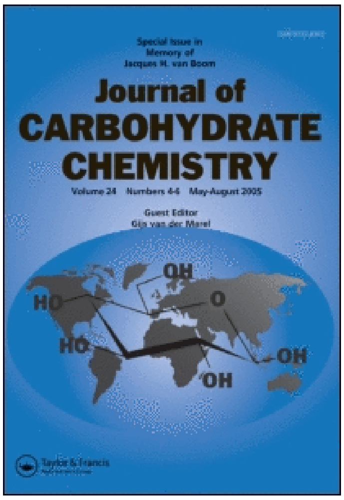

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K. Praefcke; P. Marquardt; B. Kohne; W. Stephan

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LIQUID-CRYSTALLINE INOSITOL ETHERS, THEIR SYNTHESES AND COLUMNAR MESOPHASES[1]

K. Praefcke,* P. Marquardt, B. Kohne, and W. Stephan

Institute of Organic Chemistry, C 3, Technische Universität Berlin,
D-1000 Berlin 12, Germany

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Abstract

Syntheses of selected multi-*O*-alkylethers of the stereoisomeric *myo*- and *scyllo*-inositols are described. Necessary conversions of axial hydroxyl groups into equatorial ones have been performed with either potassium superoxide (KO_2) or potassium nitrite (KNO_2) as powerful oxygen nucleophiles for this purpose. Most of the novel cyclitol ethers are thermotropic liquid crystals. Depending on the number, positions, and stereochemical arrangement of alkyl chains attached to the inositol core, these biomolecule mesogens, chemically *vicinal diols* and a *tetrol*, show interesting modes of molecular organizations in their *columnar* liquid-crystalline phases. The architectures of these mesophases are based on *hydrogen-bridged multimers*. Models for their self-assembled "*supramolecular structures*" are presented and discussed.

Introduction

During the last two to three decades scientific research in the field of liquid crystals derived from synthetic organic compounds[2] was mainly focused on their technological applications. Although studies of liquid-crystalline phenomena began on cholesterol esters about one century ago,[3] biomolecule mesogens in general have been subject to more recent scientific inquiry.[1,4-8]

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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.

Among thermotropic biomolecule liquid crystals, corresponding derivatives of sugars and inositols have gained increasing scientific interest over the last five to ten years.[4-8] During this period, it was found that *"single-tailed" rod-shaped* carbohydrate mesogens as well as recently studied[1] *"1,4-bis-single-tailed" myo*-inositol liquid crystals with *one* or *two* long alkyl chains, respectively, form solely *layer*-structured, so-called *smectic A* phases.[5,8] In contrast, numerous *"1,1-double-tailed"* (geminal) dithioacetals of various aldoses[6] or of the inosose[7] and nowadays[1] also *"1,2-double-tailed"* (vicinal) di-ethers of a cyclopentane pentol each with *two* long alkyl chains, i. e. these three families of compounds are *peg-* or *Y-shaped,*[7] exhibit thermotropic *columnar* mesophases.[1,6a,b,7] It is characteristic for these cited types of multi-hydroxy mesogens that the architectures of their mesophases are based on *hydrogen bonding networks.*[5,6b,7]

In continuation of our studies concerning the relationship between the structure and properties of liquid crystals derived from cycloalkanes in general[1,4] and from carbohydrates here in particular,[1,4,6a,b,7] we concentrated on syntheses of selected multi-ethers of two of the naturally occurring sugar-analogous hexahydroxycyclohexane isomers *myo-* and *scyllo*-inositol. In addition, the liquid-crystalline behavior of these new derivatives as well as modes of molecular organizations in their mesophases are discussed.

Results and Discussion

I. Synthesis of *myo-* and *scyllo*-inositol ethers

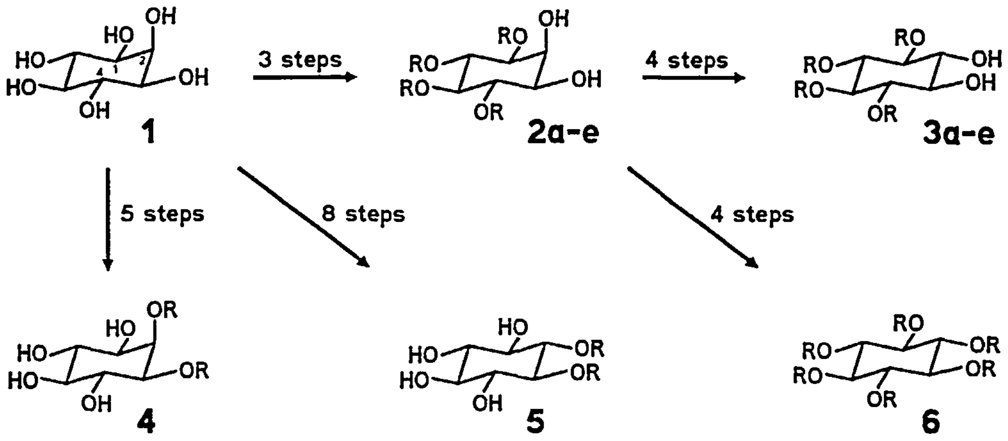
Starting from the commercially available *myo*-inositol (**1**) the multi-*O*-alkylated new inositol derivatives of type **2 - 6** were prepared as summarized in the sections A - E and depicted in Scheme 1.

The use of well established protecting groups (acetal and benzyl ether functions) allows selective *O*-alkylations of *myo*-inositol (**1**). The conversions of *myo*-inositol derivatives into *scyllo*-inositol ones were carried out employing nucleophilic substitution reactions under S_N2 conditions. In these cases, we found that potassium superoxide[9,10] (KO_2) or potassium nitrite[11] (KNO_2) were the oxygen nucleophiles of choice. The structures of the thirteen new inositol ethers **2a - e**, **3a - e**, **4**, **5**, and **6**[10] presented here have been proved by mass spectrometry, IR, ^{1}H, and ^{13}C NMR spectroscopy as well as by elemental analyses. The temperatures of phase transitions (e. g. melting and clearing points) of the ten liquid-crystalline inositol derivatives **2a - e**, **3c - e**, **5**, and **6**[10] obtained by differential scanning calorimetry (d.s.c.) are given in Table 1.

A. Preparation of the *myo*-inositol 1,4,5,6-tetra-*O*-alkylethers 2a - e (vicinal *cis*-diols)

Myo-inositol (**1**) was converted into the tetraethers of type **2** employing the following three-step sequence:

1. acetalization of *myo*-inositol (*cis*-diol groups) using cyclohexanone,[12]
2. fourfold alkylation of this protected *myo*-inositol with the corresponding alkyl bromides in the presence of powdered potassium hydroxide (KOH, cf. ref.[10]),



2,3 : R = C_nH_{2n+1}

	a	b	c	d	e
n	4	5	6	7	8

4 - 6 : R = C_6H_{13}

Scheme 1

3. liberation of the *cis*-diols **2a - e** by acidic hydrolysis.

Following this procedure, the racemic *cis*-diols **2a - e** were obtained as highly viscous oils which each solidified slowly to waxy crystals at room temperature. Their melting points (d.s.c.) are as follows: **2a** 44.8 °C, **2b** ≈20.0 °C, **2c** 27.7 °C, **2d** 34.5 °C, and **2e** 37.1 °C. The overall yields of these five compounds ranged between ca. 16 to 41 %.

B. Preparation of the *scyllo*-inositol 1,2,3,4-tetra-*O*-alkylethers 3a - e (vicinal *trans*-diols)

The syntheses of the *trans*-diols 3a - e started from the corresponding *myo*-inositol tetraethers, the *cis*-diols **2a - e**, and were performed in four steps:

1. protection of the *equatorial* hydroxyl group in **2a - e** by selective benzylation using benzyl chloride and powdered KOH in benzene as solvent (cf. ref.[9]),
2. functionalization of the remaining *axial* hydroxyl group with methanesulfonyl chloride in pyridine (CH_3SO_2Cl/py, cf. ref.[9,10]),
3. conversion of the previous axial hydroxyl group into an equatorial one by addition of KO_2[9,10] in dimethyl sulfoxide (DMSO) in the presence of small amounts of 18-crown-6 yielding (42 to 52 %) the desired *scyllo*-inositol intermediate after described work-up procedure,[10]
4. liberation of the benzyl protected equatorial hydroxyl group by catalytic hydrogenolysis (H_2, Pd/C) leading to the *trans*-diols 3a - e.

This synthetic route led to the racemic *trans*-diols 3a - e as white crystals in overall yields between 13 to 33 %. Their melting points (d.s.c.) are as follows: **3a** 137.3 °C, **3b** 117.5 °C, **3c** 48.9 °C, **3d** 39.6 °C, and **3e** 44.3 °C.

C. Preparation of the *myo*-inositol 1,2-di-*O*-hexylether (4, a "vicinal" tetrol)

The synthesis of the *myo*-inositol diether **4** was realized in five steps starting from *myo*-inositol (**1**):

1. acetalization as described in section A.1,
2. fourfold benzylation of this protected *myo*-inositol with benzyl chloride in the presence of powdered KOH,[13]
3. deprotection by acid hydrolysis,
4. simultaneous alkylation of the axial and equatorial hydroxyl group in this intermediate with bromohexane employing similar reaction conditions as given in A.2,
5. liberation of the four benzyl ether-protected hydroxyl groups by catalytic hydrogenolysis (H_2, Pd/C) generating the *myo*-inositol diether **4**.

Following this pathway the racemic *myo*-inositol diether **4** was obtained in 26 % yield as a white crystalline material melting at 110.2 °C (d.s.c.).

D. Preparation of the *scyllo*-inositol 1,2-di-*O*-hexylether (5, a "vicinal" tetrol)

The conversion of *myo*-inositol (**1**) into the scyllitol diether **5** was achieved using the following eight-step procedure:

1. to 3., reactions identical to those in section C,
4. selective acetylation of the *equatorial* hydroxyl group with acetyl chloride/pyridine (cf. ref.[9]),
5. functionalization of the remaining *axial* hydroxyl group with CH_3SO_2Cl/py (cf. ref.[9,10]),
6. here, in contrast to the reactions in sections B.3 and E.3, the conversion of the configuration of the previous axial hydroxyl group into an equatorial one was achieved by addition of KNO_2[11] (1.5 mmol; in our hands, KO_2 failed here) to the methanesulfonic acid ester (1 mmol) in dimethylformamide (20 mL), heating of this mixture at 110°C for 48 h while stirring under nitrogen, work-up in chloroform, column chromatography (petrol ether/ethyl acetate, 2:1), and recrystallization from heptane/small amounts of ethyl acetate which gave the expected intermediate as colourless needles (yield around 30 %),
7. reaction of this scyllitol derivative with bromohexane in the presence of powdered KOH led to the target dialkylated intermediate with both hexyloxy groups in vicinal equatorial arrangement (cf. C.4),
8. deprotection of the four other benzyl ether-blocked equatorial hydroxyl groups by catalytic hydrogenolysis (H_2, Pd/C) generating the scyllitol diether **5**.

According to this synthesis sequence the racemic *scyllo*-inositol diether **5** was obtained as a white crystalline material melting at 111.5°C (d.s.c.) in an overall yield of 6 %.

E. Preparation of the *scyllo*-inositol hexa-*O*-hexylether[10] (6)

Attempts to synthesize the hexaether **6** in one step by sixfold alkylation of *scyllo*-inositol with bromohexane in the presence of powdered KOH were not succesful.[10] Therefore, **6** was prepared in four steps using the *myo*-inositol tetrahexylether **2c** as starting material:

1. selective alkylation of the *equatorial* hydroxyl group of the vicinal *cis*-diol **2c** with bromohexane, powdered KOH in benzene as solvent,
2. esterification of the remaining *axial* hydroxyl group using CH_3SO_2Cl/py,
3. analogous transformation of this sulfonated hydroxyl function as outlined in section B.3 by addition of KO_2[9,10] etc. (57 % yield of the intermediate target),
4. alkylation of this transformed hydroxyl group under similar conditions as described in section A.2.

The scyllitol hexaether **6**, obtained as colourless oil in 13 % yield, solidified to a high viscous, discotic liquid-crystalline material at room temperature.

II. Liquid-crystalline properties of the synthesized *myo*- and *scyllo*-inositol ethers

All the thirteen new inositol multi-ethers presented here were studied by optical polarizing microscopy and differential scanning calorimetry (d.s.c.). In order to get further information about their mesophases we also applied (i) x-ray diffraction (**2c** and **e**, **3c** - **e**, **5**, and **6**[10]) as well as (ii) deuterium NMR spectroscopy (**2e** and **3e**). The deuterium NMR measurements were performed using two approaches:

(i) Samples of the stereoisomeric inositol tetraethers **2e** and **3e**, respectively, were doped with small amounts of deuterated benzene. The NMR spectra of the dopant were recorded within the liquid-crystalline phases of both ethers.

This method provided information on the symmetry and alignment properties as well as on specific solute-solvent interactions in the mesophases.

(ii) Direct investigations of the *cis*-diol **2e** and the *trans*-diol **3e**, respectively, but deuterated in their hydroxyl groups, revealed information on modes of motion of these molecules in their mesophase regions.

Detailed descriptions of our x-ray[10,14] and deuterium NMR[15] results are mentioned accordingly elsewhere. In section B, however, we present *models of molecular organizations* of our inositol ethers in their mesophases based on these x-ray studies.[10,14]

A. Phase types and sequences of the synthesized *myo*- and *scyllo*-inositol ethers

Finally, the phase *types* (all columnar, mostly hexagonal) and phase *sequences* of the ten thermomesomorphic inositol multi-ethers **2**, **3**, **5**, and **6** shown in Table 1 were established from results of the four physical methods applied here.

B. Molecular organizations of the *myo*- and *scyllo*-inositol ethers in their mesophases

As pointed out previously, our x-ray studies[10,14] led to assumptions about modes of molecular self-assembly of the four main groups of inositol multi-ethers **2**, **3**, **5**, and **6** in their liquid-crystalline states, all columnar and mostly hexagonal in character, depicted in **a** to **d** of Figure 1. As can be seen in this figure, the columnar phases exhibited by these four groups of inositol ethers differ essentially in their intracolumnar compositions. Thus, the hexagonal columnar phase of the scyllitol hexaether **6** is formed by a regular stacking of single *disc*-shaped molecules[10] (*monomeric*

Table 1: Temperatures of the enantiotropic (one monotropic exception: **2a**) phase transitions [°C] and types of mesophases found for the ten new inositol multi-ethers of the types **2**, **3**, **5**, and **6**. The three new non-mesomorphic inositol multi-ethers **3a**, **b**, and **4** melt at 137.3 °C, 117.5 °C, and 110.2 °C, respectively.

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. As exceptions, the transitions $D_{sq,o} \rightarrow D_{ro}$ (**3d**) and $D_1 \rightarrow D_2 \rightarrow D_3 \rightarrow D_{ho}$ (**3e**) could only be seen in the polarizing microscope (Leitz Laborlux 12 Pol equipped with a hot stage Mettler FP 82, heating rate 0.2 K/min); the same is true for the monotropic transition of **2a**.

(**Cr**: crystalline, **D**: discotic, H_X: hexagonal columnar, **I**: isotropic liquid; the indices **h**, **m**, **sq,o**, **ro** and **ho** stand for hexagonal, monoclinic, square ordered, rectangular ordered and hexagonal ordered, respectively. D_1, D_2, and D_3 represent columnar phases of hexagonal symmetry similar to D_{ho}, but with different textural features.)

Compound		Phase Transitions	
		Cr ⟶ $D_h^{*)}$ ⟶ I	
myo-inositol tetraethers **2**	**2a**	● 44.8 (● ≈ 15.0) ●	( ): monotropic transition
	b	● ≈20.0 ● 29.9 ●	
	c	● 27.7 ● 35.8 ●	
	d	● 34.5 ● 40.7 ●	
	e	● 37.1 ● 44.1 ●	
scyllo-inositol tetraethers **3**	**3c**	$Cr \xrightarrow{48.9} D_m \xrightarrow{104.4} I$	
	d	$Cr \xrightarrow{39.6} D_{sq,o}^{‡)} \xrightarrow{82.2} D_{ro} \xrightarrow{96.9} I$	
	e	$Cr \xrightarrow{44.3} D_1 \xrightarrow{55.8} D_2 \xrightarrow{69.5} D_3 \xrightarrow{78.1} D_{ho} \xrightarrow{92.7} I$	
scyllo-inositol di-ether	**5**	$Cr \xrightarrow{111.5} H_X \xrightarrow{167.1} I$	
scyllo-inositol hexaether	**6**	$Cr \xrightarrow{18.4} D_{ho} \xrightarrow{90.8} I$	

*) According to x-ray results[14] (Dr. A.-M. Levelut, Paris) the *intra*columnar order of these D_h phases is somewhat between the known ordered and disordered type, therefore, no further indication is given here.

‡) To our knowledge the tetra*heptyl*ether **3d** seems to be the first thermotropic liquid crystal of *low-molecular weight* which exhibits a mesophase of tetragonal symmetry; similar phases have been found recently in liquid-crystalline CT complexes of polymers with trinitrofluorenone, too.[16]

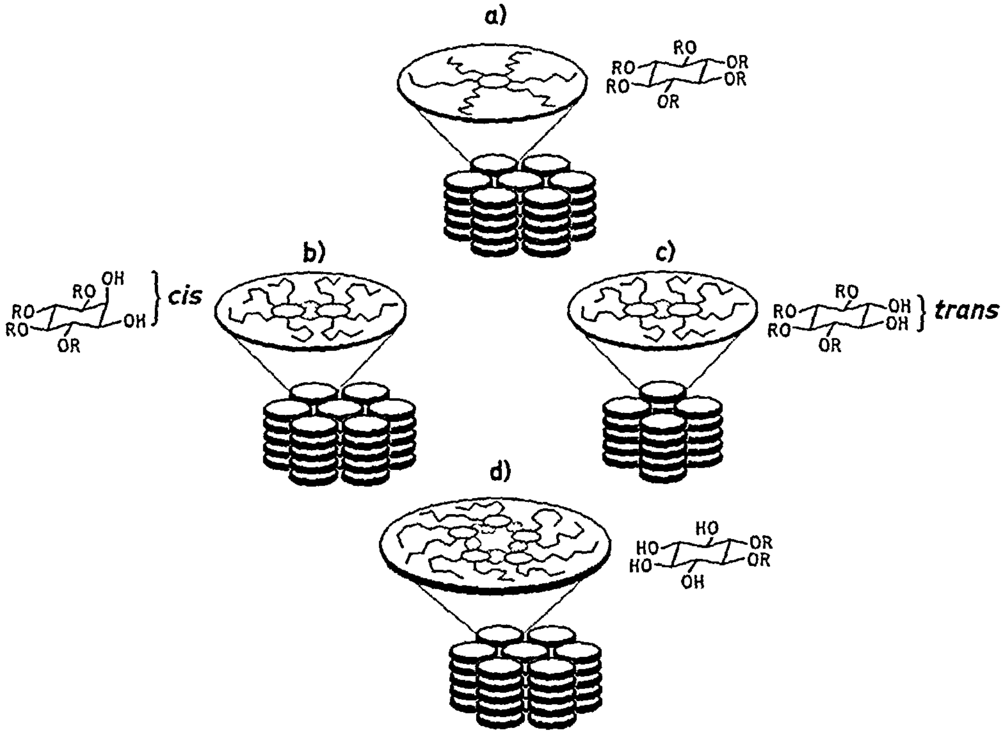


Figure 1: Models of the molecular organizations of the studied inositol multi-ethers of types **2**, **3**, **5**, and **6** in their columnar liquid-crystalline phases based on x-ray investigations.[10,14] The blown-up parts represent slices of single columns showing the differences of their compositions. The regions of hydrogen bonding between hydroxyl groups in these simplified cuts are shaded; the zigzags symbolize OR-groups (cf. Scheme 1):
a) the monomeric *scyllo*-inositol hexaether[10] **6** (D_{ho}), **b)** and **c)** the hydrogen-bridged vicinal diol dimers[14] of *myo-* and *scyllo*-inositol tetraethers of type **2** (D_h) and **3d** ($D_{sq,o}$), respectively, and **d)** the hydrogen-bridged pentamer[14,17] of the *scyllo*-inositol di-ether **5**, an all-*trans*-tetrol (H_X, cf. next page).

building units) as commonly observed for D_{ho} phases of conventional (mostly six long side chains containing) discotic liquid crystals.

In contrast, the mesophases of the *myo-* and *scyllo*-inositol ethers of types **2**, **3**, and **5** are based on *hydrogen-bridged multimers.*[14] In these cases, the lack of a sufficient number of covalently bonded long side chains which normally suppresses discotic liquid-crystalline properties[4] is overcome here by filling their open periphery through multimerization, i. e., via hydrogen-bond formation with like-molecules. In other words, the more hydroxyl groups present at the liquid crystal core instead of long paraffinic chains, the larger the *free* space in the periphery of such a core and as a consequence, the greater the degree of multimerization, as can be seen in Figure 1:
(i) *two* vicinal OH groups as present in **2** and **3** give rise to the formation of dimers,[14]

(ii) *four* vicinal OH groups as in case of **5** even result in the formation of pentamers[14] in average.[17]

It should be noted that the identified hexagonal columnar phase of the neat scyllitol diether **5** - assigned here H_X - shows structural similarities[7] to corresponding (inverted) lyotropic mesophases. Therefore, our presented model showing *distinct discs* of aggregated molecules of the scyllitol diether **5** (cf. Figure 1) is certainly idealized, i. e. for instance intracolumnar molecular fluctuations are not reflected.

Our findings presented here are in agreement with other observations[8d,10,18-21] in recent years demonstrating that various organic compounds containing hetero functions (OH or NH, possibly at least two[8c,10,21]) indeed can exhibit thermotropic liquid-crystalline phases through multimerizations based on hydrogen-bond formations. It is interesting to stress that the dimerization of the *myo-* and *scyllo*-inositol tetraethers **2** and **3** is *independent* of their different *vicinal diol* configurations: *cis* in **2** and *trans* in **3** (cf. Figure 1). On the other hand, the symmetry of the columnar networks of their liquid-crystalline phases as well as their phase transitions are affected by this difference in stereochemistry.

Whereas the *cis*-diols **2a-e** form *hexagonal* columnar phases only, the mesophase symmetries of the *trans*-diols **3c-e** are found to be *monoclinic*, *tetragonal* (similar to recently observed[16] cases in liquid-crystalline CT complexes of polymers with trinitrofluorenone), *centered rectangular*, or *hexagonal*;[14] in addition, for **3d** and **e** polymorphism is observed, too. Another dramatic stereochemical effect reveals a comparison of the properties of the *myo-* and *scyllo*-inositol dihexylethers **4** and **5**. Whereas the scyllitol diether **5** exhibits an H_X mesophase between 111.5 °C and 167.1 °C the *neat myo*-inositol diether **4** is non-liquid-crystalline, i. e. it melts at 110.2 °C directly into an isotropic liquid.

Although *thermo*mesomorphism is not found in case of **4** the addition of water leads here to the formation of a lyotropic lamellar phase (probably S_A); cf. in this context observations described in ref.[21] and other results from this group published recently. However, a precise characterization of the diether **4**/water system would require the application of pressure-resistant sample-cells.

Concluding Remarks

Our syntheses of members of five series of inositol multi-ethers led to new examples of biomolecule liquid crystals. In contrast to mostly "single-tailed" sugar and to *"1,4-bis-single-tailed" myo*-inositol mesogens which form solely *layer*-structured mesophases (cf. introduction), some selected inositol ethers of the structures **2**, **3**, and **5** studied here, having *evenly* numbered vicinal and equatorially arranged alkyl chains attached to the core, form *columnar* liquid-crystalline phases. All these mesophases are of "supramolecular designs" based on hydogen bonding networks. In the latter cases, the building units, simplified as discs in our models **b** to **d** of Figure 1, are self-assembling in columns.

This study enlarges the knowledge about the relationship between the structure and properties of discotic and carbohydrate liquid crystals.[1,4-7,10] In particular, it shows that our structural criteria[4] developed six years ago for disc-shaped liquid-crystalline molecules which exhibit columnar phases composed of *monomers* may also be valid for thermomesomorphic systems consisting of *hydrogen-bridged multimers*. Also in this section of liquid crystal research it seems to us that the moment is getting close in which predictions and observations tune in concert.

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