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Comparative lyotropy study of homologous hexaesters of hexahydroxy-benzene and -cyclohexane (scyllitol) in linear and cyclic hydrocarbons: microsegregation and mesophase formation of discotics [1]

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The investigation addressed in the title was carried out on a total of 17 members of the two disc-shaped series **1** or **2** of radial hexaesters differing only in their cyclic C_6-core units. Their lyotropic behaviour appeared to be dependent on the intracolumnar order of stacking of the respective hexaester molecules. With linear alkanes in mixtures with the phenylene centred hexaesters (series **1** derived from hexahydroxybenzene) no lyomesomorphism occurs, whereas with most of the cyclohexane centred analogues (series **2**, scyllitol derivatives) even two lyomesophases were observed: a hexagonal type and, in 49 cases, a nematic columnar (induced) phase. Here, the lyotropy demonstrates its dependence on the length of chains both of the alkanoyl groups of **2** and the solvent (the linear alkanes) used. In the case of the selected cyclic solvents, three factors proved to govern the lyotropic mesomorphism of all these disc-like hexaesters: (1) their degree of saturation, (2) their molecular size/volume, and (3) their stereostructure. Interestingly, with benzene and other (less unsaturated) monocyclic solvents, both series of hexaesters exhibit only a hexagonal type of mesophase which is induced in four cases. Saturated monocyclic hydrocarbons act on members of the aromatic centred series **1** in the same way; with cyclohexane however, two more cases of induction of a hexagonal type of lyomesophase have been observed. To our surprise, binary mixtures of most hexaesters of series **2** (scyllitol derivatives) with saturated monocyclic hydrocarbons show the same polymorphic (nematic and hexagonal) situation as that found here with linear hydrocarbons; moreover, in comparison with the results with linear alkanes, four more cases of induced phases appear with these cycloalkanes. These results, in particular the many cases of lyomesophase induction, relate to the first examples of lyotropic mesomorphism in binary systems of disc-like materials with saturated cyclic solvents/hydrocarbons. Finally, in some examples presented here it was found for the first time that bulkiness/space-filling or the stereostructure of the saturated cyclic solvents/hydrocarbons, e.g. *cis*- or *trans*-decalin, also play an important role in the lyotropic mesomorphism of their mixtures with the radial hexaesters of the two series **1** and **2**. By means of models shown here for the first time in figures 4 to 6, ideas are put forward about peculiarities due to microsegregation in relation to the (formally) very similar members of both hexaester series **1** and **2** as a key to understanding the drastic difference in their thermotropic as well as their lyotropic states.

1. Introduction

Recent work [2–5] on the lyotropic mesomorphism of aromatic macrocyclic disc-shaped materials, e.g. phthalocyanine and porphyrin derivatives, as well as large-sized metal organyls in apolar saturated organic solvents (linear alkanes only) has revealed interesting results with respect to the type, stability, and width of the lyomesophases exhibited by those binary mixtures as a function of the ratio of the length of the solvent molecules to the length of one of the alkyl chains of the various substrates. Our attention has now been drawn

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to more detailed aspects of the lyotropy of the title compounds of this paper, the already well known hexaester series **1** and **2**, both having small equally sized cyclic, flat core units, in (linear and cyclic) hydrocarbons.

The only, but decisive, structural difference between these two series lies in the saturated (cyclohexane) core of **2**, making all the members of this series equally thick both in their molecular centre and their periphery of alkyl chains, in contrast to the homologues of series **1** with their rigid and somewhat thinner aromatic (phenylene) ring (figure 1).

Historically, the three members **1d–f** were the first disc-shaped thermomesogens to be discovered [6, 7], whereas non-thermomesomorphic **1c** is also described as giving the first example of lyotropic mesomorphism for a disc-like mesogen [7, 8]: a columnar hexagonal phase is *induced* in mixtures with benzene.

The first members of homologous series **2** were first synthesized seven years later [9–13] and found to be thermotropic liquid crystalline materials; these hexaesters of naturally occurring scyllo-inositol/scyllitol show very stable and wide range thermomesophases and also interesting polymesomorphism on heating: disordered and ordered columnar hexagonal phases were observed, as well as a cubic phase [10] in one case (**2c**).

Although first indications on the lyotropic mesomorphism of the scyllitol ester series **2** in apolar organic solvents had been known to us for some time [14], a detailed study including comparisons of the lyotropic mesomorphism of members of series **2** with those of **1** has however only just been finished and is now reported here.

2. Materials and methods

The seven hexaesters of hexahydroxybenzene, the hexa-alkanoyloxybenzene derivatives **1a–g** [15], were either resynthesized by us starting from commercially available hexahydroxybenzene and the respective alkanoic acid anhydrides, following a known procedure [15], or were gratefully received from two different research groups headed by Professor S. Chandrasekhar, Centre for Liquid Crystal Research, Bangalore, India, or by Professor G. Heppke, Ivan-N.-Stranski-Institute of Physical and Theoretical Chemistry, Technische Universität Berlin, Germany.

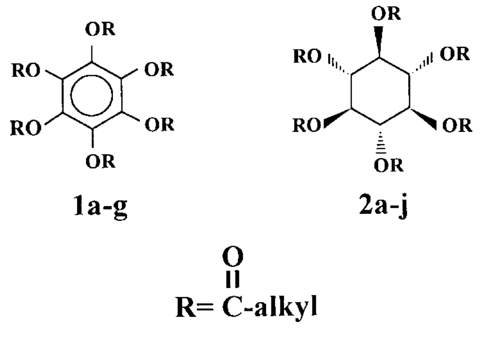


Figure 1. Structural formulae of the flat, disc-shaped hexahydroxybenzene and (saturated) scyllo-inositol hexaesters, left [6, 7, 15] and right [9–13], respectively; their alkyl groups are specified in tables 1 and 2.

The simplest method for their purification was found to be by column chromatography using silica gel 60 and methylene chloride as eluent. The synthesis and purification of our own scyllitol hexaesters **2a–j** have been described elsewhere [9, 12].

All the solvents used in this study and listed in the tables were obtained from E. Merck Ltd., Darmstadt, Germany, and employed without further purification.

The lyotropic mesomorphism was investigated using contact preparations (hexaester plus solvent). With regard to phase diagrams, mixtures of given members of series **2** and specific amounts of linear alkanes were prepared and homogenized in an ultra-sound bath for 120 min at 45°C placed in sealed cells (glue: 'Plus endfest 300'), and then studied. The thermal behaviour of these samples was investigated by polarizing microscopy (Leitz Laborlux 12 Pol microscope) with crossed polarizers and a Mettler FP 82 hot stage (heating rate: 2°C min^{-1}).

The texture photographs shown in figure 2 were taken with a 24 × 36 mm microscope camera and a Photoautomat Wild MPS 51. The coloured models were constructed manually applying the Graphical User Interface, GUI, Unichem 4.1-Suite on a Silicon Graphics Workstation R4000/50 VGX.

3. Results and discussion

3.1. *Lyomesomorphism of the **1** and **2** homologues in linear alkanes*

The results with regard to the ten disc-like (saturated) scyllitol hexaesters **2** in mixtures with various *linear* alkanes are compiled in table 1 and clearly demonstrate the dependence of their lyotropic mesomorphism on the length of chains both of the alkanoyl groups of **2** and the solvent used. Interestingly, this table reveals a sharp division of the ten hexaesters **2a–j** into three groups:

(1) three non-lyomesomorphic, short-chained esters (**2a–c** with *n* = 2, 3, or 4, respectively);
(2) five bilyomesophasic homologues (**2d–h**) forming the middle group;
(3) two monolyomesophasic members (**2i, j**) possessing the longest ester groups.

Whereas **2a–c** each display a thermotropic Col_{hd} (≡ D_1) [10, 16] or even a cubic [10] phase (**2c**), they are not lyomesomorphic in mixtures with linear alkanes from pentane to heptadecane.

The hexaesters **2d–h** in the middle section of this homologous series are the most interesting, since they

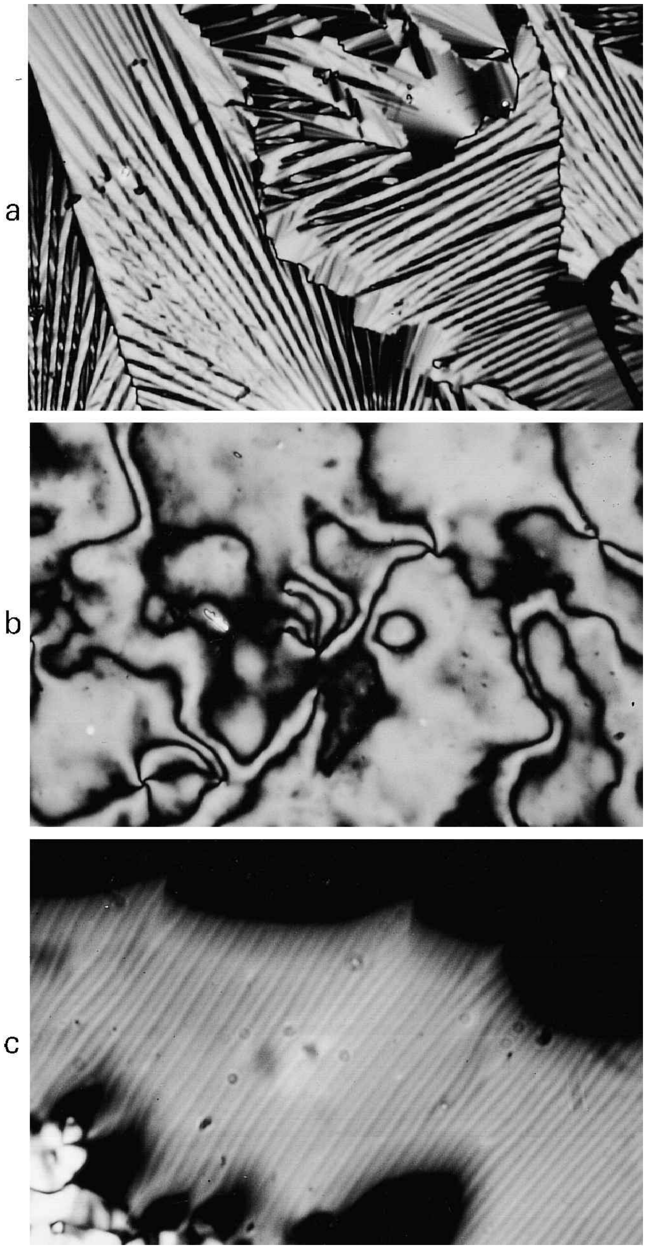


Figure 2. Photomicrographs of (*a*) herring-bone texture of a **2e**/hexane contact preparation at 58.2°C on heating, crossed polarizers; (*b*) Schlieren texture of a **2h**/octane contact preparation at 56°C on cooling, crossed polarizers; and (*c*) striped texture of a **2e**/tridecane contact preparation at 51.4°C on cooling, crossed polarizers.

exhibit thermotropically only the $\mathrm{Col}_{\mathrm{ho}}$ (≡ D_{E}) [10, 11, 16] phase, but give 49(!) cases of *induction* of a nematic phase, each one evidenced by the appearance of a Schlieren texture.

Besides these very many instances of N phase [17] induction, depicted in table 1 by vertical rectangular frames/windows, an M phase [17] shows up clearly by displaying a herring-bone or a fan-like type of texture. The border between these two kinds of mesophase is very distinct. Similarly to phase diagrams of other chromonics in water [17], the progressive increase of order with increase of concentration was observed without any peaks corresponding to the optimum composition of components for each phase. Typical textures are shown in figures 2(*a*) and 2(*b*). These pictures and the phase diagram, shown as an example in figure 3, as well as the hexagonally ordered columnar arrangement in their thermotropic mesophases [9–11] (cf. bottom part of table 1), allow us to suppose that the two lyotropic phases found here are *chromonic* in character. The Schlieren and herring-bone textures correspond to the nematic-chromonic (-columnar) and columnar hexagonal (M-chromonic) phases, respectively. This assumption also seems reasonable by comparison with cases discussed elsewhere [17].

It seems noteworthy that the hexagonal type of disordered columnar phase exhibited thermotropically by **2a–c** did not lead to any lyotropic type of mesophase with linear alkanes!

Between ordinary glass plates, the area of Schlieren texture has a tendency to become easily homeotropic. It is important to note that a shear deformation of such homeotropic domains creates a striped texture, see figure 2(*c*). Up to now, this phenomenon is not completely understood by us, and therefore further investigation of this observation seems to be necessary. Such a situation could be caused by an orientational instability, as has been described in another case, which however involved an aqueous nematic system [18].

An interesting feature about the lyotropic polymorphism observed for the (disc-like) scyllitol hexaesters forming the middle section of table 1 is caused/controlled by the difference between the chain lengths of their alkyl parts *R* and of the saturated linear hydrocarbons used as solvents in the binary mixtures: the induced N phase is stable up to a difference of five to six carbon atoms between them.

Below an oblique, widening, diffuse 'border zone' in table 1 from **2d**/dodecane down to **2g**/tetradecane-hexadecane, the polymorphism disappears. Furthermore, a difference of mainly nine carbon atoms between the two alkyl chains gives rise solely to the M phase; see the bottom part of table 1. The latter phase dominates in mixtures of **2h** and the linear alkanes: only one composition (**2h** plus pentane) allows an induced enantiotropic N phase. In seven more binary mixtures of **2h** with the relatively short hexane up to the medium-long dodecane, the induced N phase appears continuously, but only monotropically. As a result there is a second, now vertical, narrow 'border zone' between this middle group and the third group of scyllitol hexaesters made

Table 1. Amphotropic properties[a] of the scyllo-inositol hexaesters **2a–j**.

Linear alkanes	Hexaesters **2a–j** [9–13] $R = -\overset{O}{\overset{\parallel}{C}}-C_nH_{2n+1}$							
	2a,b,c $n = 2–4$	**2d** $n = 5$	**2e** $n = 6$	**2f** $n = 7$	**2g** $n = 8$	**2h** $n = 9$	**2i** $n = 10$	**2j** $n = 11$
Pentane	—	[b] N M	N M	N M	N M	N M	—	—
Hexane	—	N M	N M	N M	N M	(N) M	M	—
Heptane	—	N M	N M	N M	N M	(N) M	M	M
Octane	—	N M	N M	N M	N M	(N) M	M	M
Nonane	—	N M	N M	N M	N M	(N) M	M	M
Decane	—	N M	N M	N M	N M	(N) M	M	M
Undecane	—	N M	N M	N M	N M	(N) M	M	M
Dodecane	—	(N) M	N M	N M	N M	(N) M	M	M
Tridecane	—	M	(N) M	(N) M	N M	M	M	M
Tetradecane	—	M	(N) M	(N) M	(N) M	M	M	M
Pentadecane	—	M	M	(N) M	(N) M	M	M	M
Hexadecane	—	M	M	M	(N) M	M	M	M
Heptadecane	—	M	M	M	M	M	M	M
Thermotropy [10, 11]	Col_{hd}[c]	Col_{ho}						

[a] The lyotropic studies are based on contact preparations. Phase structures: N = nematic chromonic-like [( ) = monotropic], M = hexagonal chromonic-like. For a better overview, the cases with a monotropic phase are given on a shaded background.

[b] The vertical windows emphasise the *induced* status of the numerous N phase situations observed here (49: 33 enantiotropic and 16 monotropic).

[c] In addition, **2c** ($n = 4$) exhibits a cubic phase on heating [10].

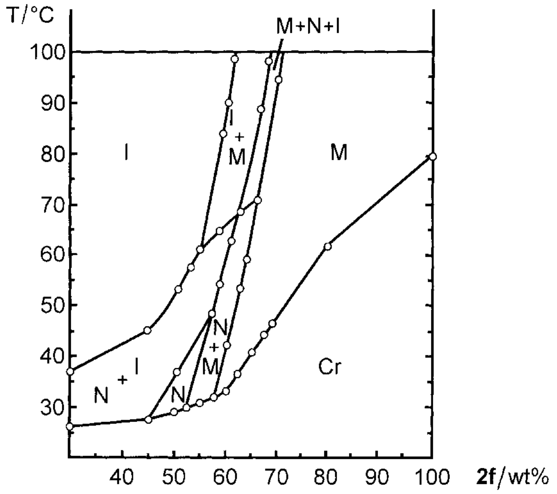


Figure 3. Simplified phase diagram of the **2f**/heptane system on cooling from the isotropic phase as determined by hot stage polarizing microscopy; Cr = crystalline, N = N-chromonic, M = M-chromonic, I = isotropic phases.

up from **2i** and **2j** which almost without exception exhibit the columnar hexagonal M phase in mixtures with the solvents of table 1.

On heating, the seven hexaesters **2d–j** each exhibit the Col_{ho} ($\equiv D_E$) phase [10, 11, 16].

Comparing members of the chemically identically functionalized series **1** [15] and **2** [9–13], the formal replacement of the saturated (cyclohexane) core of **2** by the rigid and somewhat thinner aromatic (phenylene) unit of **1**, not only reduces the number of mesomorphic homologues significantly [6, 7], but also drastically narrows the width and weakens the stability of the thermotropic columnar hexagonal phase [6, 7, 19].

Even more dramatic is the situation for members of series **1** in binary mixtures with linear alkanes compared with the behaviour of the analogous homologues of series **2** described above. In contrast to **2d–j**, with linear alkanes from pentane to hexadecane, none of the seven hexaesters of series **1** (**1d–f** each display only a disordered thermotropic Col_h phase [6, 7] as do also **2a–c**) gives rise to a lyomesophase: only in the cases of **1d** and **1e** have decreases of both their clearing and melting temperatures been observed. These findings are in good agreement with previous results published twenty years ago [7, 8], when undecane was used for the first time as a linear alkane. Moreover, the monotropic Col_{hd} phase of **1f** observed on heating [6, 7] is preserved in mixtures with octane, but has now become narrower [14].

Most probably, the reason for the different behaviour of **1d–f** and **2a–c** in comparison to **2d–j** stems from peculiarities of the interactions between these molecules within their columnar arrays which are only weak, and therefore form on heating without solvent the *disordered* type of columnar hexagonal phase.

It is known [20] that weakly segregated systems can easily be disturbed by the addition of solvents, i.e. only a direct transition from the crystalline into the isotropic state is observed. Among other reasons, stereochemical factors may be responsible for such situations, for instance in the case of the benzene derivatives **1** due to the 'dead space' existing on both sides of the somewhat thinner phenylene centre after these disc-like molecules have stacked in columns [19]. Obviously, this circumstance leads to weaker core–core interactions and, consequently, to a reduction in the intermolecular contact within their columnar aggregates.

On the other hand, only members of these series with an *ordered* columnar array, Col$_{ho}$ and having the thicker cyclohexane centre, e.g. the scyllitol hexaesters **2d–j**, exhibit lyotropic phases in mixtures with linear alkanes. Even the induction of a nematic type of phase is now possible and controlled by the length of the alkyl groups (the 'internal, covalently bound, substrate's-own solvent' [21]) of the promesogenic material and the ('external') solvent forming the binary mixture.

3.2. *Lyomesomorphism of the **1** and **2** homologues in cyclic hydrocarbons*

Although the first example of lyotropic mesomorphism for a disc-shaped thermomesogen was described twenty years ago [7, 8] in the case of mixtures of members **c–f** of series **1** with benzene, to the best of our knowledge [22], no other *cyclic* solvent has been applied since then in order to study binary mixtures with organic materials of discotic molecular structure. Because of this, and to satisfy our curiosity in this matter, we have used ten cyclic solvents—except for one (cyclohexanone), all of them are non-polar hydrocarbons—as components for binary mixtures with all seventeen members of both hexaester series **1** and **2**. Including benzene, seven of the solvents are monocyclic, whereas the remaining four (*cis*- and *trans*-decahydronaphthalene, naphthalene and 1,2,3,4-tetrahydronaphthalene) are bicyclic in shape. The members of the first group differ in their degree of saturation and ring size/volume and are made up of five, six, eight, or ten carbon atoms. The difference between the four bicyclic hydrocarbons, each containing ten carbon atoms, stems not only from their different degrees of saturation but also, for instance in the cases of the two isomeric decalins, from another important aspect—their fixed stereostructures either *cis*- or *trans*-configurated and therefore different in space-filling.

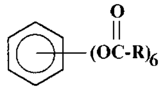
The space-filling models of the molecules of the eleven cyclic solvents shown in figure 4 serve to illustrate their electronic and geometric/space-filling differences. For the selected solvents, three factors proved clearly to govern the lyotropic mesomorphism observed for each hexaester of both these series differing only in the core unit: their degree of saturation, molecular size, and stereostructure.

In the following sections, results supporting these conclusions are presented and discussed.

3.2.1. *Binary mixtures based on the benzene derivatives **1a–g***

In table 2 and its footnotes, our results regarding series **1** having an aromatic (phenylene) core are summarized. The four benzene derivatives **1a**, **1b**, and in part **1c** carrying short alkanoyl groups, as well as **1g** with the longest side chains of all the members of this series, are non-mesomorphic, i.e. neither on heating [6, 7], nor in binary mixtures with all or most of the ten cyclic or bicyclic solvents used in this study.

Table 2. Lyomesomorphism[a] of the hexakis(alkanoyl)benzene derivatives **1a–g**[b] in some cyclic (mainly saturated) hydrocarbons.

	Solvents				
1a–g[b] [6, 7, 15]	Benzene[c]	Cyclohexene[d]	Cyclohexane	Cyclooctane	Cyclodecane[e]
1a,b (*R* = propyl, butyl)	—	—	—	—	—
1c (*R* = pentyl)	[f] $\boxed{\text{M}}$	$\boxed{\text{M}}$	$\boxed{\text{M}}$	—	—
1d (*R* = hexyl)	M	M	M	M	M
1e (*R* = heptyl)	M	M	M	M	M
1f (*R* = octyl)	(M)	(M)	$\boxed{\text{M}}$	(M)	(M)
1g (*R* = nonyl)	—	—	—	—	—

[a] Contact preparations: M = hexagonal chromonic-like [() on shaded background = monotropic].

[b] Whereas **1a–c**, and **1g** are not thermomesomorphic, **1d–f** are (**1f** monotropically) [6, 7]; the three latter materials each exhibit a disordered Col$_h$ phase, cf. their transition data [6, 7].

[c] No mesophase formation arose with the bicyclic arenes naphthalene or 1,2,3,4-tetrahydronaphthalene (tetralin)!

[d] The same results were obtained using cyclohexanone.

[e] No mesophase formation occurred with most of these homologues in mixtures with the bicyclic alkanes *cis*- or *trans*-decahydronaphthalene (decalin). One exception only (**1d**) plus each of the latter two fully saturated bicyclic solvents (cf. models shown in figure 4) also exhibits the M phase enantiotropically!

[f] The M phase shown here in windows is *induced*! See also footnote [b].

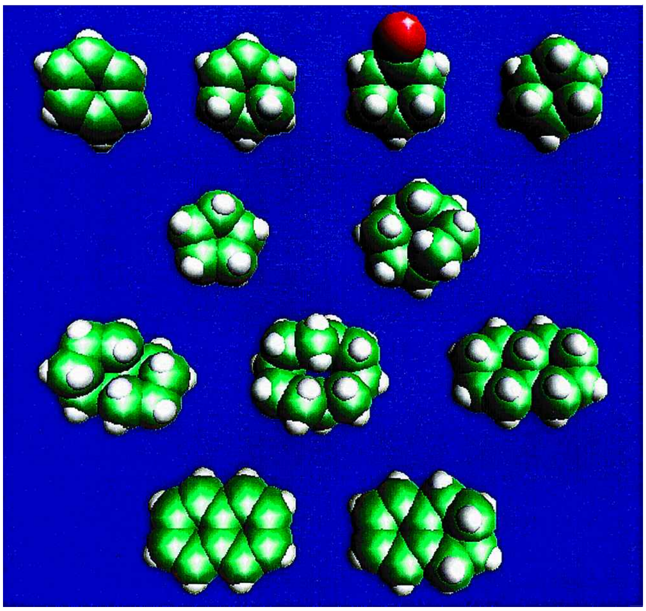


Figure 4. Space-filling models in demonstrating the shape and size of the molecules of eleven cyclic organic solvents used to make binary mixtures with the disc-/star-shaped hexaesters of series **1** and **2** depicted in Figure 1: f.l.t.r. (row 1) benzene, cyclohexene, cyclohexanone, and cyclohexane; (row 2) cyclopentane, and cyclooctane; (row 3) *cis*-decahydronaphthalene (*cis*-decalin), cyclodecane, and *trans*-decahydronaphthalene (*trans*-decalin); (row 4) naphthalene and 1,2,3,4-tetrahydronaphthalene (tetralin). Assignment of colours: carbon—green, hydrogen—white, and oxygen—red (in carbonyl, C=O group).

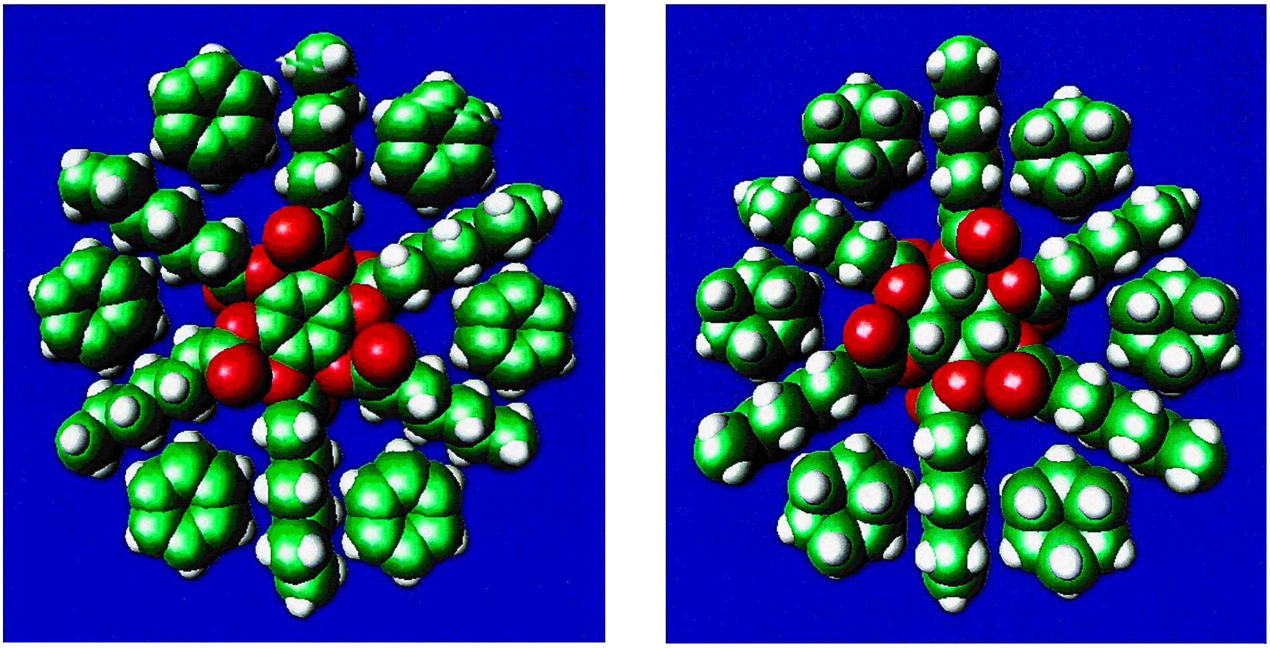


Figure 5. Space-filling models illustrating two arbitrarily chosen examples of disc-like 'supramolecular assemblies' assumed to be possible as such, and each to form a columnar array by stacking on top of each other with the absorbed solvent remaining in the periphery and not intercallated in between the core units; the latter situation would weaken the columnar stability [20]. The two particular discs depicted each consist of star-shaped hexaesters, e.g. the heptanoates **1d** or **2e**, respectively, of the two hexols: hexahydroxybenzene (left) or 1,2,3,4,5,6-hexa(eq)-hydroxycyclohexane, i.e. scyllo-inositol or scyllitol (right), and of six cyclic solvent molecules, benzene (left) or cyclohexane (right), equal in scale. Naturally, the solvent molecules of the binary mixtures under study here—placed in the space in between the relatively stretched alkanoyl chains—certainly rotate and may be different in number. Assignment of colours used: carbon—green, hydrogen—white, and oxygen—red (in carboxylate, $-CO_2-$ groups).

Surprisingly (see table 2), the hexaester **1c** is an exception: it becomes lyomesomorphic not only on addition of benzene [7, 8] but also in mixtures with the two only partly unsaturated solvents of equal ring size, namely cyclohexene and cyclohexanone, or even with cyclohexane. These results mean that in addition to the very early discovery of mesophase induction in the system **1c**/benzene [7, 8], three more cases of such induction based on **1c** have now been found. In this connection it is worth stressing that these three monocyclic six-membered solvents have fewer or even no π-bonds compared with the aromatic solvent benzene or the core unit of series **1**.

The three thermomesomorphic hexaesters **1d–f** [6, 7] not only exhibit the same type of disordered columnar hexagonal phase both in the pure state and in mixtures with benzene [7, 8], but also with five more monocyclic solvents—**1d** also in (the bicyclic) *cis*- or *trans*-decalin—mentioned in table 2 and two of its footnotes. These solvents: cyclo-hexane, -octane and -decane, and both decalin isomers are fully saturated, demonstrating again that aromaticity of a solvent is not required.

The textures these contact preparations developed are the same without doubt. Very interestingly, the optimal effect occurs with cyclohexane(!) which turns the monotropic mesophase of **1f**—characteristic for this hexaester both on heating [6, 7] and in mixtures not only with benzene [7, 8, and table 2], but also, as found here, with five more monocyclic solvents—into an enantiotropic mesophase, thereby constituting a phase stabilization or, in other words, an induction.

Finally, we emphasize that steric/space-filling effects on the part of solvent molecules are also involved here! For instance, neither cyclo-octane, -decane nor both decalin isomers which are all bulkier than cyclohexane (cf. the models shown in figure 4) give rise to lyotropic mesomorphism of mixtures with **1c** (cf. table 2). A second case has been found with the non-appearance of any lyomesophase using the bicyclic aromatic solvents naphthalene or 1,2,3,4-tetrahydronaphthalene (tetralin), both very much larger than the positively-acting benzene.

3.2.2. *Binary mixtures based on the cyclohexane derivatives 2a–j*

As pentane is the shortest linear alkane in our lyotropy study of scyllo-inositol hexaesters **2d–j**, for which results are compiled in table 1, we started our investigations in this part with cyclopentane, for comparative reasons.

At a first glance at tables 2 and 3, one notices that the three monocyclic aromatic/unsaturated solvents benzene, cyclohexene, and cyclohexanone give similar results. Their mixtures with single members of both series **1** and **2**, each possessing either an aromatic or a saturated cyclic C_6-core (see figure 1), uniformly exhibit the hexagonal M phase. Exceptionally, so also does tetralin with **2g** (see table 3, footnote e). However, apart from the first two homologues of both series of hexaesters (**1a, b** and **2a, b**), the number of members of the 'aromatic' series **1**, all forming this one type of lyotropic phase, is almost half compared with that of the 'saturated' series **2**. Moreover, differences in the M phase stability also show the advantage of the cyclohexane derivatives **2**. Further, it is important to note from table 2 that the saturated monocyclic hydrocarbons produce the same results as the (three) unsaturated solvents in mixtures with members of series **1**.

In compiling observations on series **2** for table 3, however, a significant difference between these two groups of solvents comes to light, i.e. the saturated solvents give rise to two mesophases. In other words, saturated cyclic or linear hydrocarbons show a similar preference in the formation of lyotropic mesophases with the cyclohexane derivatives **2** (compare tables 1 and 3). Moreover, a comparison of cyclopentane and cyclohexane with the respective linear alkanes and their effect on series **2** members, clearly reveals that these cycloalkanes have the power to extend the lyomesomorphism beyond the borders set by the linear hydrocarbons, independent of the length of the side groups in **2**. In this way, **2c** becomes lyomesomorphic both in cyclo-pentane and -hexane as also do **2i** and **2j**, exhibiting now the hexagonal type of columnar phase. These extensions of lyomesomorphism are new examples of induction of which five are presented in the frames/windows; the description of a sixth case of mesophase stabilization/induction is included in footnote e of table 3: **2g** with the bulky *cis*-decalin yields the same pair of mesophases as with cyclodecane, the nematic phase being monotropic. However, using the (flat) *trans*-isomer, the N phase becomes enantiotropic, as achieved with octane (table 1) or cyclo-octane (table 3, footnote).

This stabilization of the nematic phase of **2g** due to the change from *cis*- to *trans*-decalin is clearly a case of induction and simultaneously an example of a stereochemical effect on mesophase formation from the solvent; cf. two more cases discussed at the end of the previous section.

3.3. *Peculiarities of microsegregation as a key towards understanding the striking difference in mesomorphic behaviour between members of series 1 and 2*

For about two decades it has been evident [23–29] that microsegregation, creating interfaces between chemically different (e.g. polar or non-polar) molecular regions, is one of the main driving forces for the development of liquid crystalline properties of disc-like [26] materials. In view of this background we feel encouraged to explain in a similar way our findings from this comparative lyotropy study of the two hexaester series **1** and **2** in the apolar solvents used.

The six hexaesters **1d–f** and **2a–c**, each forming a disordered type of columnar hexagonal phase on heating, are non-lyomesomorphic in binary mixtures with linear alkanes. The polar and apolar parts of their columns are only slightly segregated and their weak intracolumnar interactions can therefore be affected easily and disturbed

Table 3. Lyomesomorphism[a] of the scyllo-inositol hexaesters **2a–j**[b] in some cyclic (mainly saturated) hydrocarbons.

Scyllitol hexaesters[b]	Solvents Benzene[c]	Cyclohexene[d]	Cyclohexane	Cyclopentane	Cyclodecane[e]
2a,b	—	—	—	—	—
2c	[f] $\boxed{\text{M}}$	—	$\boxed{\text{N}}$	$\boxed{\text{N, M}}$	—
2d	M	M	N, M	N, M	N, M
2e	M	M	N, M	N, M	N, M
2f	M	M	N, M	N, M	N, M
2g	M	M	(N), M	(N), M	(N), M
2h	M	M	M	M	M
2i	M	M	M	$\boxed{\text{M}}$	M
2j	M	M	$\boxed{\text{M}}$	—	M

[a] Contact preparations. Details on phase structures—see footnote [a] of table 1, [() on shaded background = monotropic].

[b] The aliphatic chains of the alkanoate functions of the hexaesters **2a–j** are given in table 1.

[c] No mesophase formation with the bicyclic arene naphthalene! In the contact zone, immediate crystallization takes place.

[d] The same results were obtained in cyclohexanone!

[e] The three homologues **2a–c** also did not exhibit any lyotropic phase in mixtures with either *cis*- or *trans*-decahydronaphthalene (decalin) or 1,2,3,4-tetrahydronaphthalene (tetralin), cf. models of these three solvents shown in figure 4. However, the same results, but with an enantiotropic N phase for **2g**, were obtained using cyclooctane or *trans*-decalin as solvents. On the other hand, the *cis*-isomer of the fully saturated naphthalene in mixtures with **2g** gave the same result as with cyclodecane: each formed an (N) and M phase. When tetralin was used instead, only an M phase for **2d–j** was exhibited.

[f] The M and N phases in windows are *induced* phases compared with the situations for mixtures with linear alkanes, see table 1.

completely by addition of solvent [20]. Moreover, **2a–c** possess alkyl chains that are too short, preventing the inclusion of linear solvent molecules which could act by filling space between them and stimulate the formation of mesophases made up by columns as in the case of N_{Col} and Col_h phases and the phases from **2d** upward.

Whereas the hexaesters **1c–f** in mixtures with cyclic hydrocarbons give rise to only one (a 2-dimensionally ordered) lyomesophase, the saturated esters (**2c–j**) may even form two lyomesophases under identical conditions, see tables 2 and 3. This difference in behaviour between series **1** and **2** can only be caused by their different cores which are very different not only in space filling [19], but also in the area and density/number of mobile (π and lone pair) electrons, the direction of micropolarization, and, eventually, in microsegregation.

Electronic effects between the oxycarbonyl functions and the aromatic carbocycle in the cases of **1c–f** result in a strongly enlarged molecular core ($\varnothing \sim 7$ Å, shown by Dreiding models made up of a benzene ring and O–C=O– groups *para*-attached to it) stabilized by mesomerism, giving a wide, flat disc-like 'cloud' of π and lone pair electrons. The micropolarization of this system has its main direction within the molecular plane (see figures 5 and 6), i.e. *perpendicular* to the axis of a columnar array of these molecules stacked on top of each other in a disordered manner.

The microsegregation within these stacks gives rise to one massive spinal, columnar, polar block surrounded by a wide cylindrical interface (see figure 6, sketch I) with the hydrophobic alkyl chains on the outer (peripheral) side.

In contrast, the six (polar) oxycarbonyl functions (length of each ~ 2.5 Å, taken from Dreiding models) located at the cyclohexane ring of series **2**, and in this situation electronically isolated, show mesomerism only within each single O–C=O–unit. As space filling models display, their micropolarization is oriented somewhat *parallel* to the column axis, but alternatingly in two opposite directions due to the fact that the carbonyl parts of neighbouring oxycarbonyl functions of each hexaester molecule point obliquely up- or down-ward (figure 5).

These six polar, more strand-shaped 'blocks' formed spontaneously in the stacking process for members of series **2** are rope-like, surrounding the columnar centre, made up here by stacked (apolar) cyclohexane units, and separating from it the alkyl chains (in these cases the second apolar area) on their outer, peripheral side. This unique supramolecular assembly of disc-like hexaesters of type **2** is of high stability, certainly stemming from its inherently polar and helical type of 'corset' in between the two inner and outer apolar columnar regions. Furthermore, on the basis of the two above sets of molecular considerations, simple calculations reveal that the total of the apolar–polar interfaces existing in the columns formed by members of series **2** are more than double in size compared with the single, large interface for members of series **1** (figure 6).

Thus, in comparison with columns made up by the benzene hexaesters of type **1**, the six polar 'blocks' in columns of **2** are smaller (strand-like), but their number as well as the difference in micropolarization between

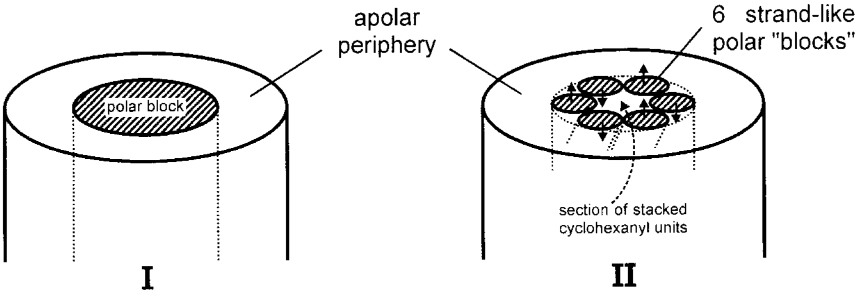
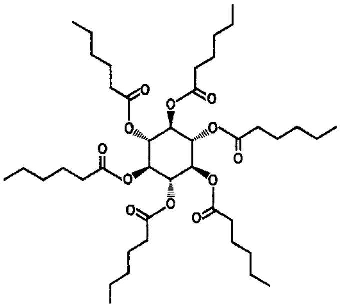


Figure 6. Sketches I and II of cross-sections of columns composed of vertically stacked molecules of the hexaester series **1** or **2**, respectively, revealing our conception of the construction of their central regions. Their architectural characteristics depicted here are seen to be responsible for the difference in microsegregation and consequently for the divergent mesogenic behaviour between these two families of disc-like compounds. Sketch I shows a spinal polar block formed by the electron rich aromatic centre and the six oxycarbonyl groups in each molecule of the homologues **1** surrounded by an apolar periphery consisting of alkyl chains. Sketch II represents an equivalent view of a somewhat more complicated column made up by the scyllitol hexaesters **2** giving rise to three columnar sections instead of only two in the case of sketch I. The tube-like polar region present in II, arising from six more or less distinct strand-like 'blocks' inside the columns, and constituted by the electronically isolated oxycarbonyl groups attached here to cyclohexanyl units, segregates two apolar molecular regions from each other: the cyclohexane part in the molecular centre and the area of alkyl chains in the periphery. The oxycarbonyl groups of all molecules point alternatingly up- or down-ward, indicated here by arrows at the six small ellipses of sketch II. Due to the tilt of these functions with respect to the average molecular plane, the polar strand-like 'blocks' of sketch II are arranged in a rope-like manner so forming an intracolumnar scaffolding, a kind of inner 'corset'.



2d

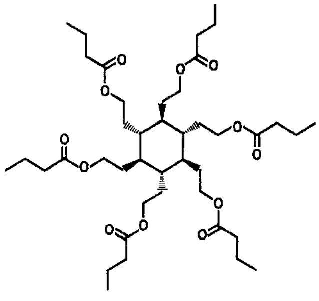


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Figure 7. Comparison of two cyclohexane centred, disc-like, and radially-symmetric hexaesters isomeric in their molecular structures: the mesomorphic scyllo-inositol hexahexanoate (**2d**), see [9–13] as well as tables 1 and 3 of this paper; and the non-mesomorphic hexaester [26] (1α,2β,3α,4β,5α,6β)-hexa(2-butanoyloxyethyl)cyclohexane (**3**).

their polar and apolar sections increases, i.e. the number and total area of interfaces within their columns is enhanced. All these factors intensify the process of microsegregation and make the columnar arrangement of members of series **2** very stable.

In order further to support our findings and the discussion of them, we feel it interesting to compare the two constitutionally isomeric, aliphatic, and equally disk-like hexaesters **2d** and **3** [26] shown in figure 7. Whereas **2d** is mesomorphic as quoted [9–13] and reported in tables 1 and 3 of this paper, the hexaester **3** is not [26], obviously due to the fact that its six oxycarbonyl functions are each two methylene groups removed from the cyclohexane ring forming the molecular centre. Apparently, the oxycarbonyl units of **3** are now too 'dilute', i.e. are too far away from each other and have therefore become too flexible, discouraging the formation of a narrow, stable polar interface between the two (unbalanced) apolar regions of that isomeric disc-like hexaester. Note that substitution of the six butanoyloxy parts of **3** by 4-(heptyloxy)benzoyloxy groups, each additionally equipped with a large, unsaturated (phenylene) segment as compared with the small oxycarbonyl groups present in **3**, does not induce mesomorphic properties in this type of hexaester [26].

Our foregoing explanations have the following consequences:

(a) the short chained homologues **2a–c** are thermomesomorphic, but the analogues of series **1** are not;
(b) thermotropically, the homologues **2e–g** ($n = 6$–8) exhibit the $\mathrm{Col_h}$ in an ordered fashion, whereas similar homologues of series **1** ($n = 6$–8) display this type of phase only in a disordered manner;

(c) due to strong intracolumnar interactions, lyopolymorphism occurs with several members of series **2** in mixtures with saturated cyclic hydrocarbons, while under the same conditions members of series **1** develop only one (a 2-dimensionally ordered) lyomesophase;

(d) the weakly segregated esters **1d–f** and **2a–c** (each displaying a disordered type of Col_h phase in their pure states) are non-lyomesomorphic in mixtures with linear alkanes, whereas the higher homologues of series **2** (each with an ordered Col_h phase) do show lyomesomorphism.

On increasing the solvent concentration in mixtures of scyllitol hexaesters **2** with linear or saturated cyclic hydrocarbons (tables 1 and 3) the intercolumnar distance is enhanced. Since the intracolumnar interaction remains strong, the solvent molecules insert into the hydrophobic (apolar) periphery, i.e. are between the columns, but are *not* intercalated between the stacked hexaester molecules. Moreover, in the cases of **2d–h** the intercolumnar interaction may even vanish with formation of the N_{Col} (N chromonic-like) phase.

However, under the above conditions, binary mixtures from phenylene centred hexaesters **1** and each of the cyclic hydrocarbons of table 2 give only the columnar hexagonal chromonic M phase or the isotropic phase.

With regard to five members (**1c, f** and **2c, i, j**) of our two series, it is important to stress that cyclic hydrocarbons, e.g. benzene, cyclohexene, or cyclohexane, can induce lyomesomorphic behaviour, even in case of the non-thermomesomorphic hexaester **1c**!

Obviously, good miscibility of the paraffinic moiety of the respective solute with cyclic hydrocarbons, suitable in size and therefore easily able to fill space in the columnar periphery, advantageously increases the difference between the polar and apolar parts of the hexaester molecules and, thus, improves the mesomorphic properties of the system as a whole. Nevertheless, in mixtures with unsaturated cyclic hydrocarbons, the homologues of series **2** are *mono*lyomesomorphic. One of the reasons for this could lie in a special electronic interaction between the ester functions and unsaturated solvent molecules, transforming the six more strand-like polar 'blocks' into a unified cylindrical, tube-like polar block remaining between the two intracolumnar (central and peripheral) aliphatic sections. In conjunction with this, the direction of the micropolarization could also be perturbed in its uniformity, resulting in a weakening of the very important microsegregation.

In general, for members of the hexaester series **2** it is noted that the difference in contrast in the intramolecular polarity causes the difference in the lyotropic mesomorphism in linear alkanes. Extending our previous comments on the phase behaviour of **2a–c**, it is consistent to state that the difference in phase behaviour of the homologues **2d–h**, as well as of **2i** and **2j** in their mixtures with linear alkanes (table 1) is a consequence of the competition between the inter- and intra-columnar forces. This means that the longer the (ester) chains are, the more stable the 2-dimensional order of the mesophase becomes.

Up to a certain concentration, linear apolar saturated solvents (dependent on their molecular length) do not disturb the intercolumnar cohesive strength apart from the possibility that some swelling may occur. However, above this concentration two different routes of breakdown of order can take place: (1) the whole ordered arrangement is simultaneously and completely destroyed in both dimensions, transforming the distinctive M phase directly down into an isotropic liquid (cf. the lower part of **2d–h**, as well as **2i** and **2j** in table 1) which can no longer develop a nematic phase; or (2) the mesophase changes gradually but in a stepwise manner by losing the intercolumnar association giving rise—parallel to the already existing M phase—to the formation of single columns which form a nematic phase (most probably of N_{Col} type) which is eventually destroyed due to intercalation of solvent molecules, subsequently disappearing, because of strong dilution with the respective alkane, and becoming an isotropic liquid.

4. Conclusion

This comparative investigation has dealt with the lyotropic mesomorphism of 17 homologous members of two disc- or star-shaped amphotropic mesogenic series **1** and **2**; these are equally simple in their molecular structure, containing a flat C_6-carbocyclic core, aromatic in series **1** or fully saturated in series **2**. The exhibition of differently ordered columnar hexagonal phases on heating was known [6, 7, 9–13] for members of both series. The large number of linear or cyclic organic solvents, apart from one (cyclohexanone), utilized here are non-polar hydrocarbons among which were also a few unsaturated cyclic hydrocarbons.

The results are compiled in three tables demonstrating that the cyclohexane centred derivatives (series **2**) develop a lyomesomorphism in mixtures with saturated *linear* hydrocarbons, richer than shown by representatives of both hexaesters series **1** and **2** in mixtures with analogous *un*saturated *cyclic* solvents. Whereas compounds of series **2** characteristically display two lyomesophases (a nematic and a hexagonal chromonic phase), members of the aromatic series **1** form only the latter type of lyomesophase.

For the first time since the introduction of the two series of mesogens in 1977 [6] and 1984 [9], respectively, the radical differences in stability of their thermotropic as well as their lyotropic states has now been explained in terms of peculiarities due to microsegregation in a similar way to one earlier example [26] and later cases [23–25, 27–29] in the literature. This background was the key for the understanding of manipulation/induction phenomena with respect to the mesomorphic behaviour observed for members of both hexaester series. In contact preparations, many examples of induction of the nematic columnar phase have been observed within the contact zone between solvent and the majority of members of series **2**.

For the first time, we have observed the *induction/stabilization* of mesomorphism in mixtures of disc-like materials with saturated *cyclic* organic solvents/hydrocarbons.

Interestingly, stereochemical effects on the part of some solvents have also been found relevant to the formation of the mesophases—for example, those originating from differences in molecular size and configuration, as in *cis*- and *trans*-decahydronaphthalene used as solvents.

A last but not least important influence on the development of mesophases was found to be the degree of saturation of the apolar organic solvents used in our comparative lyotropy study.

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