Attempts Towards Novel Cycloalkane Liquid Crystals

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ATTEMPTS TOWARDS NOVEL CYCLOALKANE LIQUID CRYSTALS[1]

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Abstract

This paper is concerned with the relationship between molecular structure and liquid-crystalline properties of two types of functionalized cycloalkanes, i.e. cyclopentanes and cyclohexanes, in the latter case *myo-* and *scyllo*-inositol. The occurence of *columnar* or *lamellar mesophases* is discussed for a variety of new compounds in relation to: 1) the role of heteroatoms in side chains, 2) the core size and stereochemical arrangement of heteroalkyl side chains, and 3) the replacement of such side chains by hydroxyl groups. Both in the cyclopentane and inositol series various interesting examples of new multihydroxy liquid crystals have been synthesized and studied. Their mesophases are of *supramolecular* architecture based on hydrogen bonding networks.

Introduction

Although research on liquid crystals (mesogens) started on a cycloalkane system more than one hundred years ago,[2] compounds with such moieties came into the focus of interest in science and technology only in recent time.[3-7] The most thermomesomorphic materials investigated since research in this field began have been aromatic and *rod*-shaped.[8] The first *disc*-shaped cycloalkane (-hexane) liquid crystals published[6a-d] are homologous aliphatic hexa*esters* of the naturally occurring *scyllo*-inositol (e.g. 1 of this series in Figure 1 and Table 1) which exhibit very interesting, unexpected properties compared to those with a phenyl core.[6b] Moreover, a discotic mesophase was also observed in the

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* Dedicated to OStR *Bodo Michels* on the occasion of his retirement in August 1991 from his teaching position in chemistry at the EOS Goethe-Oberschule, formerly Gymnasium Friderico Francisceum, Bad Doberan in Mecklenburg-Vorpommern, Germany.

1

2

7

8

9a

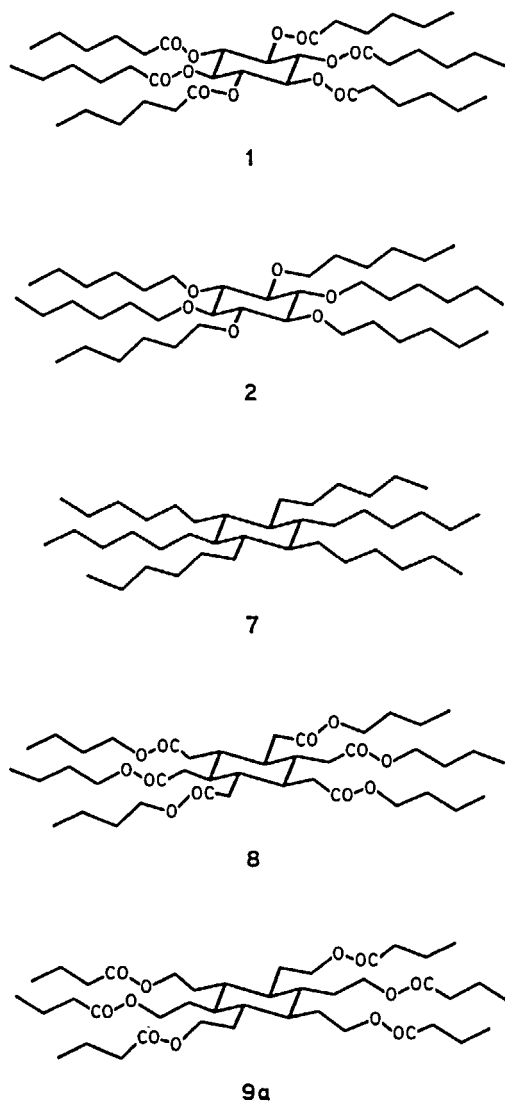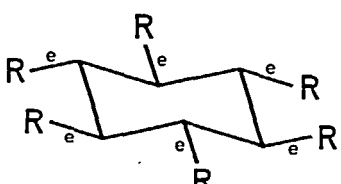**Figure 1.** The structures of five of the discussed cyclohexane derivatives in comparison to one another, 1) *scyllo*-inositol hexahexanoate (**1**), 2) *scyllo*-inositol hexa(hexyl)ether (**2**), 3) (1α, 2β, 3α, 4β, 5α, 6β)-hexa(hexyl)cyclohexane (**7**), 4) (1α, 2β, 3α, 4β, 5α, 6β)-hexa(butoxy-carbonylmethyl)cyclohexane (**8**), 5) (1α, 2β, 3α, 4β, 5α, 6β)-hexa(2-butanoyloxyethyl)cyclo-hexane (**9a**).

Table 1. Temperatures of phase transitions [°C] and types of mesophases found for the disc-shaped cyclohexane derivatives **1, 2**, and **7-9** with identical (*equatorial*) substitution pattern, cf. Figure 1 and Scheme 1. The structures of the four new compounds **7-9b** have been proved by mass spectrometry, IR, ^{1}H & ^{13}C NMR spectroscopy as well as by elemental analyses. The temperature values were obtained by differential scanning calorimetry (d.s.c.) using a Mettler TA 3000/DSC 30 S with GraphWare TA 72, heating rate 5 K/min (**8**: 1 K/min). The judging of the textures, i.e. the determination of the D_{ho}-phases was carried out with a polarizing microscope Leitz Laborlux 12 Pol equipped with a hot stage Mettler FP 82. (Cr: crystalline, D_{ho}: discotic, hexagonal ordered, I: isotropic liquid)

Comp.	R	Geometrical Form	Phase Transitions
1	O-CO-C$_5$H$_{11}$ [6a,b]	disc	Cr $\xrightarrow{68.5}$ D$_{ho}$ $\xrightarrow{199.5}$ I
2	O-C$_6$H$_{13}$ [6e-g]	disc	Cr $\xrightarrow{18.4}$ D$_{ho}$ $\xrightarrow{90.8}$ I
7	CH$_2$-C$_5$H$_{11}$	disc	Cr $\xrightarrow{66.2}$ I
8	CH$_2$-COO-C$_4$H$_9$	disc	Cr $\xrightarrow{-6.7}$ I
9a	CH$_2$-CH$_2$-OOC-C$_3$H$_7$	disc	Cr $\xrightarrow{52.6}$ I
b	CH$_2$-CH$_2$-OOC-⟨O⟩-OC$_7$H$_{15}$	disc	Cr $\xrightarrow{104.5}$ I

fully O-alkylated *scyllo*-inositol, the hexa*ether* **2**,[6e-g] but the stability and width of its mesophase appeared distinctly weaker and smaller as found for the corresponding hexa*ester* **1**[6e] with an identical number of carbon atoms in the side chains.

The fast development in this field of saturated liquid crystals and its growing significance for the understanding of properties of carbohydrates and related compounds gives rise to new questions on structural conditions for the exhibition and stability of mesophases in general or for discotic ones in particular, for instance as regarding:

1) the role of heteroatoms in side chains,

2) the core size and stereochemical arrangement of heteroalkyl side chains, and

3) the replacement of heteroalkyl side chains by hydroxyl groups.

Our paper deals with these topics of current interest. The results presented here contribute to the research into the scope and limitations of the liquid-crystalline behaviour in cycloalkane derivatives.

Results and Discussion

I. Heteroatom Effect: Oxygen Atoms in Side Chains

In agreement with earlier findings[6b,e,f,9-14] regarding liquid-crystalline behaviour of some other rod- or disc-shaped compounds, we consider the difference in occurrence and stability of the discotic phases in the two scyllitol derivatives 1 and 2 to depend strongly on the number, kind,[14b,c] position, and stereochemical arrangement[6b,e,f] of the hetero- (here: oxygen-) atoms in their side chains. On this basis we think that this dependence is determined particularly by electronic effects of the π- and lone-pair electrons of these oxygen functions.

A logical consequence of this research was an investigation of at least one "oxygen-free scyllitol derivative" which prompted us to synthesize and to study the 1,2,3,4,5,6-hexahexyl substituted cyclohexane 7. This model compound does possess the same stereochemistry as the fully functionalized scyllitol derivatives depicted in Figure 1 and Table 1, i.e. all six hexyl groups of the saturated, disc-shaped hydrocarbon 7 are in equatorial arrangements.

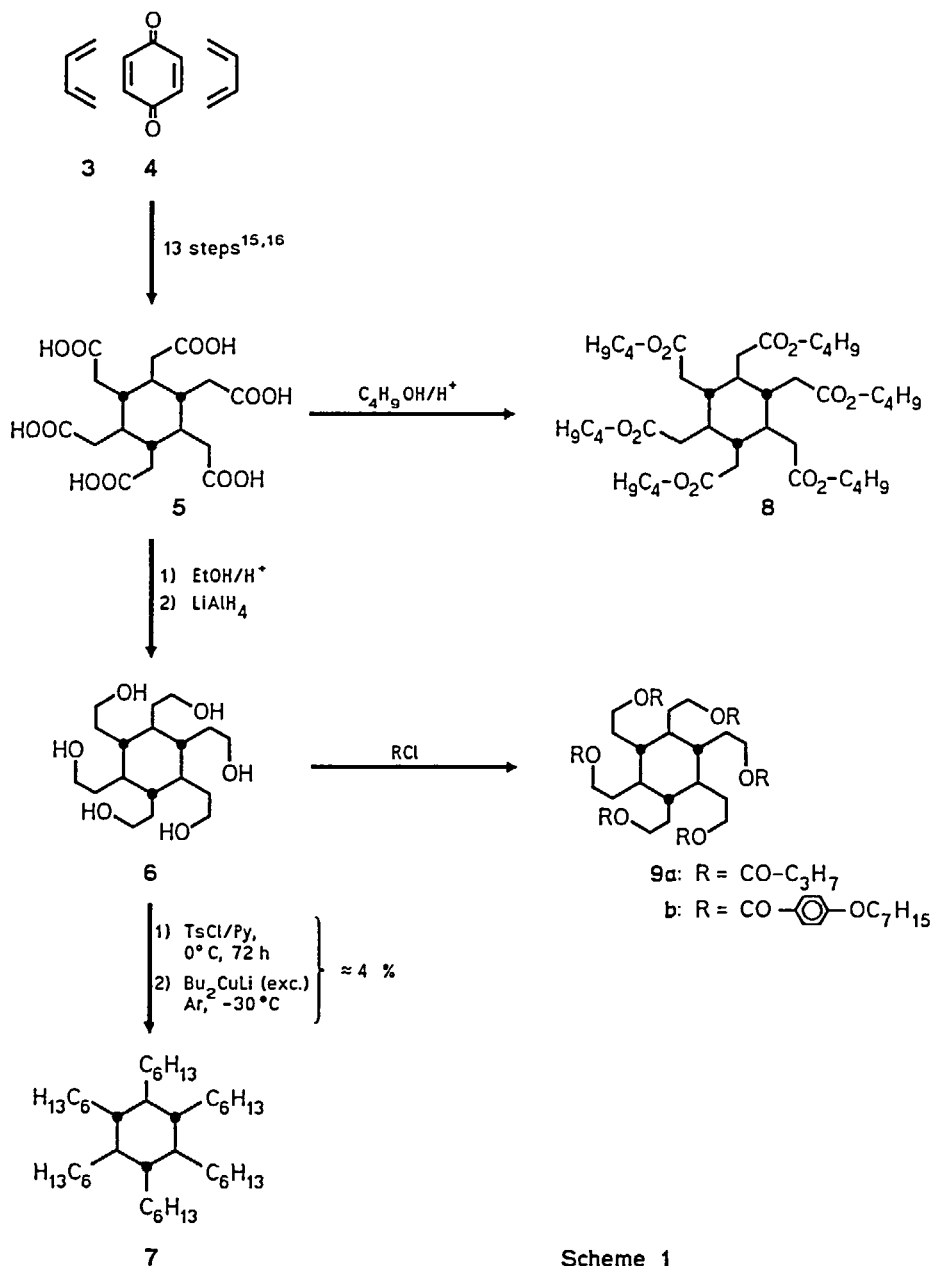Our 17-step synthesis of this hitherto unknown hydrocarbon 7 in an over-all yield of 0.3 % via the key compounds 5 and 6, whose structures were assigned inter alia by ^{1}H and ^{13}C NMR, followed a stereospecific route described only sketchily[15] and improved by us.[16] The starting materials for this project summarized in Scheme 1 were 1,3-butadiene (3) and 1,4-benzoquinone (4).

Furthermore, the availability of the two cyclohexane derivatives 5 and 6 provided the opportunity to prepare the three esters 8, 9a, and b in yields ranging between 39 and 61 %, cf. Scheme 1.

The ^{13}C NMR spectrum of 7 is shown in Figure 2. The presence of only seven peaks in the spectrum clearly proves the high symmetry of this disc-shaped compound. An analogous situation occurs in the spectra of compounds 5, 6, 8, and 9. As was to be expected, their methine carbon NMR resonances are close to 39.23 ppm (6 and 9a,b) or about 2 ppm higher for 5 and 8.

None of the four new compounds 7-9 showed liquid-crystalline behaviour as can be seen from their phase transition data presented in Table 1 and obtained by differential scanning calorimetry (d.s.c.). The results of our investigations demonstrate that the exhibition of thermomesomorphism in this series of all-*trans* hexasubstituted cyclohexane derivatives, identical in geometry (cf. Figure 1 and Table 1), depends on the presence *and* position of oxygen in their structures. The optimal structural condition is given with this heteroatom being bonded equatorially[6b,e,f] to the cyclohexane core, cf. 1 and 2 on the one hand with 7 or with 8 and 9 on the other.

It appears to us that these oxygen atoms in 1 and 2 play not only a simple role as a bridging function between their cores and their side chains, but also play a role in generating amphiphilic character. Thus, this "ring" made up with six oxygen atoms creates an intramolecular interface between the two moieties, covalently bonded,

3   4

13 steps[15,16]

HOOC ... COOH
... COOH
HOOC ... COOH
HOOC ... COOH
5

C_4H_9OH/H^+

$H_9C_4-O_2C$ ... $CO_2-C_4H_9$
... $CO_2-C_4H_9$
$H_9C_4-O_2C$ ...
$H_9C_4-O_2C$ ... $CO_2-C_4H_9$
8

1) EtOH/H$^+$
2) LiAlH$_4$

OH ... OH
HO ... OH
HO ... OH
6

RCl

OR ... OR
RO ... OR
RO ... OR
9a: R = CO-C$_3$H$_7$
b: R = CO—⬡—OC$_7$H$_{15}$

1) TsCl/Py,
   0° C, 72 h
2) Bu$_2$CuLi (exc.)
   Ar, -30 °C   ≈ 4 %

C$_6$H$_{13}$
H$_{13}$C$_6$ ... C$_6$H$_{13}$
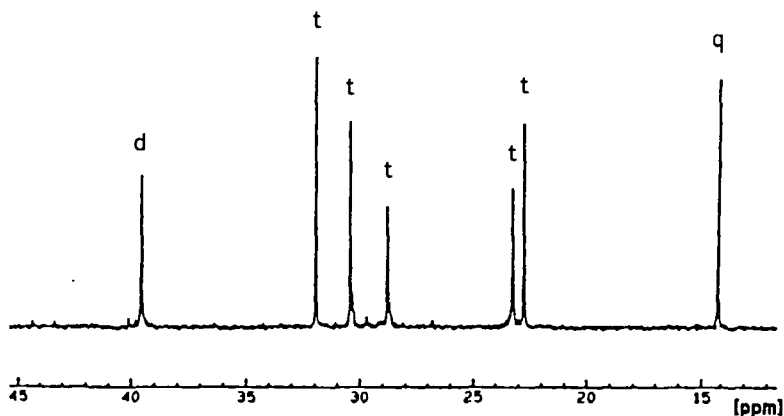H$_{13}$C$_6$ ... C$_6$H$_{13}$
C$_6$H$_{13}$
7

Scheme 1

Figure 2. The ^{13}C NMR spectrum (Bruker AM 270, CDCl$_3$) of the disc-shaped hydro-carbon **7**, (1α, 2β, 3α, 4β, 5α, 6β)-hexa(hexyl)cyclohexane, with the following assignment of the observed resonance peaks: 1) a doublet at 39.5563 ppm (the methine carbons), 2) five triplets at 31.9397, 30.4150, 28.7964, 23.2758, and 22.7981 ppm (the five types of methylene carbons), and 3) a quartet at 14.1341 ppm (the methyl carbons).

but suitably separated into two distinct microdomains, one consisting of flexible hydro-carbon chains and the other built up by a rigid cyclohexane ring. In other cases[9,17,18] of mesophase formation initiated by microphase separation, the incompatibility of the constituent parts of such molecules must be related not to solubility or insolubility in water, but certainly to van der Waals repulsions due to different polarizabilities. Changes in conformation and space filling due to altered bond angles and lengths are also consequences of the introduction of heteroatoms as constituent elements other than carbon in side chains, and oxygens surely play an additional role on the formation and stability of thermotropic mesophases. This must be valid too for influences of dipolar interactions between the heteroatom positions in side chains and between other parts of the molecules compared to compounds without hetero substitution.[19] Here and in general, an important factor is the phenomenon of aggregation of electrically neutral molecules which is said to be based almost solely on hydrophilic–lipophilic interactions[20] and therefore should also be taken into consideration.

As can be seen from Figure 1 and Table 1, comparing the scyllitol derivatives **1** with **2**, carbonyl groups in **1** neighbouring the bridging (ether) oxygen atoms opposite to the cyclohexane ring improves the liquid-crystalline property drastically. However, no liquid crystallinity is observed in this series of compounds if the oxygen atoms are not bonded directly to the core, but for instance separated by two carbon atoms, cf. examples **8, 9a**, and **b** in Table 1. One has reason to believe that boundaries between their microdomains shifted disadvantageously into the very flexible periphery of the molecules foiling the

possibility for establishing sharp interfaces and stable states of balance between them. In these latter cases, when carbonyl functions were added on inner or outer sides of the oxygen atoms within the chains of **8** or **9**, respectively, there was no improvement of the phase behaviour.
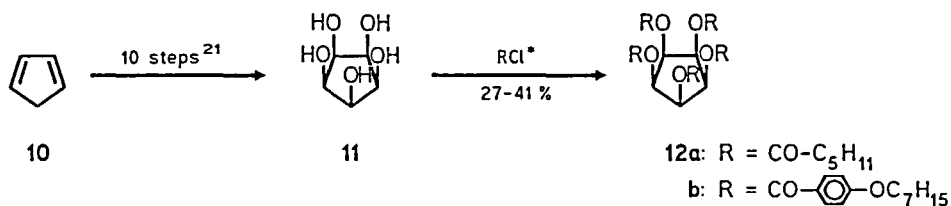
Concluding this chapter we want to emphasize that to the best of our knowledge never before has a series of disc-shaped compounds in the following alteration of their (e.g. six) side chains from

<p align="center">alkanoyloxy → alkyloxy → alkyl</p>
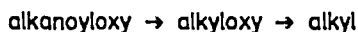
at a suitable core, most likely for simple synthetic reasons, been discussed in the literature.

II. Core Size and Stereochemical Arrangement of Heteroalkyl Side Chains

Another line of interest in our liquid crystal work aimed at the reduction of the size of the saturated molecular core, i.e. to study the four *cyclopentane* centered model compounds **12a,b** and **15a,b** fully covalently functionalized similarly to **1** and **9**. Their preparations were easily possible from the well described[21,22] pentols **11** and **14**, respectively (Schemes 2 and 3).

12a: R = CO-C$_5$H$_{11}$
 b: R = CO-⟨◯⟩-OC$_7$H$_{15}$

Scheme 2

15a: R = CO-C$_5$H$_{11}$
 b: R = CO-⟨◯⟩-C$_8$H$_{17}$
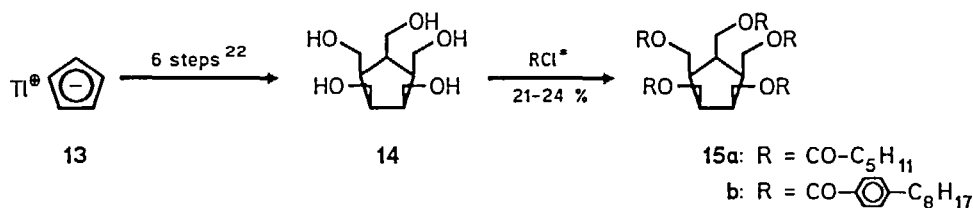
* Esterification towards **a** in CF$_3$-COOH or towards **b** in pyridine, respectively.

Scheme 3

As space filling models prove, in contrast to the all-*trans* situation in the series **1,2,7-9** the substitution pattern of the new cyclo*pentane* derivatives **12** and **15** must be *all-cis* allowing them to be flat and radialsymmetric in structure. Despite this stereochemical arrangement in a favourable conformation these *penta*esters are characterized by:

1) having a relatively flat core somewhat humpbacked on one side and
2) a star-like periphery covered less completely because of only *five* side chains compared to six in **1**.

Because of negative influences[6b,e,f,23] on the exhibition of discotic phases due to the introduction of a disturbance, we did not expect this type of mesophase, but did not exclude the possibility of the occurrence of a *pyramidic*[24] phase in principle. Nevertheless, strong doubts also remained about this alternative mainly because the cores of **12** and **15**, hardly *bowl*-shaped, are too different in geometry and very much less hollow as known for typical pyramidic mesophases.[24]

Results from the polarizing microscopy of the four pentaesters led to the conclusion that none of them exhibit a mesophase, neither enantio- nor monotropically. Whereas **12a**, **15a**, and **15b** are oily liquids at room temperature, **12b** melts at 76.5°C into an isotropic liquid; the structures of these latter compounds have been proved by spectroscopic methods (mass spectrometry, ^1H and ^{13}C NMR) and elemental analyses.

It is interesting to stress that the five phenyl rings present both in **12b** and **15b** apparently don't improve the phase behaviour of these compounds, e.g. by forming a space filling "ring of rings" which would lead to a kind of "super-disc core", as was found advantageously in other cases.[6b] It seems to us that broader substituents[25] as periphery filling side arms probably must be introduced in suitable stereochemical arrangement to yield a novel family of radialsymmetric liquid crystals, fully covalent in structure and based on cyclopentane as a core.

## III. Replacement of Heteroalkyl Side Chains by Hydroxyl Groups

In this chapter we focus on new cycloalkane derivatives which lack heteroalkyl side chains, but possess hydroxyl groups instead. Because of this situation, the various geometrical forms of such compounds are not disc-like anymore as were characteristic of those described in the two previous chapters.

The mesophases of such multiol compounds presented here are *supramolecular* in structure, i.e. they are composed of hydrogen-bond assisted multimers organized in *layers* or *columns*. In such systems similar to other examples studied recently,[6e,f,g,26] the lack of a sufficient number of covalently bonded long heteroalkyl side chains, leading to suppression of any liquid-crystalline property,[6b,f] was compensated for by filling their uncovered peripheries through multimerization, i.e. enlarging the promesogenic units via *inter*molecular hydrogen-bridge formation between their hydroxyl functions.

Thus we selected cyclo*penta*diene (**10**) and the naturally occurring cyclo*hexane* derivative *myo*-inositol (**16**, commercially available) as our starting materials from which

we synthesized eight new multiol model compounds in multi-step sequences and yields summarized in Schemes 4 and 5.

As can be seen from their structures these compounds are *rod-* or, as in case of **25**, *peg*-shaped. All of them but one (**21**), are liquid-crystalline. Our assignments of the geometrical forms, the temperatures of phase transitions, and the types of thermotropic mesophases of these eight cycloalkane derivatives can be seen in Table 2. The six *rod*-shaped pentols and tetrols **18a-c**, **20a,b**, and **24**, respectively, exhibit *smectic A*, i.e. *layer*-structured mesophases, whereas that one of the *peg*-shaped triol **25** is *hexagonal columnar*. Both kinds of textures are characteristically different and can be distinguished by polarizing microscopy.
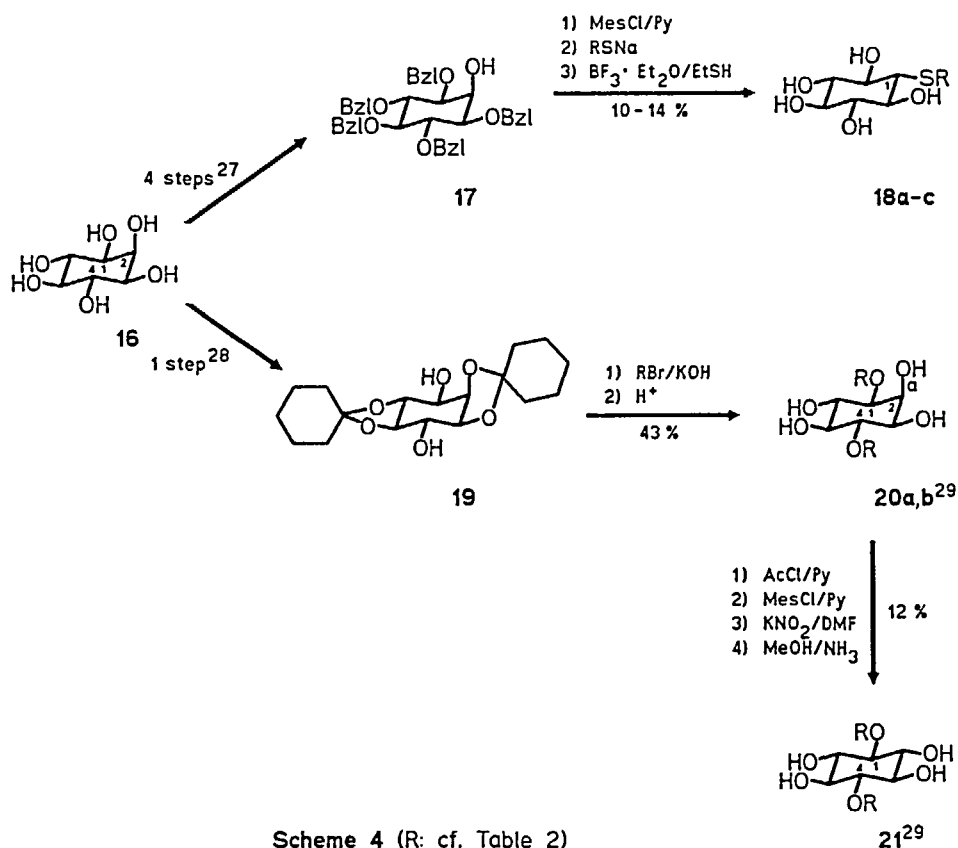
Scheme 4 (R: cf. Table 2)

As is known from derivatives of inosose[30] and various sugars,[31,32] here too, the different ways of molecular organization leading to these two types of mesophases are determined by the *number* of heteroalkyl side chains attached to the cycloalkane multiols. It doesn't matter whether in case of *two* of such side chains these are vicinally or geminally attached to the ring. Examples of this are various "*1,1-double-tailed*"
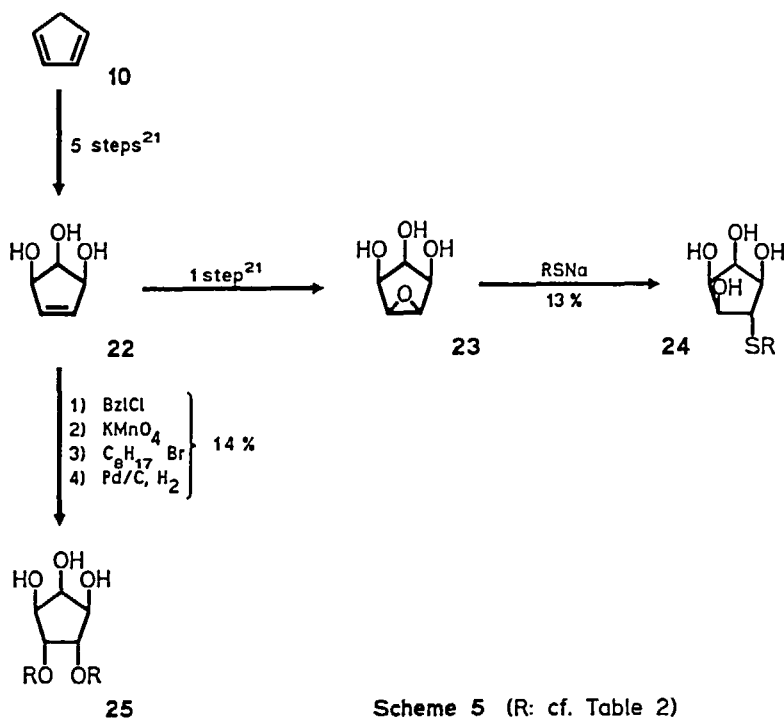
Scheme 5 (R: cf. Table 2)

carbohydrate derivatives[30,31] or a "*1,2–double–tailed*" *scyllo*-inositol diether[6f] and the cyclopentane triol **25** presented here, respectively.

The mesophase of **25** turned out to be miscible (polarizing microscope, contact method) and, therefore, is identical with the one from the D–xylose S,S–dioctyl acetal[31] and the *scyllo*-inositol 1,2-dihexylether[6f] which had been established as hexagonal columnar (H_x-phase) by x-ray diffraction[6f,31] and consisting each of five multiol molecules (hydrogen–bridged pentamers) on average for a cross–section of columns. A photograph of the H_x-phase of **25** is shown in Figure 3, as compared with that of another sugar S,S-dioctyl acetal published earlier.[31]

It should be mentioned that this thermotropic, metastable H_x-phase of the *peg*-shaped triol **25** (see Table 2) is stabilized by addition of water, forming now a *stable lyotropic* mesophase with a maximum clearing temparture of about 90°C and probably with the same symmetry as for the water-free sample.

On the other hand, the *smectic* type phase of the four *mono*thioethers **18a–c** and **24**, all "*single-tailed*", consist most likely of *bi*molecular layers with partially overlapping cyclomultiol moieties in the core of the layer (a hydrogen–bond supported interdigitated bilayer; smectic A_d) and the alkyl chains pointing outwards. For instance, by far most of the known liquid crystals derived from carbohydrates[32] exhibit this smectic A_d phase of published texture.[32b-d] In contrast to the smectic A_d phases of **18** and **24**, the smectic A hase of the 1,4-diethers **20a** and **b** of *myo-* inositol must be composed of *mono*molecular layers (x-ray investigations are in progress).

Table 2. Temperatures of phase transitions [°C] and types of mesophases found for the eight new rod- or peg-/Y-shaped inositol and cyclopentane multiol ethers or thioethers **18, 20, 21** (non-liquid-crystalline), **24**, and **25**, cf. Schemes 4 and 5. The structures of these compounds have been proved by mass spectrometry, IR, ^{1}H & ^{13}C NMR spectroscopy, as well as by elemental analyses. The instruments and conditions applied for these determinations are given in Table 1, but with deviations for 1) **18a**: because of fast crystallization the $S_A \longrightarrow I$ transition temperature of ≈220°C could be found by microscopy only, 2) **25**: in this case the heating rate in the d.s.c. was 1 K/min. (Cr: crystalline, S_A: smectic type A, H_X: hexagonal columnar, I: isotropic liquid)

| Comp.	R	Geometrical Form	Phase Transitions
18a	C_8H_{17}	rod	Cr $\xrightarrow{223.8}$ { S_A $\xrightarrow{\approx 220}$ } I
b	C_9H_{19}		Cr $\xrightarrow{223.4}$ S_A $\xrightarrow{224.4}$ I
c	$C_{12}H_{25}$		Cr $\xrightarrow{217.4}$ S_A $\xrightarrow{229.6}$ I
20a	C_6H_{13}	rod	Cr $\xrightarrow{144.8}$ S_A $\xrightarrow{176.9}$ I
b	C_8H_{17}		Cr $\xrightarrow{141.2}$ S_A $\xrightarrow{170.1}$ I
21	C_6H_{13}	rod	Cr $\xrightarrow{265.2}$ I
24	C_8H_{17}	rod	Cr $\xrightarrow{76.4}$ S_A $\xrightarrow{144.8}$ I
25	C_8H_{17}	peg	Cr $\xrightarrow{63.3}$ { H_X $\xrightarrow{54.8}$ } I

{ }: monotropic transition

Because of their *trans*-1,4-dialkylation pattern, these molecules are also *rod*-shaped and can be considered as "*bis*-single-tailed", i.e. created formally by pushing the cores of two "single-tailed" molecules into each other and generating this "internally interdigitated *mono*molecular situation" present in **20** (in **21**, too, see later). From another point of view their molecular structures could be put together from two halves, each a glycerol monoether, but *non*-liquid-crystalline by itself,[14b-c] connected via two carbon-carbon bonds (C-1—C-6 and C-3—C-4), cf. Scheme 4.

Preliminary investigations of **20b** and **24** with a polarizing microscope demonstrated that their smectic phases are miscible (contact method). This observation is interesting since these two smectic A phases are of different structure (**20b** forms *mono*- and **24** *bi*molecular layers). However, an ultimate decision about this finding is not easy since both compounds develop different textures, e.g. the one, **20b** a focal-conic fan texture[33] (see Figure 3), whereas the other one of **24** is homeotropic.

We believe that this conspicuous difference in texture must mainly be caused by their difference in general shape: **20b**, a more or less *flat* tetrol because of the equatorial arrangement of all but one (the hydroxyl group at C-2) substituent contains a hydrophilic region in the center of the molecule between two lipophilic chains, whereas the all-*cis*
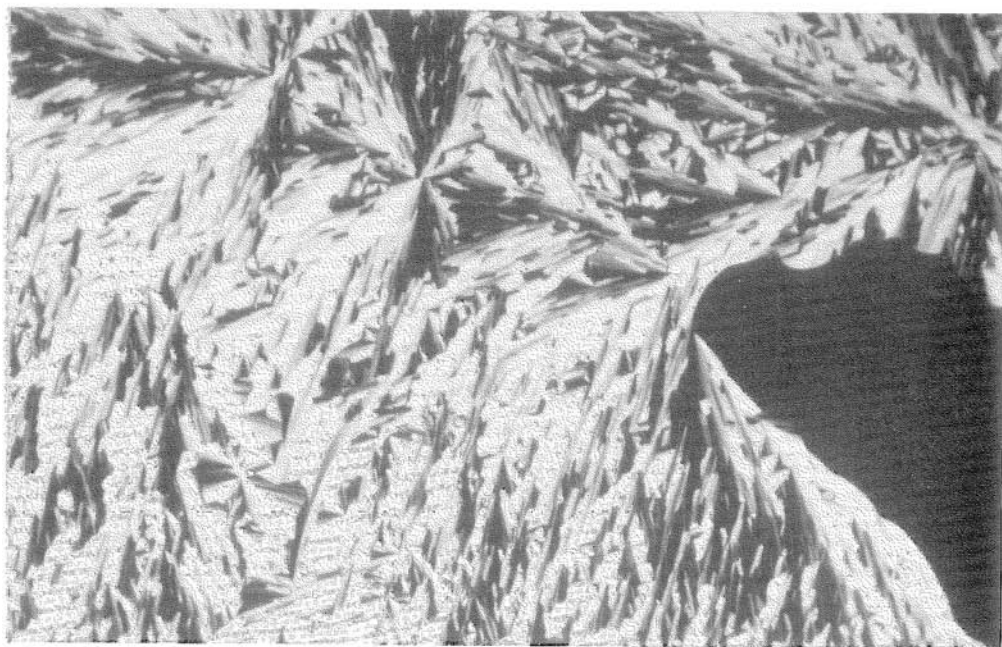
20b
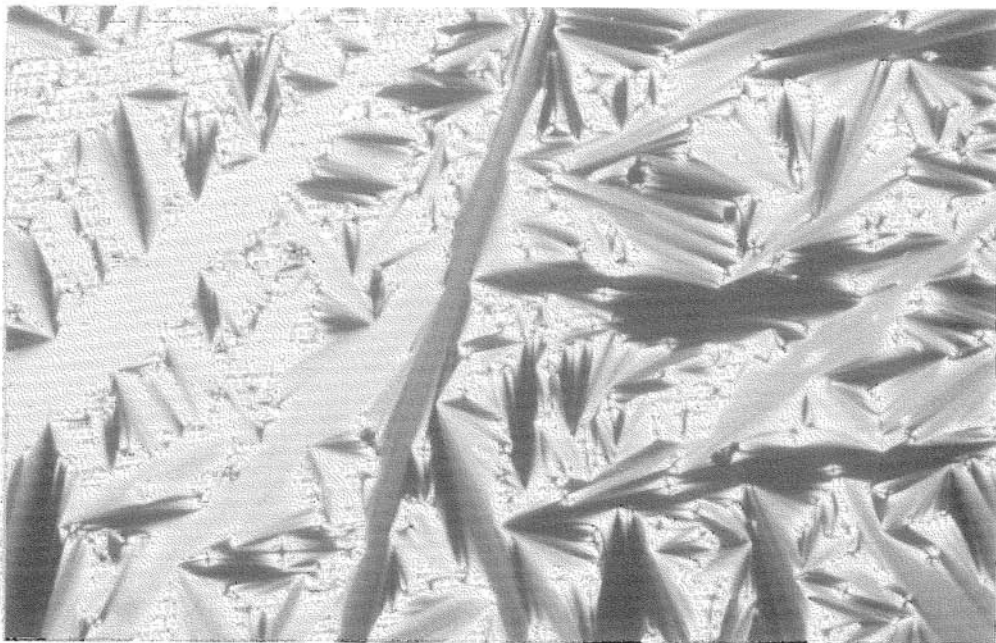
25

Figure 3. Textures of 1) the *smectic A* phase of *myo-*inositol 1,4–dioctylether (**20b**) at 168°C, and 2) the *hexagonal columnar* (H_x) phase of (1α, 2α, 3α)-trihydroxy-(4β, 5β)-dioctyloxy-cyclopentan (**25**) at 53°C with a homeotropic (black) region.– These photographs were taken in a 24x36 mm camera (enlargement 32x), photoautomat WILD MPS 51, crossed polarizers, polarizing microscope Leitz Laborlux 12 Pol equipped with a hot stage Mettler FP 82.

crown-like tetrol **24**, so to speak a crown on top of a stick (the stretched alkylthio chain), owns a hydrophilic head group connected to a lipophilic tail and, therefore, can adhere better at the polar glass surface forcing the smectic layers to be built parallel to it. Further microscopic studies concerning this topic are in progress as with the three thioscyllitol derivatives **18a-c**.

Concerning the *rod*-like, *"bis-single-tailed"* molecular structure of **20a** and **b** discussed above, the same is true for the *non*-liquid-crystalline *scyllo*-inositol 1,4-diether **21**; however, as it melts at a very high temperature of 265.2 °C (cf. Table 2) it is understandable that an enantiotropic mesophase fails to be exhibited. On the other hand, the observation of a monotropic one is complicated due to fast crystallization of this particular dihexylether. We hope to be succesful soon in lowering the melting point by lengthening the alkyl chains in this stereochemical series of 1,4-diethers and hereby further producing a new type of natural product liquid crystal. It should be noted here that the difference in behaviour between **20a** and **21** (equal length of their alkyl chains, cf. Table 2) is caused by a different stereochemical orientation of only *one* hydroxyl group, see Scheme 4.

The various new types of mostly liquid-crystalline cyclic, rod- or peg-shaped multiols synthesized and discussed in this last chapter demonstrate that:

1) their thermomesogenic properties (stability and mesophase range) are strongly influenced by the size of the ring and the stereochemistry at the ring, cf. **18** with **24** and **20a** with **21** in Table 2,

2) the number and position of heteroalkyl side chains are important, because both determine the type of the exhibited mesophase, cf. for instance **24** with **25**, and

3) the formation of the lamellar and columnar mesophases, here too, is based on hydrogen bonding networks as was found essential in other recent investigations.

Acknowledgement

References and Footnotes

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