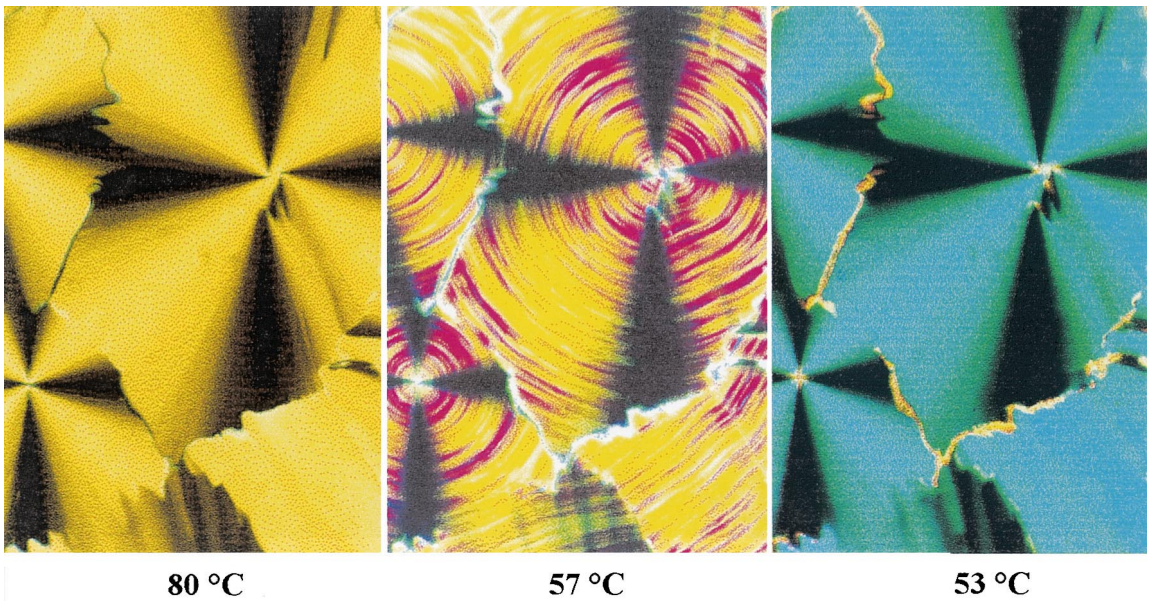


Fig. 6. Textures of compound **8** [37] (Leitz Laborlux 12 Pol microscope equipped with a Mettler hot stage FP 90 and a Leica WILD MPS 52 for photomicrographs). For thermal data, see Table 2.

22 show, on cooling, a slight continuous change of texture [34]. The melting and clearing temperatures of **18**–**22** are higher compared to the fluorine-free compounds with an equivalent alkyl chain length [39]. The F-alkyl-substituted mesogens **16** and **17** present sharper peaks and larger enthalpies than the compounds **18**–**22** that contain spacers between the aryl and *F*-alkyl moiety. However, only their melting temperatures are significantly higher than those of the corresponding fluorine-free amphiphiles [40,41]. The authors explain the similar clearing temperatures by a balance due to the weakening of the van der Waals forces resulting from the conformational stiffening of F-alkyl chains (for further details see Ref. [34]).

The amphiphilic (3-perfluorooctyl-propyl) 6-*O*-dodecanoyl-β-D-glucopyranoside (**8**) shows very interesting thermal properties [37]. The compound also contains, besides a perfluoroalkyl chain, a lipophilic hydrocarbon part in the molecule. On heating, compound **8** forms only one columnar mesophase, which is stable up to 147 °C. When this phase was cooled below 57 °C, a metastable phase of a type still unknown was observed (Table 2). The latter seems not to be induced by absorption of water. The textures of these phases are shown in Fig. 6.

4. Thermal properties of non-amphiphilic (monophilic) derivatives

Calamitic, non-amphiphilic mesogens containing deoxygenated carbohydrate moieties are good prospects to give cholesteric or smectic C*-phases. Some models of this type of chiral liquid crystals have been described (see e.g., Ref. [42,43]). The introduction of fluorine may improve the chemical stability and the thermal properties of non-amphiphilic mesogens [44]. Fluorinated materials have even higher and broader temperature ferroelectric phases with larger spontaneous polarisation. Furthermore, the small fluorine atom does not impair the formation of mesophases, even while fitting in a lateral position. Fluorine-containing carbohydrate-based liquid crystals should rather be non-amphiphilic (monophilic) because such mesogens meet the requirements for the formation of chiral smectic C phases (S_C^*).

The non-amphiphilic mesogens **27a**,**c**, **29**, and **31a**,**c** show, like the amphiphile **8**, changes of their mesophase type (polymorphism), i.e., formation of S_C^* and S_A phases [37,45], whereas the cyanophenyl derivative **28** forms exclusively a smectic A phase (Table 4).

Thus, a smectic C* phase is observed above the melting point of **27a** (134 °C), **27c** (155 °C)

31a (147–149 °C), and **31c** (155–156 °C). On further heating, a phase transition $S_C^* \rightarrow S_A$ occurs at 170 °C (**27a**), 205–206 °C (**27c**), 157 °C (**31a**) and 191 °C (**31c**), respectively (for the clearing points (cp) see Table 4). Nice coloured textures [fan shaped texture (S_A), broken fan shaped texture (S_C^*) and striated fan-shaped texture (S_C^*)] of **27a** and **31a,c** [37,45] were observed with a polarising microscope. For photographs of the textures of **27a** and **31a**, see Figs. 7 and 8. The left picture shows the typical striated fan-shaped texture of an S_C^*-phase caused by helical supramolecular structures; the right one shows the 'normal' fan-shaped texture of an S_A-phase. The pictures were taken nearly the transition temperature $S_A \rightarrow S_C^*$. The texture of the corresponding C_8F_{17}-derivative **27c** shows below 205 °C a broken fan-shaped texture with only a few striated regions [37].

In the case of the cyanobiphenyl derivative **29**, the smectic C* phase is metastable (Table 4), i.e., it is only observed at supercooling of the melt. The $S_A \rightarrow S_C^*$ phase transformation was observed at about 120 °C perceptible by formation of transverse-banded lines within

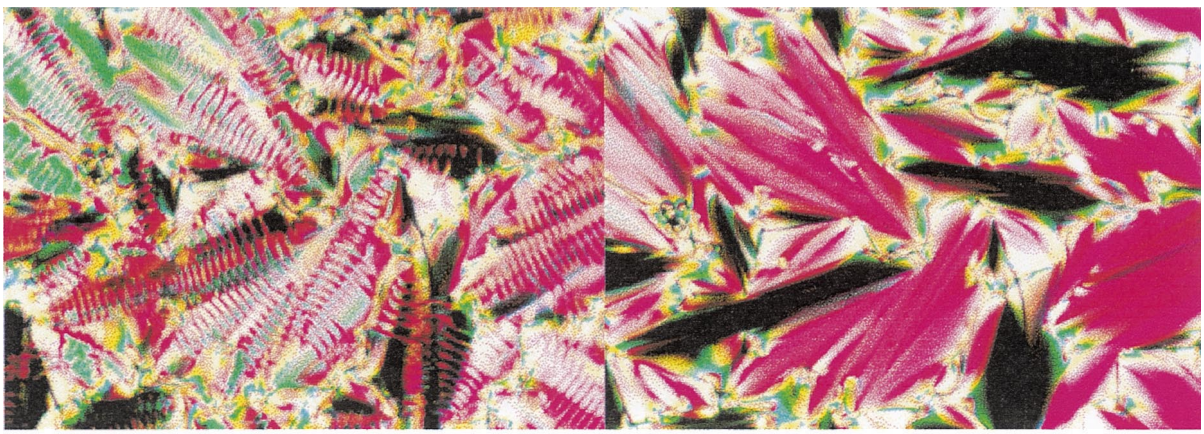


Fig. 7. Polymorphism of compound **27a** [37] (Leitz Laborlux 12 Pol microscope equipped with a Mettler hot stage FP 90 and a Leica WILD MPS 52 for photomicrographs). For thermal data see Table 4.

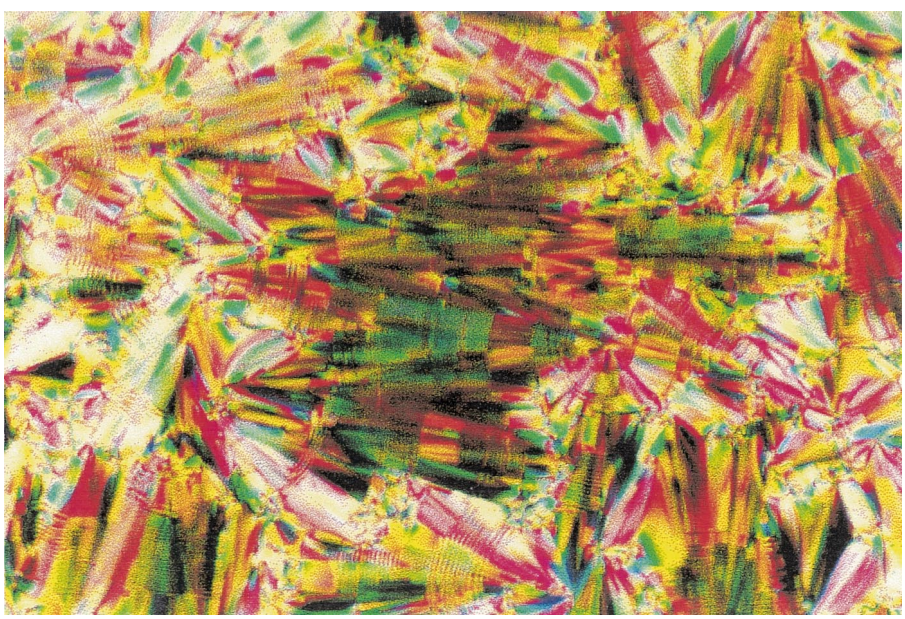


Fig. 8. S_C^*-phase of compound **31a** at 156.6 °C [45] (Leitz Laborlux 12 Pol microscope equipped with a Mettler hot stage FP 90 and a Leica WILD MPS 52 for photomicrographs). For thermal data see Table 4.

the texture. We estimated the molecular length of compound **29** (about 30 Å) using a molecular structure model set, i.e., always two calamitic molecules of **29** are required to explain the thickness of the S_A layer (48.5 ± 0.5 Å) as determined by X-ray measurement [37].

It is well known that chiral compounds may induce helically organised supramolecular architectures in a non-chiral nematic host phase. The helicity may be detected by polarising microscopy with help of the typical 'fingerprint' texture. A qualitative miscibility experiment of the optically active mesogen **27a** with the non-chiral nematic 1,4-di-(4-heptyloxybenzoyloxy)-benzene resulted in such a cholesteric phase. Using a microscope with vertical illumination but without polarising filter, the rainbow-coloured selective reflection could be observed along the concentration gradient of the two mesogens as a result of a high helicity induction. Moreover, a blue phase could be observed on this contact preparation.

Compound **30** (mp 104–105 °C) is not liquid crystalline, probably due to the unfavourable three-dimensional orientation of the molecules [37]. The miscibility experiment of **30** with 1,4-di-(4-heptyloxybenzoyloxy)-benzene likewise gave the expected chiral induction [45].

5. Conclusions

It is known that the miscibility of alkyl- and perfluoroalkyl compounds is restricted because perfluoroalkyl chains are both hydrophobic and lipophobic [13] (for a monograph on mixed surfactant systems, see Ref. [46]). Contact preparations of amphiphilic perfluoroalkyl substituted mesogens and non-fluorinated liquid crystals are obviously suitable to assign the type of a mesophase, e.g., the two smectic A type mesogens **15b** and dodecyl α-D-galactopyranoside were totally miscible. 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 (Ref. [13] and papers cited therein).

The thermal properties of the perfluoroalkyl substituted non-amphiphilic mesogens **24**–**27** confirm the observation of Liu and Nohira [47] that the stability of smectic phases increases with increasing fluorination extent. Whereas comparably structured non-fluorinated compounds tend to form cholesteric phases above the smectic A phase and a chiral smectic C phase below the smectic A, the perfluoroalkyl substituted compounds seem to favour chiral smectic phases including smectic C*.

Various families of mesogens, except carbohydrate-based compounds, have practical importance as materials in liquid crystal displays (LCD). One of the latest developments on this field is the ferroelectric liquid crystal display (FLC–LCD) technology which employs the higher ordered smectic S_C^* phase [48]. In a S_C phase the molecules are tilted at an angle Θ with respect to the layer normal. The helicoidal structure is a bulk property of the S_C^* material, which is present when no external fields or boundary conditions are applied. Ferroelectrics are materials that exhibit a permanent polarisation when subjected to an electric field. A rewarding objective in carbohydrate chemistry is to find carbohydrate-based mesogens that form S_C^* phases. Fluorine atoms, strategically positioned in the target molecules, may significantly support the polarisation effect.

6. Typical procedures

*6.1. (4′*R*)-4′-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononyl)-2′,3′,4′,5′-tetrahydro-{3,4-anhydro-1,2-dideoxy-α-*D*-allopyranoso}-[2,3-*b*]furan* (**26c**)

To a stirred solution of KO^{t}Bu (130 mg, 116 mmol) in dry MeOH (15 mL) **23c** [28] (400 mg, 0.49 mmol) was added in solid form at rt. Then the mixture shortly warmed-up to 40–50 °C to dissolve **23c** completely, and stirring was continued for 30 min at rt. After concentration of the mixture to a volume of about 5 mL, satd aq NaCl soln (10 mL) was added, **26c** was extracted with EtOAc (3×30 mL), the organic phase was dried (Na_2SO_4),

the solvent was evaporated, and the residue was purified by column chromatography (1:1 heptane–EtOAc). Yield of **26c** 270 mg (91%), mp 115 °C, cp 142 °C, $[\alpha]_D^{24}$ −29.3° (*c* 1.01, MeOH).

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.50 (d, 1 H, $^3J_{1,2}$ 5.6 Hz, H-1), 3.83–4.03 (m, 4 H, H-5, H-6a, H-6b, H-5′a), 3.75 (dd, 1 H, $J_{H,H}$ 7.6, $J_{H,H}$ 10.8 Hz, H-5′b), 3.31 (dd, 1 H, $^3J_{4,5}$ 1.6, $^3J_{3,4}$ 4.5 Hz, H-4), 3.25 (t, 1 H, $^3J_{2,3}$ 4.3 Hz, H-3), 2.94 (m, 1 H, H-4′), 2.54 (ddd, 1 H, $^3J_{2,4'}$ 7.7 Hz, H-2), 2.24–2.78 (m, 2 H, CH_2CF_2). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 99.7 (m, $^1J_{C,H}$ 174.7 Hz, C-1), 72.2 (m, $^1J_{C,H}$ 149.5, $^4J_{C\text{-}5',F}$ 2.0 Hz, C-5′), 68.6 (m, $^1J_{C,H}$ 148.4 Hz, C-5), 63.8 (m, $^1J_{C,H}$ 144.2 Hz, C-6), 51.2 (m, $^1J_{C,H}$ 179.9 Hz, C-4), 48.3 (m, $^1J_{C,H}$ 181.9 Hz, $^5J_{C\text{-}3,F}$ 1.5 Hz, C-3); 36.7 (m, $^1J_{C,H}$ 133.9 Hz, C-2), 34.1 (m, $^1J_{C,H}$ 131.6, $^3J_{C\text{-}4',Fa,b}$ 2.0 Hz, C-4′), 28.2 (m, $^1J_{C,H}$ 129.9, $^2J_{C,Fa,b}$ 22.0 Hz, CH_2CF_2). ^{19}F{^{1}H} NMR (235 MHz, $CDCl_3$): δ −80.5 (t, $^3J_{F,F}$ 9 Hz, CF_3), −111.7 to −114.6 (m, $^3J_{Fa,F} = {}^3J_{Fb,F}$ 13, $^2J_{Fa,Fb}$ 267 Hz, α-CF_2), −121.3, −121.6, −121.6, −122.4, −123.1, −125.9 (m, 6 CF_2); Anal. Calcd for $C_{17}H_{13}F_{17}O_4$ (604.3): C, 33.79; H, 2.17. Found: C, 33.55; H, 2.15.

*6.2. (4′*R*)-4′-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononyl)-2′,3′,4′,5′-tetrahydro-{3,4-anhydro-1,2-dideoxy-6-*O*-[4-(4-heptyloxybenzoyloxy)phenyl]-α-*D*-allopyranoso}-[2,3-*b*]-furan* (**31c**)

To a stirred mixture of PPh_3 (85 mg, 0.32 mmol) and 4-(4-heptyloxybenzoyloxy)phenol (160 mg, 0.49 mmol) in dry toluene (5 mL) DIAD (75 μL, 0.36 mmol) was dropwise added at rt under an argon atmosphere and vigorous stirring. Subsequently, **26c** (190 mg, 0.31 mmol) was added in solid form, and stirring was continued. After 2 h again PPh_3 (20 mg, 0.08 mmol) and DIAD (20 μL, 0.10 mmol) were added. This make-up was repeated every 2 h until complete turnover was detected by thin-layer chromatography (TLC). After dilution with EtOAc the mixture was filtered through Celite, the filtrate was concentrated under reduced pressure and the residue was recrystallised from MeOH/EtOAc Yield: 250 mg (87%), mp 155–156 °C, cp 210 °C, $[\alpha]_D^{23}$ −26.3° (*c* 1.00, $CHCl_3$).

^{1}H NMR (250 MHz, $CDCl_3$): δ 8.08–8.15 (m, 2 H, aromatic H), 7.09–7.16 (m, 2 H, aromatic H), 6.92–7.01 (m, 4 H, aromatic H), 5.54 (d, 1 H, $^3J_{1,2}$ 5.5 Hz, H-1), 4.24–4.33, 3.97–4.07 (m, 6 H, H-5, H-6a, H-6b, H-5′a, $ArOCH_2$), 3.79 (dd, 1 H, $J_{H,H}$ 7.7, $J_{H,H}$ 10.7 Hz, H-5′b), 3.44 (dd, 1 H, $^3J_{4,5}$ 1.2, $^3J_{3,4}$ 4.4 Hz, H-4), 3.33 (t, 1 H, $^3J_{2,3}$ 4.3 Hz, H-3), 2.96 (m, 1 H, H-4′), 2.64 (ddd, 1 H, $^3J_{2,4'}$ 8.2 Hz, H-2), 2.26–2.84 (m, 2 H, CH_2CF_2), 1.75–1.87 (m, 2 H, CH_2), 1.26–1.53 (m, 8 H, 4 CH_2), 0.89 (t (br), $^3J_{H,H}$ 6.7 Hz, CH_3); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 165.2, 163.5 (s, CO, quat. C_{arom}), 156.0 (s, quat. C_{arom}), 145.2 (s, quat. C_{arom}), 132.2 (s, 2 aromatic CH), 122.7 (s, 2 aromatic CH), 121.6 (s, quat. C_{arom}), 115.4 (s, 2 aromatic CH), 114.3 (s, 2 aromatic CH), 99.5 (s, C-1), 72.2 (d, $^4J_{C\text{-}5',F}$ 2.3 Hz, C-5′), 69.1, 68.3 (s, C-6, $ArOCH_2$), 67.0 (s, C-5), 51.0 (s, C-4), 48.6 (d, $^5J_{C\text{-}3,F}$ 1.2 Hz, C-3) 37.0 (s, C-2), 34.1 (t, $^3J_{C\text{-}4',Fa,b}$ 1.9 Hz, C-4′), 31.7, 29.1, 29.0 (s, 3 CH_2), 28.4 (t, $^2J_{C,Fa,b}$ 22.1 Hz, CH_2CF_2), 25.9 (s, CH_2), 22.6 (s, CH_2), 14.0 (s, CH_3). ^{19}F{^{1}H} NMR (235 MHz, $CDCl_3$): δ −80.6 (t, $^3J_{F,F}$ 10 Hz, CF_3), −111.7 to −114.7 (m, $^3J_{Fa,F} = {}^3J_{Fb,F}$ 13, $^2J_{Fa,Fb}$ 271 Hz, α-CF_2), −121.4, −121.7, −121.7, −122.5, −123.1, −125.9 (m, 6 CF_2). Anal. Calcd for $C_{37}H_{35}F_{17}O_7$ (914.7): C, 48.59; H, 3.86. Found: C, 48.51; H, 4.04.

7. Supplementary material

Crystallographic data for the structures of **6b** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-118767. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

We thank our dedicated co-authors, whose names appear in the references. Furthermore, we are very grateful to Professor Dr Helmut Reinke (Fachbereich Chemie, Universität Ro-

stock) for X-ray measurements and interpretation of compound **6b** and to Professor Dr Wolfgang Weissflog and Dr Siegmar Diele (Institut für Physikalische Chemie, Martin-Luther-Universität Halle-Wittenberg) for X-ray measurements of **25c**, and **27c**. Last but not least, we are grateful to Dr H. van Doren (Netherlands Institute for Carbohydrate Research TNO, Groningen) for fruitful discussions and the 'Fonds der Chemischen Industrie' and the 'Deutsche Forschungsgemeinschaft' for support.

References

[1] H. Prade, R. Miethchen, V. Vill, *J. Prakt. Chem.*, 237 (1995) 427–440.
[2] C.M. Paleos, D. Tsiourvas, *Angew. Chem., Int. Ed. Engl.*, 134 (1995) 1696–1712.
[3] J.W. Goodby, M.J. Watson, G. MacKenzie, S.M. Kelly, S. Bachir, P. Bault, P. Gode, G. Goethals, P. Martin, G. Ronco, P. Villa, *Liq. Cryst.*, 25 (1998) 139–147.
[4] J.W. Goodby, G.H. Mehl, I.M. Saez, R.P. Tuffin, G. Mackenzie, R. Auzely-Velty, T. Benvegnu, D. Plusquellec, *Chem. Commun. (Cambridge)*, (1998) 2057–2070.
[5] M. Veber, E. Cheylan, S. Czernecki, J. Xie, *Liq. Cryst.*, 21 (1996) 197–201.
[6] H.A. van Doren, L.M. Wingert, *Mol. Cryst. Liq. Cryst.*, 198 (1991) 381–391.
[7] G.A. Jeffrey, L.M. Wingert, *Liq. Cryst.*, 12 (1992) 179–202.
[8] J.W. Goodby, *Mol. Cryst. Liq. Cryst.*, 110 (1984) 205–219.
[9] G.A. Jeffrey, *Mol. Cryst. Liq. Cryst.*, 185 (1990) 209–213.
[10] G.A. Jeffrey, S. Bhattacharjee, *Carbohydr. Res.*, 115 (1983) 53–58.
[11] G.A. Jeffrey, in A. Meister (Ed.), *Advances in Enzymology and Related Areas of Molecular Biology*, Vol. 65, Wiley, New York, 1992, pp. 217–254.
[12] I.P. Street, C.R. Armstrong, S.W. Withers, *Biochemistry*, 25 (1986) 6021–6027.
[13] E. Kissa, *Fluorinated Surfactants. Synthesis, Properties, Applications*, Marcel Dekker, New York, 1994.
[14] G.J. Tiddy, in H.F. Eicke (Ed.), *Modern Trends of Colloid Science in Chemistry and Biology*, Birkhäuser, Basel, 1985, p. 148.
[15] R. Miethchen, H. Prade, J. Holz, K. Praefcke, D. Blunk, *Chem. Ber.*, 126 (1993) 1707–1712.
[16] R. Miethchen, C. Zur, *J. Prakt. Chem.*, 337 (1995) 189–195.
[17] R. Miethchen, H. Prade, *Carbohydr. Lett.*, 1 (1994) 19–26.
[18] R. Miethchen, H. Kowalek, A. Niemann, S. Diele, Chr. Schick, *Liebigs Ann. Chem.*, (1997) 279–284.
[19] P. Kováč, *Carbohydr. Res.*, 153 (1986) 168–170.
[20] T. Ido, C.-N. Wan, J.S. Fowler, A.P. Wolf, *J. Org. Chem.*, 42 (1977) 2341–2342.
[21] G. Rong, R. Keese, *Tetrahedron Lett.*, 31 (1990) 5615–5616.
[22] W.-Y. Huang, F.-H. Wu, *Israel J. Chem.*, 39 (1999) 167–170.
[23] W.-Y. Huang, *J. Fluorine Chem.*, 58 (1992) 1–8.
[24] R. Miethchen, M. Hein, H. Reinke, *Eur. J. Org. Chem.*, (1998) 919–923.
[25] B. Yu, J. Zhang, S. Lu, Y. Hui, *Synlett*, (1998) 29–30.
[26] M. Hein, R. Miethchen, *Tetrahedron Lett.*, 39 (1998) 6679–6682.
[27] M. Hein, R. Miethchen, D. Schwäbisch, *J. Fluorine Chem.*, 98 (1999) 55–60.
[28] M. Hein, R. Miethchen, *Eur. J. Org. Chem.*, (1999) 2429–2432.
[29] S. Zhu, C. Qing, J. Zhou, J. Zhang, B. Xu, *J. Fluorine Chem.*, 79 (1996) 77–79.
[30] V.N. Boiko, G.M. Shchupak, *J. Fluorine Chem.*, 69 (1994) 207 and papers cited therein.
[31] C. Zur, R. Miethchen, *Eur. J. Org. Chem.*, (1998) 531–539.
[32] D. Peters, C. Zur, R. Miethchen, *Synthesis*, (1998) 1033–1038.
[33] C. Zur, A.O. Miller, R. Miethchen, *J. Fluorine Chem.*, 90 (1998) 67–76.
[34] H.L. Nguyen, J. Dedier, H.T. Nguyen, J.-C. Rouillon, G. Sigaud, *Liq. Cryst.*, 26 (1999) 1637–1644.
[35] V. Vill, T. Böcker, J. Thiem, F. Fischer, *Liq. Cryst.*, 6 (1989) 349–356.
[36] V. Vill, T.K. Lindhorst, J. Thiem, *J. Carbohydr. Chem.*, 10 (1991) 771–786.
[37] M. Hein, R. Miethchen, D. Schwäbisch, Chr. Schick, *Liq. Cryst.*, 27 (2000) 163–168.
[38] C. Zur, A.O. Miller, R. Miethchen, *Liq. Cryst.*, 24 (1998) 695–699.
[39] E. Smits, J.B.F.N. Engberts, R. Kellogg, H.A. van Doren, *Liq. Cryst.*, 23 (1997) 481–488.
[40] C. Tschierske, A. Lunow, H. Zaschke, *Liq. Cryst.*, 8 (1990) 885–888.
[41] L.M. Wingert, G.A. Jeffrey, Jahangir, D.C. Baker, *Liq. Cryst.*, 13 (1993) 467–470.
[42] (a) P. Pudlo, J. Thiem, V. Vill, *Chem. Ber.*, 123 (1990) 1129–1135. (b) V. Vill, H.W. Tunder, *Liebigs Ann. Chem.*, (1995) 1055–1060.
[43] E. Smits, J.B.F.N. Engberts, R.M. Kellogg, H.A. van Doren, *Mol. Cryst. Liq. Cryst.*, 260 (1995) 185–199.
[44] (a) G. Nestor, G.W. Gray, D. Lacey, K. Toyne, *Liq. Cryst.*, 7 (1990) 669. (b) G.W. Gray, M. Hird, K.J. Toyne, *Mol. Cryst. Liq. Cryst.*, 204 (1991) 43–64, 91–110. (c) R. Twieg, K. Betterton, R. DiPietro, D. Gravert, C. Nguyen, H.T. Nguyen, A. Babeau, C. Destrade, G. Sigaud, *Mol. Cryst. Liq. Cryst.*, 217 (1992) 201–206. (d) V. Faye, J.C. Rouillon, C. Destrade, H.T. Ngyuen, *Liq. Cryst.*, 19 (1995) 47–56.
[45] M. Hein, Ph.D. *Thesis*, University of Rostock, 1999.
[46] K. Ogino, M. Abe (Eds.), *Mixed Surfactant Systems, Surfactant Science Series*, Vol. 46, Marcel Dekker, New York, 1993.
[47] H. Liu, H. Nohira, *Liq. Cryst.*, 22 (1997) 217–222.
[48] U. Finkenzeller, A.E. Pausch, E. Poetsch, J. Suermann, *Kontakte (Darmstadt)* (1993) 3–14.