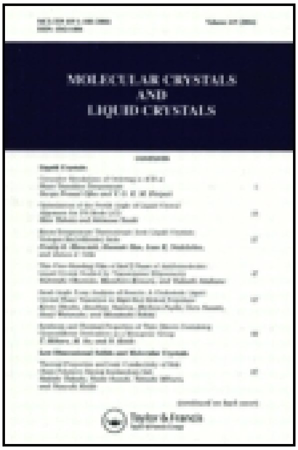

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Amphotropic Properties of Cyclic Scyllitol Hexaesters [1]

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Amphotropic Properties of Cyclic Scyllitol Hexaesters [1]

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The new Scyllitol hexaesters with *cyclic* fragments in lateral substituents of series **1** were synthesized and their thermo- and lyotropic properties (with various organic linear or cyclic solvents) have been studied. It was established that the presence of benzene fragments in the substituents of the scyllitol hexaesters (**1a-e**) reduces the ability of the mesophase formation. The cyclohexane unit instead (sf. **1f**) increases the thermostability of mesophase. While using above mentioned solvents a lot of cases of the *induction* of mesomorphic properties for *non-mesogenic* compounds of series **1** have been described. With cyclic solvents lyotropic mesophases were induced in binary mixtures of the hexaester **1a** which showed mesomorphic properties neither under thermotropic conditions nor in binary mixtures with linear alkanes.

Keywords: scyllitol hexaesters; organic solvents; mesophase; amphotropy; microsegregation

INTRODUCTION

Recently, we analyzed the lyotropic mesomorphism of linear hexahydrobenzene and scyllitol hexaesters correspondingly in binary

systems with linear, mono- or bicyclic hydrocarbons [3]. Hexaesters of the natural occurring *scyllo*-Inositol (Scyllitol) represent typical examples of classical disc-like mesogens. Their thermotropic mesomorphism was already described about seventeenth years ago [4, 5] and show stable columnar mesophases over wide ranges of temperature. In addition, we have found that their lyotropic mesomorphism depends on 1) the intracolumnar order of theses molecules in their thermotropic state (either ordered or disordered), 2) the ratio of the number of carbon atoms in their lateral hexaester alkyl chains and the linear alkanes used as solvents, and 3) the type of the solvent, either linear or cyclic, mono- or bicyclic, saturated or non-saturated, polar or apolar [3].

Their lyomesomorphic characteristics have been discussed from the point of view of conception of microsegregation [3, 6], based on the idea of unification of homogeneous parts of the molecules with an interface formation between these molecular parts. Thus, we have compared the thermo- and lyomesomorphic properties of hexaalkyl esters of both series with a phenyl [7, 8] or a cyclohexanyl ring [4, 5] in their molecular centres, respectively. The phenyl centred species possess a noticeably reduced capability for the development of mesomorphic properties. It has been concluded that the cyclohexanyl fragment as a core of this disc-like type of molecule is more favorable for a mesophase formation compared to the analogues having a central phenyl fragment. Microsegregation peculiarities of such inositol or hexahydroxybenzene derivatives were proposed as one of the most probable reasons of such a drastic difference between their mesomorphic properties [3]. Besides, investigations of linear hexaesters of scyllitol revealed that a cyclic structure of solvents is more preferable for the lyomesophase formation. Saturated cyclic hydrocarbons (cyclohexane in particular) are the best organic solvents for such studies. The contribution of cyclohexane molecules to the formation of lyomesophase may be explained by the effect of filling vacant volumes of the hydrophobic periphery present in these disc-like molecules as demonstrated in Figure 1.

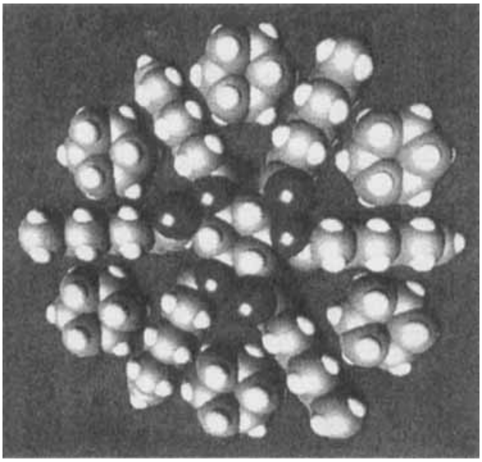


FIGURE 1. Space-filling model illustrating possible arrangement of linear scyllitol hexaester (n=6) and cyclohexane molecules [3]. See Color Plate II at the back of this issue.

Hence, it has become possible to induce a lyotropic columnar nematic mesophase on the basis of the well established microsegregation principle [6] using suitable apolar organic solvent. As our experiments with the lyomesomorphism of palladium organyls show, a lateral substituent may be treated as "internal" [9] solvent for columnar aggregates forming mesophases. The interaction of such "internal" solvent with the "external" one (the linear alkanes) greatly influence the mesomorphism of these compounds. All this mentioned above was a strong impetus on our new step of investigation of further, but different inositol hexaesters.

In this paper we present our data on thermomesomorphic properties of six other scyllitol hexaesters each with cyclic fragments (phenyl or cyclohexanyl rings, respectively) in their star-like arranged substituents. Besides, the lyotropic mesomorphism of these compounds in binary mixtures with various apolar organic solvent will also be reported.

Thermomesomorphism of scyllitol hexaesters containing variously substituted linear ester functions, i.e., carrying for example covalently bound space filling alkyl groups, has been studied by other people [10-12]. However, lyotropic mesomorphism of these latter compounds has not yet been studied.

MATERIALS AND METHODS

The new and not yet published scyllitol hexaesters **1a-f** have been synthesized like procedure described before [4]. The structure and purity have been characterized by elemental analysis, NMR- and Mass-spectroscopy. The solvents (linear alkanes: from pentane to hexadecane, mono- or bicyclic hydrocarbons) were obtained from Merck Ltd., Darmstadt, Germany, and employed without further purification. The thermal behaviour was investigated by differential scanning calorimetry (Mettler TA 300/DSC 30S with Graph Wave TA 72.5, heating rate 10 ^{0}C/min) and polarizing microscopy (Leitz

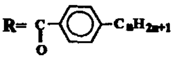
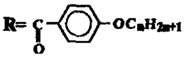
Laborlux 12 Pol microscope with crossed polarizers and a Mettler FP 82 hot stage, heating rate 2 ^{0}C/min). The lyotropic mesomorphism was investigated using contact preparations. The texture photographs were taken with a 24 x 36 mm^2 microscope camera and a Photoautomat Wild MPS 51.

RESULTS AND DISCUSSION

Thermotropic mesomorphism

The data of the thermotropic mesomorphism of **1a-f** are listed in Table 1.

Table 1. Thermotropic Mesomorphism of the Scyllitol Hexaesters **1a-f**.

Scyllitol Hexaester	**R**	**Thermotropic mesomorphism**[a]
1a-c	 **1a** (n=7) **1b** (n=8) **1c** (n=9)	Cr 223.5 Iso[b] Cr_1 100.8 Cr_2 129.9 Cr_3 207.7 Iso Cr 120 M_1 1805 M_2 192 Iso[b]
d-e	 **d** (n=8) **e** (n=10)	Cr_1 107.4 Cr_2 238.9 Iso Cr_1 93.4 Cr_2 208.8 Iso
f		Cr 150.2 M 272.7 Iso

[a] Transition data obtained by d.s.c.

[b] Transition data obtained by polarizing microscopy only.

M = mesophase

Only two of these hexaesters (**1c** and **f**) are mesomorphic on heating. The homologue **1c** exhibits 2 types of mesophases: i) M_1 with a marble texture between 120 to 185 ^{0}C (Fig. 2); ii) M_2 with a mosaic or herring bone texture between 185 to 192 ^{0}C (Fig. 3). Hexaester **1f** shows only one thermotropic mesophase with a herring bone texture between 150.2 to 272.2 ^{0}C. The mesophase structures cannot yet be characterized. The similarity of the textures of **1c** or **1f** with that one of linear hexaesters [5] lets us suggest a columnar type of supramolecular packing for them. The hexaesters **1a**, **b**, **d** and **e** are not mesomorphic and show several crystalline modifications.

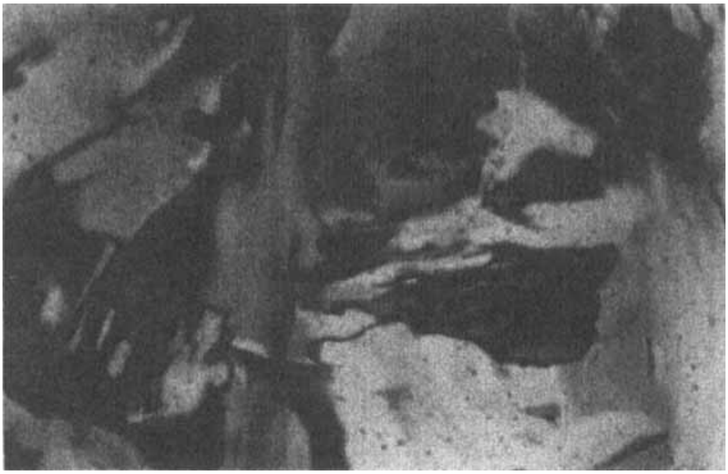


FIGURE 2. Marble texture of the thermotropic mesophase (M_1) of **1d** at 178 ^{0}C on cooling, crossed polarizers, x 250.
See Color Plate III at the back of this issue

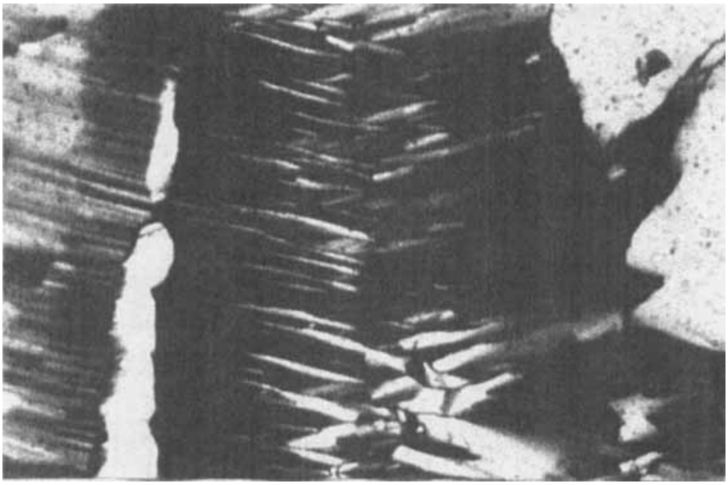


FIGURE 3. "Herring-bone" texture of the thermotropic mesophase (M_2) of **1c** at 187 ^{0}C on heating, crossed polarizers, x 250. See Color Plate IV at the back of this issue.

Lyotropic Mesomorphism

In Table 2 our data on lyotropic mesomorphism of the hexaesters **1a-f** with *linear alkanes* are compiled. The table shows that non-mesogenic homologue **1a** does not possess lyomesogenic properties with any of the alkanes used. However, both of the thermotropic mesogenes (**1c** and **f**), as well as the non-mesogenic **1b**, **d** and **e** form two types of lyotropic mesophases. The first phase is more viscous and has either a herring bone or a non-geometrical texture. The second one is more fluid and is characterized by a Schlieren or homeotropic texture. Probably, most mesophases are of a columnar type and belong to chromonics since the molecules have disc-like shape and are analogous to the inositol hexaesters of linear carboxylic acids having a columnar type of thermotropic phase. Hence, they are called M- and N-phase, respectively.

Table 2. Types of Mesophases of the Scyllitol Hexaesters **1a-f** in Binary Mixtures with *Linear* Alkanes.

Solvent	**Radial Haxaester**					
	1a n=7	**1b** n=8	**1c** n=9	**1d** n=8	**1e** n=10	**1f** n=9
Pentane	-	-	-	-	N, M	N, M
Hexane	-	-	-	-	N, M	N, M
Heptane	-	N, M	N, M	N, M	N, M	N, M
Octane	-	(N),M	N, M	N, M	N, M	N, M
Nonane	-	M	N, M	N, M	N, M	N, M
Decane	-	M	N, M	N, M	N, M	N, M
Undecane	-	-	(N) M	N, M	N, M	N, M
Dodecane	-	-	M	-	N, M	N, M
Tridecane	-	-	M	-	N, M	N, M
Tetradecane	-	-	M	-	N, M	N, M
Pentadecane	-	-	-	-	N, M	N, M
Hexadecane	-	-	-	-	N, M	N, M
Heptadecane	-	-	-	-	M	N, M
Thermotropy	-	-	+	-	-	+

☐ The vertical windows show the *induced* lyotropic mesomorphism in comparison with the thermotropic one.

Thus, in 40 cases the induction of lyotropic M- and N-phases became possible in binary systems with linear alkanes including even those hexaesters not exhibiting thermomesomorphic properties (**1b**, **d** and **e**). In all these cases, the temperature of the crystal → mesophase transition was considerably lower than under thermotropic conditions.

Following previous experience about inductions of mesomorphic properties using cyclic solvents we managed here also to induce lyotropic mesophases in case of **1a** which does not exhibit mesomorphic properties in any of the formerly applied linear alkanes. Lyomesophases can be observed in most binary systems using cyclic hydrocarbons, see Table 3, Figure 4. Interestingly, in some cases (e.g., using benzene or cyclohexane) lyomesophases do exist even ***at room temperature.***

Table 3. Types of Possible Mesophases of Compound **1a** in Binary Mixtures with *Cyclic* Hydrocarbons.

Solvent	**1a**
Cyclooctane	**N♦ , M**
Cyclodecane	**(N) , M**
Cyclohexene	**N , M**
Benzene	**M**
Hexafluorobenzene	**-**
Cyclohexanone	**M**
***cis*-Decaline**	**(N) , M**
***trans*-Decaline**	**(N) , M**
Tetraline	**M**

♦This phase is *monotropic* on first heating but appears *enantiotropic* on repeated heatings.

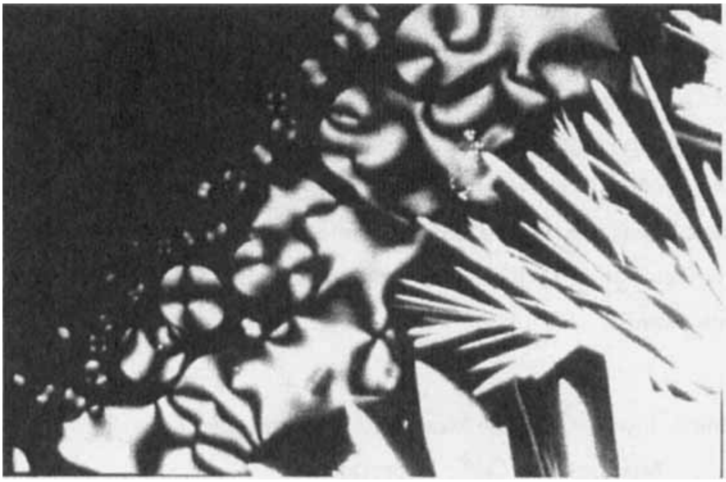


FIGURE 4. Contact preparation of the binary system **1a**/cyclodecane, at 73 ^{0}C on cooling, crossed polarizers, x 250. From left to right: the isotropic region, the nematic and crystal phase. See Color Plate V at the back of this issue.

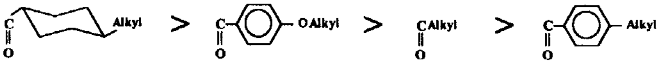
We found out that compound **1f** possessing *cyclohexane* fragments in its lateral substituents show the strongest ability to develop lyomesomorphism if one considers the number of lyotropic mesophases. Probably, the most distinct mesomorphism (both thermo- and lyotropic) of compound **1f** in comparison to **1a-e** and linear scyllitol hexaesters studied earlier [3] connected with the presence of wide peripheral apolar block in supramolecular ensembles and also with a good filling of vacant volume on the columnar periphery caused by bulky cyclohexane fragment included in lateral substituent. All these factors lead to microsegregation increase based on strengthening of apolar/polar disbalance inside of the column.

According to the discussion in the beginning of this article, it seems noteworthy to others that the presence of ***benzene*** fragments in the substituents should lead to a decrease of mesogenic properties. This proved to be right for the hexaesters **1a-c**. One of the homologues (**1c**, n=9) is mesomorphic in a narrower temperature range compared to the analogous homologue **1f** (ΔT=72 and 122 ^{0}C, respectively). The number of binary mixtures of **1b-d** with linear alkanes exhibiting lyomesomorphic properties is also limited, see Table 2.

CONCLUSION

1. The presence of benzene fragments in the substituents reduces the ability of the *scyllo-inositol* hexaesters to form thermotropic mesophases: all the homologues of linear scyllitol hexaesters [3] (n=2-11) are mesomorphic, whereas only one (**1c**) of the three investigated homologues **1a-c** (n=7-9) possesses mesomorphic properties.
2. The cyclohexane unit instead (sf. **1f**) increase the thermostability of the mesophase.
3. The lyomesomorphic state has been induced in binary mixtures of 22 cases **non-mesomorphic** hexaesters of type **1b, d** and **e** with linear alkanes. In 19 cases **two types** of lyomesophases (nematic and two-dimensional columnar) have been observed.
4. In binary systems with **linear alkanes 1c** and **f** display a *lyotropic nematic* phase side by side with the two-dimensional columnar one, typical for their thermotropic mesomorphism.

5. On the basis of this investigation and previous one [3] the following consequence for scyllitol hexaesters with respect to their ability of exhibiting of lyomesomorphism in binary mixtures with linear alkanes was found:



1f **1d-e** see [3] **1a-c**

The evaluation has been performed according to the number of lyotropic polymorphic modification formed in each mixture and to the number of mesogenic binary mixtures displayed each compound (hexaester) with various solvents.

6. Lyotropic mesophases were *induced* in binary mixtures of the hexaesters **1a** with cyclic solvents neither shown under thermotropic conditions nor in binary mixtures with linear alkanes.

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