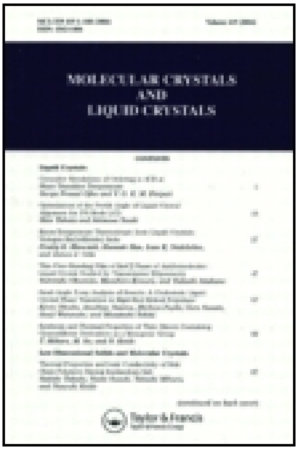

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Induction/Variation of Mesomorphic Properties of Disc-Like Materials in Binary Systems with Solvents

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INDUCTION/VARIATION OF MESOMORPHIC PROPERTIES OF DISC-LIKE MATERIALS IN BINARY SYSTEMS WITH SOLVENTS

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This work summarises for the first time the authors' results in the field of lyotropic mesomorphism dealing with the study of disc-like compounds (benzene, scyllitol, benzenehexamine, triphenylene, phthalocyanine, triazacyclononane derivatives and dendrimers) in organic solvents. The authors answer a number of key-questions, connected with induction/variation of lyotropic liquid crystal properties of above mentioned mesomorphic and non-mesomorphic materials. A comprehensive survey of the data is the basis for prediction of new lyotropic compositions with induction/variation of mesomorphic properties for disc- and lath-like hydrophobic compounds.

Keywords: discotics; lyotropic mesomorphism; organic solvents; induction/variation of mesomorphic properties; microsegregation

INTRODUCTION

For a long time classical amphiphiles, so-called "conventional lyomesogens" (rod-like materials, which have both polar and apolar groups in a molecule) have been the main compounds giving lyotropic liquid crystals. Lyotropic mesomorphism of traditional amphiphilic mesogens (salts of fatty acids, lipids, alkylsulfates of alkaline metals) is a considerable topic in the field

We are thankful to all the colleagues who contributed to our investigations and whose names are mentioned in the list of references. We would like to express our special gratitude to Prof. K. Praefcke, Prof. P. Espinet, Prof. H. D. Koswig, Dr. G. Lattermann, the long-term co-operation and fruitful discussions with whom gave the opportunity to realise our researches. Financial support for this work by the Russian Foundation for Basic Research (Grant No 9603-00091 G), Moscow, Russia, in conjunction with the projects Pr 116/18 -1 to 3 of the Deutsche Forschungsgemeinschaft, Bonn, Germany, is gratefully acknowledged as well as support by the INTAS Program (Grant No 99-00365), Brussels, Belgium, and by the Ministry of Education of Spain.

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of liquid crystal state research. Such questions as structure-property relationship, types of supramolecular self-organisation, etc. for amphiphilic molecules were developed in detail [1,2].

But besides the type of self-aggregation via micelle formation, there is another type of supramolecular lyotropic packing—formation of columns similar to stack of coins by the molecules with lath- or disc-like molecular shape. The first attempt in this field was connected with the investigation of association or pseudo-polymerisation processes of dyes (due to π-electron interactions directed perpendicular to the plane of such molecules) [3]. But at that moment the connection between this type of association and liquid crystal state had not been reported yet.

Later on it was stated, that increasing of the dye concentration leads to the formation of supramolecular columnar aggregates, which can be organised in N- or M-chromonic lyomesophases. The first compound with such type of self-aggregation known in the literature is disodium cromoglycate [4], that gives the name "chromonics" for this new lyomesogens and the name "chromonic phases" for this new type of lyotropic mesophases: N and M chromonic ones. Then chromonic lyomesophases were found for lath-shaped dyes, for example, Sirius Supra Brown RLL or Red 151 [5]. In N-phase columns have orientational order, in more concentrated M-phase columns are arranged in two-dimensional ordered hexagonal lattice. Normally, under polarising light N phase shows Schlieren-texture, while M-phase is characterised by grainy or herring-bone textures [6].

During the period since 1977 (when first disc-like mesogens were discovered by S. Chandrasekhar [7]) till the present time an enormous number of thermotropic mesogens, mostly hydrophobic, with disc-like shape of molecules have been synthesized.

15 years ago when we began our research, there were known only very few literature data concerning lyotropic mesomorphism of disc-like compounds:

- S. Chandrasekhar et al. [7] discovered induction of lyomesomorphism in mixtures of hexa(alkanoyloxy)benzene derivative with benzene or undecane;
- S. Gaspard et al. [8] reported about birefringent textures displayed by the aqueous systems of tetra(carboxy)phthalocyanine copper complex with additives of Li^+ or Na^+;
- N. Boden et al. [9] studied lyotropic mesomorphism of aqueous systems of triphenylene substituted with oligo(ethyleneoxy)chains;
- N. B. McKeown and J. Painter [10] found lyotropic mesomorphism for phthalocyanine ligand substituted with four oligo(ethyleneoxy)chains in ethanol;

- K. Praefcke et al. [11] used some aliphatic or cyclic hydrocarbons as solvents for lyotropic study of benzenehexamides.

In this paper we draw your attention to the data of our systematic investigation on induction/variation of mesomorphic properties of non-conventional materials with the help of suitable solvents using several series of different disc-like compounds **1**–**20** (molecular formulas, see below). The studied compounds are differentiated by the ***type of central core*** (small or large, hard or flexible, distinctly determined or not clearly expressed, containing metal atom(s) or without them) and in the ***length*** or ***number of lateral substituents***. We have studied them in mixtures with various ***organic solvents*** in order to establish the influence of the type of solvent on mesomorphic properties of disc-like materials.

MATERIALS AND METHODS

The studied compounds were synthesized, characterized and in some cases investigated from thermomesomorphism point of view in different scientific groups. But their lyotropic properties had mostly not been investigated.

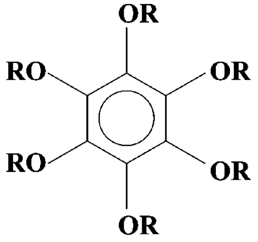
Hexaesters of hexahydroxybenzene **1** were either resynthesized by Prof. K. Praefcke's group (Germany) or were gratefully received from research groups headed by Prof. S. Chandrasekhar (India) or by Prof. G. Heppke (Germany). Various scyllitol hexaesters **2**–**5** and benzenehexamine derivatives **6** were obtained from Prof. K. Praefcke's group. Metal organyls **14**–**18** were synthesized by Prof. P. Espinet's group (Spain) and Prof. K. Praefcke's group. Triphenylene derivatives **7**–**9** were synthesized by Dr. C. H. Erdelen (Germany). Octa(octyloxy)phthalocyanine **10a** and its metal complexes **10b**–**c** were produced by Aldrich Chemie company. Other octa- and tetra-substituted phthalocyanine derivatives **10d**–**e**, **11**–**13** were synthesized in Ivanovo State University or in collaboration with our colleagues from Ivanovo State University of Chemistry and Technology (Russia). 1,4,7-triazacyclononane derivatives **19** as well as all dendrimers **20** were obtained from the group of Dr. G. Lattermann (Bayreuth University, Germany).

All solvents (linear alkanes: from pentane to heptadecane; cyclic hydrocarbons: cyclohexane, cyclohexene, cyclohexanone, benzene; bicyclic hydrocarbons: decalin, tetralin, naphthalene; chloroform, DMF, DMSO, THF etc.) were obtained from E. Merck Ltd., Darmstadt, Germany or Aldrich Chemie company and employed without further purification.

The lyotropic mesomorphism of studied mixtures was investigated by the methods of polarising microscopy (contact preparations and construction of phase diagrams), differential scanning calorimetry (DSC), X-ray analysis, UV VIS-spectroscopy and others.

Thermotropic Mesomorphism of Compounds Under Study and Some of their Lyotropic Properties Known up to the Moment of our Investigations

Hexaesters of Hexa(hydroxy)benzene (series 1)



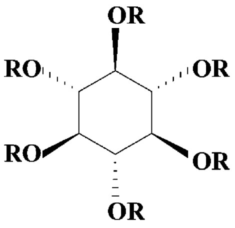
1

1: R= COC$_n$H$_{2n+1}$

1a: n=3;
1b: n=4;
1c: n=5;
1d: n=6
1e: n=7
1f: n=8
1g: n=9

Historically, three members of series **1** (**1d-f**) were the first disc-shaped thermomesogens displaying columnar hexagonal phase of disordered type (Col$_{hd}$), which were discovered in 1977 by S. Chandrasekhar [7]. Non-thermomesomorphic **1c** was also described as giving the first example of lyotropic mesomorphism for a disc-like mesogen [7]: a columnar hexagonal phase is *induced* in mixtures with benzene or undecane.

Hexaesters of Hexa(hydroxy)cyclohexane (scyllitol) (series 2) and Relative Scyllitol Hexaesters with Cyclic Fragments in their Lateral Substituents (3–5)

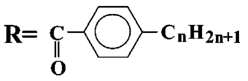


2-5

2: R= COC$_n$H$_{2n+1}$

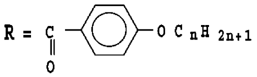
2a: n=2;
2b: n=3;
2c: n=4;
2d: n=5;
2e: n=6;
1f: n=7
1g: n=8
2h: n=9
2i: n=10
2j: n=11

3:



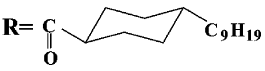
3a: n=7
3b: n=8
3c: n=9

4:



4a: n=8
4b: n=10

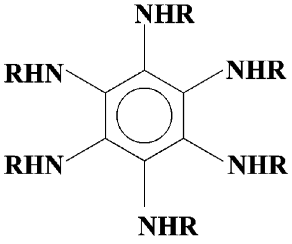
5:



The members of homologous series **2** were synthesized in 1984 [12] and found to be thermotropic liquid crystalline materials. These hexaesters of naturally occurring *scyllo*-inositol (scyllitol) show very stable and wide range mesophases on heating: disordered ($\mathrm{Col_{hd}}$) and ordered ($\mathrm{Col_{ho}}$) columnar hexagonal phases were observed, as well as a cubic phase (Cub) in one case (**2c**) [13]. Although first indications of the lyotropic mesomorphism of the scyllitol ester series **2** in apolar organic solvents have been known to us for some time. However a detailed study including the comparison of the lyotropic mesomorphism of members of series **2** with those of **1** has just been finished [14].

Moreover in this paper we consider some scyllitol hexaesters **3**–**5**,pospossessing *cyclic* fragments in lateral substituents, from lyotropic mesomorphism point of view.

Hexamides of Benzenehexamine (series 6)



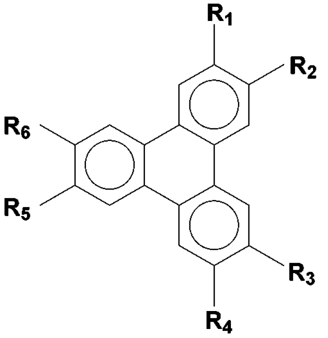
6

6a: R=-CO-CH_2-CH(CH_3)$_3$
6b: R=-CO-C_6H_{13}
6c: R=-CO-C_8H_{17}
6d: R=-CO-$C_{11}H_{23}$
6e: R=-CO-$C_{15}H_{31}$

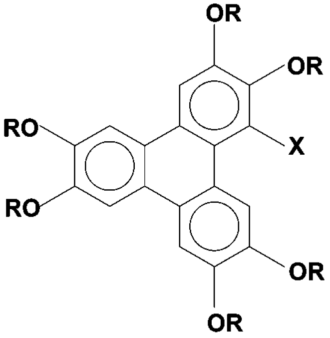
These compounds have been known for more than 60 years [15]. But their mesomorphic properties have been found quite recently [11]. Due to steric reasons, i.e., because of the presence of six *tert.*-butyl groups, homologue **6a** exhibits no mesomorphic behaviour. Previously it has already been shown, that **6b** forms a gel-phase with decalin [11]. At certain concentrations and temperatures the homologue **6e** with longest substituents (R = -CO-$C_{15}H_{31}$) forms two lyomesophases – a nematic phase and a hexagonal one – in binary mixtures with chloroform, decalin, isooctane, decane, dodecane, toluene or cyclohexane [11].

Triphenylene Derivatives (series 7–9)

Triphenylene derivatives are other disc-like compounds whose mesomorphic properties were thoroughly investigated [16]. In this article we concentrate our attention on triphenylene derivatives **7**–**9** (the formulae and thermotropic mesomorphism data see in Tables 7 and 8). The aim of our work was to study the influence of triphenylene structure peculiarities: introduction in triphenylene ring of polar groups (NO_2 or NH_2), asymmetric substitution by lateral chains or dimerisation of triphenylene ring, on mesomorphic properties.



7-8



9

The first three lower homologues of 2,3,6,7,10,11-hexa(alkoxy)-triphenylene derivatives **7a**–**c** (n = 1–3) are non-mesomorphic on heating, while higher analogues **7d**–**k** (n = 4–11) form thermotropic columnar hexagonal ordered (Col_{ho}) mesophase [16], the members **7l** and **7m** of this series with n = 12 or 14, correspondingly display thermotropic *poly*-mesomorphism [17].

None of the studied asymmetrically substituted triphenylene derivatives of series **8** possesses thermotropic mesomorphism, except compound **8d**, which forms columnar hexagonal thermomesophase with flower-like texture.

The other types of triphenylenes studied by us were nitro- (**9a**) and amino- (**9b**) as well as azomethine spatially-deformed dimer (**9c**) of hexa-(alkoxy)triphenylene derivatives. The first two homologues of series **9a** with the shortest lateral chains (n = 1 or 2) do not possess mesomorphic properties, while the next representatives of this type with n = 3-12 display thermotropic columnar mesophase. It is interesting to note that thermostability of mesophase and its temperature range for nitro-triphenylenes **9a** are higher than for the analogue ethers of series **7**. Such influence can be explained by the action of acceptor (NO_2-group) introduced in the triphenylene core, which leads to the displacement of electronic density from triphenylene ring and therefore decreases π-π-interactions between neighbouring triphenylene cores. As a consequence the temperature range of columnar phase is extended. Moreover, it seems that sterical factor also plays an important role, because bulky NO_2-group loosens the supramolecular structure.

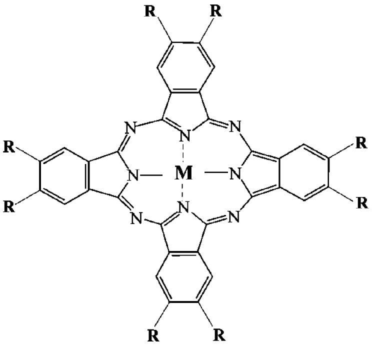
Both of amino-substituted triphenylenes **9b** (n = 7, 10) form thermotropic columnar mesophase. In contrast to NO_2-acceptor function, the donor NH_2-group displaces electronic density to triphenylene ring and increases π-π-interactions between triphenylene cores and therefore leads to decreasing of temperature range of columnar phase and increasing of clearing points.

Based on the interval of mesophase existence the investigated triphenylenes can be arranged in the following sequence: $-NH_2$ (**9b**) < ether (**7**) < NO_2 (**9a**).

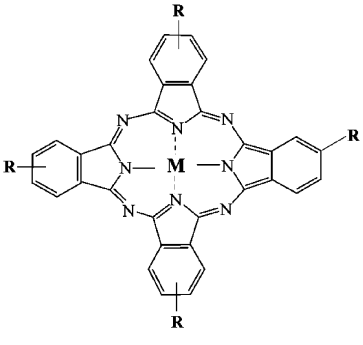
Dimerisation of triphenylene rings (compound **9c**) does not result in significant reorganisation of supramolecular structure and leads only to broadening of the temperature range of mesophase (from 60°C – for amino-triphenylene **9b** within = 7 to 97°C – for **9c**).

Phthalocyanine Derivatives (10–13) The first information about the thermotropic phase behaviour of phthalocyanine (Pc) derivatives and related compounds was published in 1982 [18]. Further researches stated that the number or length of the side chains as well as metal atom in the middle of macrocyclic ring determines thermotropic mesomorphism of these compounds [19].

Nevertheless, lyotropic properties of phthalocyanine derivatives are less studied than thermotropic ones. Although, some data about lyotropic mesomorphism have been already known at the moment when our work began. For example, it had been known about lyotropic properties displayed by phthalocyanine (Pc) substituted with four carboxylate groups. However, at that time the structures of this lyomesophase was not investigated and in the ternary systems with sulfonate Pc derivatives the lyotropic phase behaviour was not found [8].



10-11



12-13

Moreover, for hydrophobic phthalocyanine derivatives it was commonly accepted that they possessed columnar mesomorphism if their molecules contained six to eight lateral substituents [20]. Nevertheless, several compounds of this class with only four substituents and exhibiting mesomorphism have been found later [21] and only two of them are amphotropic [10], i.e., possess both thermo- and lyomesomorphism.

Several years ago we had already summarised the data of our research on ***hydrophilic*** Pc derivatives in ***aqueous*** solutions [19]. In this article we present the results of our investigations on lyotropy of ***hydrophobic octa***- and *tetra*-substituted phthalocyanine derivatives (**10**–**13**) with ***organic*** solvents.

The thermotropic mesomorphism of 2,3,9,10,16,17,23,24-octa(alkoxy)-substituted phthalocyanines and their metal complexes **10** was known before our work [22]. The compounds of this series with octyloxy-lateral chains **10a**–**c** display thermotropic columnar hexagonal phase of ordered type (Col_{ho}) [22–23]. X-ray investigation of the mesogenic structure of dodecyloxy-substituted complexes **10d** and **10e** has showed that they form thermotropic columnar hexagonal phases (ordered or disordered correspondingly) [24].

Octa-substituted copper (II) phthalocyanines of series **11** possessing four carboxyl and four alkoxycarbonyl substituents also display thermotropic columnar mesophase [25].

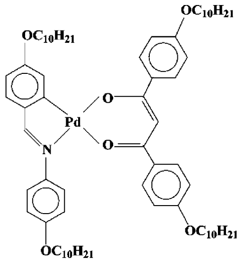
With the aim of searching *tetra*-substituted mesomorphic Pcs, we considered copper (II) complexes of 2,9,16,23-tetra(decylthio)phthalocyanine **12** and tetra-4-(*n*-alkoxycarbonyl)phthalocyanines **13**. In [26] it was supposed that compound **12** has columnar hexagonal type of mesomorphic packing with the disordered arrangement of molecules in columns (Col_{hd}). Some homologues of series **13** (n = 4,6,8,10) were used for the formation of Langmuir-Blodgett films [27], but their mesomorphism had not been studied before. As we established later [28], the lower homologues of this series **13a**–**b** (n = 1,2) are not thermotropic mesogens. Other members **13c**–**k** (n = 3–16) form columnar mesophase of ordered type with rectangular or hexagonal arrangement of columns in two-dimensional lattice (Col_{ro} or Col_{ho}) depending on the length of aliphatic part of lateral substituents [28].

Mono-, Di- and Tetra-metal Organyls (14–18)

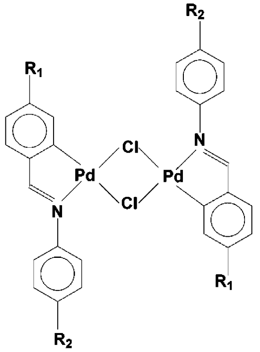
The ***mono***-palladium organyl **14** in thermotropic state displays SmC, SmA and N phases [29]. Nematic phase was observed in a very short temperature range (*ca.* 1°C only).

Di-palladium organyls **15a**–**b** exhibit thermotropic smectic A phase, whereas **15c** possesses both smectic C as well as SmA [29]. The non-planar ***di***-nuclear Pd complex **16** at heating besides SmA shows nematic phase [29].

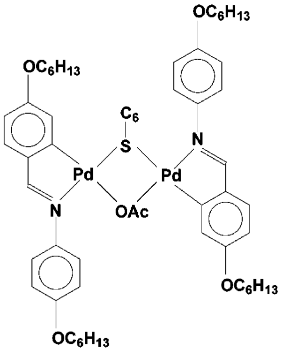
All the ***tetra***-nuclear palladium or platinum organyls of type **17** and **18** display extremely viscous thermotropic mesophase with fan-shaped texture ($Col_{ob,d}$), except the chloro-bridged hexyloxy-palladium compound **17** [30].



14

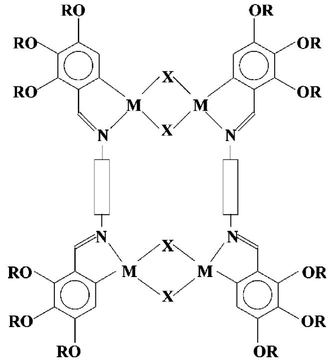


15



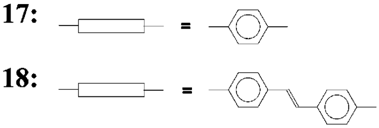
16

15a: $R_1=OC_{10}H_{21}$, $R_2=C_6H_{13}$
15b: $R_1=OC_6H_{13}$, $R_2=C_6H_{13}$
15c: $R_1=OC_{10}H_{21}$,

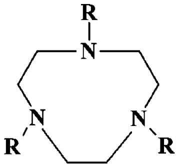


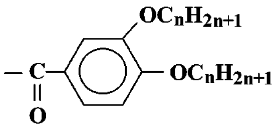
17-18

M= Pd, Pt
X= Cl, Br, I
R= C_6H_{13}, $C_{12}H_{25}$



Triazacyclononane Derivatives (19)



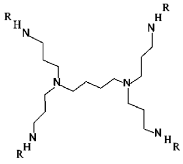


19a: n=1;
19b: n=3;
19c: n=5;
19d: n=6;
19e: n=8;
19f: n=10

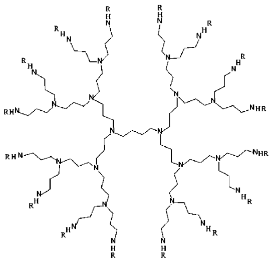
19

1,4,7-triazacyclononane derivatives **19** possessing nine-membered flexible hetero-atomic central fragment were chosen as "transitional" compounds from low-molecular discotic mesogens to dendrimers, in order to investigate the influence of structure of mesogen or solvent molecules on lyotropic mesomorphism. Moreover, compounds of series **19** have the same lateral substituents as dendrimers, which will be described below. The data on thermotropic mesomorphism of compounds **19** were published elsewhere [31]: two first homologues **19a–b** are non-mesogenic; **19d** possesses *monotropic* mesophase; the rest of the members of this homologous series (**19c, e** and **f**) display enantiotropic thermomesophase.

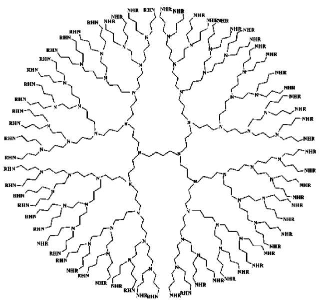
Poly(propylene imine) Dendrimers (20)



1st generation



3rd generation



5th generation

For the thermotropic state of studied poly(propylene imine) dendrimers **20** it was found that such factors as increasing number of generation, branching of lateral substituents or protonation of dendritic matrix increase the stability of mesophases with respect to the crystalline phase [32].

RESULTS AND DISCUSSION

Actually, the detailed data on amphotropic (both thermo- and lyotropic) properties of each of the compounds mentioned above could be a theme of special article and they have already been presented in many publications. Therefore here we shall speak about their peculiarities very briefly. We would rather try to answer some of the key-questions:

1) *Why have hydrophobic solvents been applied for the lyomesophase formation?*

2) *Does the common feature exist in the influence of hydrophobic solvents?*
3) *Is the chemical structure of organic solvents important for the lyomesophase formation?*
4) *Does the intracolumnar interaction of the entitled materials play any role in the lyomesophase formation?*

As for the first question it can be noted that up to now, nearly all investigations of lyotropic mesomorphism were connected with the phase behaviour of rod- or disc-like mesogens in aqueous solutions. Therefore, the lyotropic properties of differently structured hydrophobic compounds, such as **1**–**20** are more or less unexplored. To fill this gap, we have been studying the lyotropic mesomorphism of hydrophobic disc- or lath-like compounds in organic solvents. Besides these two-component systems seem to be bridges between the investigations of the thermotropic and lyotropic mesomorphism, because lateral substituents of discotic compounds can represent to a certain extent as an "internal" solvent [33]. Such kind of investigations can be very important for the development of general notion in the field of liquid crystal state.

To answer the next key-questions let us start with disc-like materials, which possess a *small* central core: benzene **1**, scyllitol **2**–**5** and benzenehexamine **6** derivatives. The detailed description of their lyotropic properties has been already published, therefore we concentrate attention only at the moment on points which are important for answering the above key-questions.

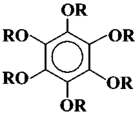
As is well known, linear alkanes are the most common solvents for hydrophobic materials. That is why we have started our systematic investigations with such hydrocarbons.

It has been found that none of the seven hexaesters of series **1** gives rise to a lyomesophase. In the cases of **1d** and **1e** only the decrease of their clearing and melting temperatures has been observed [14]. These findings are in a good agreement with the previous results published more than twenty years ago [7], when undecane was used as a solvent for the first time.

To the best of our knowledge, no other *cyclic* solvent (except benzene [7]) has been applied in order to study binary mixtures of **1** with organic solvents. Therefore, we have used cyclic non-polar hydrocarbons in binary mixtures with hexaesters of series **1** (see Table 1 and its footnotes) [14].

The four benzene derivatives of series **1** (**1a**–**b** and in part **1c** carrying short alkanoyl groups as well as **1g** with the longest side chains) are non-mesomorphic in binary mixtures with all of the ten cyclic or bicyclic solvents used in this study. The non-mesomorphic hexaester **1c** becomes

TABLE 1 Lyomesomorphism[a] of the Hexakis(alkanoyl)benzene Derivatives **1a**–**g**[b] in some *Cyclic* (mainly Saturated) Hydrocarbons [14]

	Solvents				
$R = COC_nH_{2n+1}$	Benzene[c]	*Cyclo*-hexene[d]	*Cyclo*-hexane	*Cyclo*-octane	*Cyclo*-decane[e]
1a, b (R = 3–4)	–	–	–	–	–
c (R = 5)	[f] $\boxed{\text{M}}$	$\boxed{\text{M}}$	$\boxed{\text{M}}$	–	–
d (R = 6)	M	M	M	M	M
e (R = 7)	M	M	M	M	M
f (R = 8)	M	M	$\boxed{\text{M}}$	M	M
g (R = 9)	–	–	–	–	–

[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); the three latter materials each exhibit a disordered Col_h phase, cf. their transition data.

[c] No mesophase formation arose with the bicyclic arenes naphtalene or tetralin.

[d] The same results were obtained with cyclohexanone.

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

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

lyomesomorphic not only on addition of benzene [7] but also in mixtures with the two partly unsaturated solvents (cyclohexene or cyclohexanone) and with cyclohexane [14].

The results on lyotropic mesomorphism of disc-like (saturated) scyllitol hexaesters **2** in mixtures with various *linear* alkanes are compiled in Table 2. They clearly demonstrate the dependence of the lyotropic mesomorphism on: i) type of columnar arrangement in thermotropic mesophase (disordered or ordered), ii) the number of carbon atoms both of the alkanoyl groups of **2** and the solvent used [14].

As we have already observed for the series **1** the hexagonal type of *disordered* columnar phase exhibited thermotropically by **2a**–**c** did not lead to any lyotropic type of mesophase with linear alkanes from pentane to heptadecane [14].

But the hexaesters **2d**–**h** (see the middle section of Table 2) possessing thermotropic hexagonal *ordered* columnar phase, induced a nematic phase, evidenced by the appearance of a Schlieren texture. It has been shown that the induced N phase is stable when the difference between the chain length of alkyl part of lateral substituent R and length

TABLE 2 Amphotropic Properties[a] of the *Scyllo*-inositol Hexaesters **2a–j** [14]

	Hexaesters 2a–j			$R = \text{-COC}_nH_{2n+1}$				
Linear alkanes	**a,b,c** $n = 2–4$	**d** $n = 5$	**e** $n = 6$	**f** $n = 7$	**g** $n = 8$	**h** $n = 9$	**i** $n = 10$	**j** $n = 11$
Pentane	–	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	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.

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

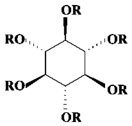
of the saturated linear hydrocarbons used as a solvent is no more than five or six carbon atoms [14].

Similar to series **1**, and in order to obtain more cases of induced lyomesophases for compounds of series **2**, we used the above mentioned *mono- or bicyclic* hydrocarbons as solvents (see Table 3 and its footnotes). Several cases of induction of N or M lyomesophases were found, even for homologue **2c**, which does not show any lyotropy in the mixtures with linear alkanes [14].

In other words, saturated cyclic or linear hydrocarbons show a similar preference in the formation of lyotropic mesophases with derivatives **2**. Moreover, the comparison of cyclopentane and cyclohexane with the respective linear alkanes and their effect on series **2** members clearly reveals that these cycloalkanes can extend the lyomesomorphism in **2**. In this way, compound **2c** becomes lyomesomorphic both in cyclo-pentane and –hexane as **2i** and **2j** also do, exhibiting now the hexagonal type of columnar lyomesophase [14].

One more case of mesophase induction (monotropic N phase) was found in the system of **2g** with the bulky *cis*-decalin. However, using the (flat)

TABLE 3 Lyomesomorphism[a] of the *Scyllo*-inositol Hexaesters **2a**–**j**[b] in some Cyclic (Mainly Saturated) Hydrocarbons [14]

	Solvents				
	Benzene[c]	*Cyclo*-hexene[d]	*Cyclo*-hexane	*Cyclo*-pentane	*Cyclo*-decane[e]
2a,b(n = 2, 3)	–	–	–	–	–
c (n = 4)	[f] $\boxed{\text{M}}$	–	$\boxed{\text{N}}$	$\boxed{\text{N, M}}$	–
d (n = 5)	M	M	N, M	N, M	N, M
e (n = 6)	M	M	N, M	N, M	N, M
f (n = 7)	M	M	N, M	N, M	N, M
g (n = 8)	M	M	(N) M	(N) M	(N) M
h (n = 9)	M	M	M	M	M
i (n = 10)	M	M	M	$\boxed{\text{M}}$	M
j (n = 11)	M	M	$\boxed{\text{M}}$	–	M

[a] Contact preparations. Details on phase structure - see footnote [a] of Table 2, [( ) on shaded background = monotropic]

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

[c] No mesophase formation with the bicyclic arene naphthalene.

[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). However, the same results, but with 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 results as with cyclodecane: each formed (N) and M phase. When tetralin was used instead, only M phase for **2d**–**j** was exhibited.

[f] The M and N phases in windows are *induced* phases compared with the situation for mixtures with linear alkanes, see Table 2.

trans-isomer, the N phase becomes *enantiotropic*, as achieved with octane (Table 2) or cyclooctane (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 stereo-chemical effect on mesophase formation produced by the solvent [14].

In order to continue our investigations on influence of phenyl or cyclohexanyl rings on mesomorphism of disc-like compounds, we studied six other scyllitol hexaesters **3**–**5** each containing the above mentioned *cyclic fragments* in their star-like arranged substituents in binary mixtures with various apolar organic solvents [34] (see Table 4).

Table 4 shows that only two of the compounds were thermomesomorphic. Nevertheless, the induction of two types of lyotropic mesophases (N- or M-chromonic phases) has been observed both for two

TABLE 4 Types of Mesophases of the Scyllitol Hexaesters **3**–**5** in Binary Mixtures with *Linear* Alkanes [34]

	Hexaesters **3**–**5**					
Solvent	**3a** n = 7	**3b** n = 8	**3c** n = 9	**4a** n = 8	**4b** n = 10	**5** 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.

mesomorphic and for three non-mesomorphic homologues. Non-mesogenic **3a** does not possess lyomesogenic properties with any of the alkanes used. The M phase is more viscous and has either herring-bone or non-geometrical texture. The N-phase is more fluid and characterised by a Schlieren or homeotropic texture. Thus, the induction of lyotropic M- and N-phases became possible in binary systems with linear alkanes including even hexaesters not exhibiting thermomesomorphic properties (**3b**, **4a** and **4b**). In all these cases, the temperature of the crystal → mesophase transition was considerably lower than under thermotropic conditions.

Following our previous experience concerning the induction of mesomorphic properties using *cyclic solvents* we managed here also to induce lyotropic mesophases in case of **3a** which does not exhibit mesomorphic properties in any of the formerly applied linear alkanes. As has been expected lyomesophases can be observed in most binary systems of **3a** with cyclic hydrocarbons, see Table 5. Interestingly, in some cases (e.g., using benzene or cyclohexane) lyomesophases do exist even *at room temperature* [34].

As we can see from Table 4, compound **5** possessing *cyclohexane* fragments in its lateral substituents shows the strongest ability to develop lyomesomorphism (if one considers the number of lyotropic mesophases).

TABLE 5 Types of Possible Mesophases of Compound **3a** in Binary Mixtures with *Cyclic* Hydrocarbons [34].

Solvent	**3a**
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 heating.

Probably, the most distinct thermo- and lyotropic mesomorphism of compound **5** in comparison to scyllitol hexaesters of series **2**, **3** or **4** is connected with the presence of wide apolar periphery in supramolecular ensembles and also with a good filling of vacant volume on the columnar periphery caused by bulky cyclohexane fragment included in the lateral substituent. All these factors lead to microsegregation increase based on strengthening of apolar/polar disbalance inside the column [35].

The presence of *benzene* fragments in the substituents should lead to a decrease of mesogenic properties. This proved to be right for the hexaesters **3a**–**c**. One of the homologues (**3c**, $n = 9$) is mesomorphic in a narrower temperature range compared to the analogous homologue **5**. The number of binary mixtures of **3b**–**c** and **4a** with linear alkanes exhibiting lyomesomorphic properties is also limited, see Table 4.

Hence, from the comparative data on lyotropic mesomorphism of scyllitol derivatives **3**–**5** presented in this part of the article with hexaesters of series **2** described above it can be concluded that:

- the *two types* of lyomesophases (nematic and two-dimensional columnar) have been induced in binary mixtures of *non-mesomorphic* hexaesters **3b, 4a**–**b** with linear alkanes;
- in binary systems with linear alkanes the *mesomorphic* compounds **3c** and **5** display a *lyotropic nematic* phase side by side with the two-dimensional columnar one, typical for their thermotropic mesomorphism;
- the following consequence for scyllitol hexaesters with respect to their ability of exhibiting lyomesomorphism in binary mixtures with linear

alkanes has been found:

- lyotropic mesophases were ***induced*** in binary mixtures of the hexaesters **3a** with *cyclic* solvents though they had been observed neither under thermotropic conditions nor in binary mixtures with linear alkanes [34].

Compounds **6** represent another very interesting case of disc-like materials with small central “hard” benzene core studied by us. The detailed study on lyotropic mesomorphism of benzenehexamide derivatives of type **6** with number of organic solvents [36], allowed us to state, that the variety of lyomesomorphic modifications increases so as the length of the alkyl chain of their amido-functions (see Table 6).

The presence of Schlieren or herring-bone textures proves the formation of a nematic and a hexagonal lyotropic phase, respectively, in binary compositions earlier described only for **6e** [11]. As known from the literature, the tendency of compounds with similar structures to form columnar aggregates allows us to suppose that the columnar mesophases discussed above are also of the N- or M-chromonic type. The intermediate phase “X” with fan-like texture appearing at the border between the hexagonal and nematic phases of **6d** demands the further characterisation [36].

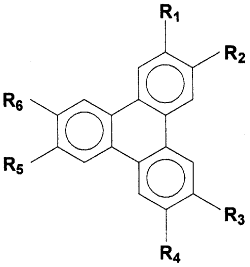
A special interest is attracted by the textures exhibited by **6c** or **6d** possessing some additional defects in binary systems with linear alkanes (Table 6): linear type of spirals or vortex defect. It has been proved that the mesophases with such defects are chiral. Computer simulations of the hexapropionyl hexamide of **6** chosen by us as a model compound for computing, prove that the formation of intramolecular hydrogen bridges

TABLE 6 The Types of Lyomesophases Observed in Contact Preparations of the Four Hexamides **6a**–**d** and a Polar Organic Solvents [36]

Solvent	**6a**	**6b**	**6c**	**6d**
Chloroform	–	–	M	M^*, N^*,X
Hexane	–	M	M	M^*, N^*,X
Nonane	–	M	M, (M^*)	M^*, N^*,X
Decane	–	M	M^*	M^*, N^*,X
Dodecane	–	M	M^*, N^*	M^*, N^*,X

M – hexagonal phase of chromonic type; M^* – hexagonal phase of chromonic type with chiral defects; N^* – nematic phase of chromonic type with chiral defects; X – intermediate phase with yet known supramolecular organisation; ( ) – monotropic character of the mesophase indicated.

TABLE 7 Amphotropic Properties of Triphenylene Ethers **7–8**

Structural formula	Compound	n	Thermotropy	Lyotropy*
	**7a–c:**	n = 1–3	–	–
	7d–k:	n = 4–11	Col_{ho}	+
	7l–m: $R_1 = R_2 = R_3 = R_3 = R_4$ $= R_5 = R_6 = C_nH_{2n+1}$	n = 12–14	Polymorphism	–
	8a: $R_1 = R_4 = R_5 = R_6 = C_5H_{11}$ $R_2 = R_3 = CH_3$		–	–
	8b: $R_1 = R_3 = R_4 = R_6 = C_5H_{11}$ $R_2 = R_5 = CH_3$		–	–
	8c: $R_1 = R_3 = R_4 = R_6 = C_5H_{11}$ $R_2 = R_5 = CH_3$ or $R_1 = R_3 = R_4 = R_5 = C_5H_{11}$ $R_2 = R_6 = CH_3$ (mixture of isomers)		–	–
	8d: $R_1 = R_3 = R_4 = R_6 = C_5H_{11}$ $R_2 = R_5 = OC(O)CH_3$		–	–
	8e: $R_1 = R_2 = R_4 = R_5 = R_6 =$ $= C_5H_{11}$ $R_3 = OCH_2CH(CH_2CH_3)_2$		Col_h	+

*Solvents used for: **7** – linear alkanes, cyclohexane, cyclohexene, benzene, chloroform; **8** – the same, plus tetralin, *trans*-decalin.

leads to a non-planar arrangement of its substituents at the central ring [36]. The formation of chiral lyomesophases in this case is not connected with the presence of a chiral centre in the mesogenic molecule. Presumably, it is the formation of stable conformational isomers due to intramolecular hydrogen bonds and their self-assembly in columns forming the base of a chiral order. In these binary systems both the length of the solvent molecule and the length of lateral substituents in compounds **6** influence the formation of chiral defects as well as the type of lyotropic mesophase (Table 6).

So, giving the answer to the above key-questions, for discotic compounds of series **1**–**6** with a relatively small central fragment it can be noted, that their common feature is expressed in the possibility of mesomorphic state induction in non-mesomorphic homologues due to the formation of binary systems with organic solvents. In this case the chemical structure of organic solvents plays a very important role: the probability of induction increases with the usage of cyclic solvents. Lyomesogenity is also sensitive to the stereoisomery of a solvent. The inducing ability of linear alkanes depends on the correlation of number of carbon atoms in a molecule of a solvent with the number in a lateral substituent of mesogen. For such kind of compounds the intracolumnar interaction influences the lyomesophase appearance: strong molecular interactions inside columnar packing of mesogen, observed in an *ordered* type of mesophase, are more favourable for mesophase formation, than a *disordered* type of packing.

It would be interesting to check these conclusions for compounds with other types of central fragments: triphenylene **7**–**9**, phthalocyanine **10**–**13** or metal organyl **14**–**18** derivatives.

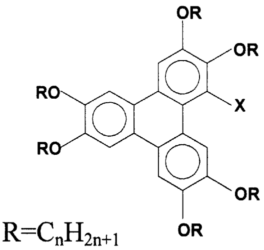
From all the compounds of series **7**–**9** the lyotropic mesomorphism (see Tables 7–8 and their footnotes) in mixtures with different solvents (even with the cyclic ones) was found only for *mesogenic* homologues, in some cases at room temperature [17].

Octa-substituted phthalocyanine (Pc) derivatives of two types: with identical lateral substituents **10** and with alternated carboxyl and alkoxycarbonyl substituents **11** are presented in Table 9.

For all *mesogenic* homologues **10** in the mixtures with linear or cyclic hydrocarbons (Tables 9 and 10) the two types of lyomesophases (N- and M-chromonic) were observed. The N-phase was an *induced* one. Based on the obtained results for compounds **10a**–**c**, it was concluded that the metal atom influenced not only thermo-, but also lyotropic mesomorphism. The following consequence of lyomesophase appearance for Pc derivatives: $Cu^{2+} > (2H^{+}) > Zn^{2+}$, was established [23].

The *non*-mesomorphic compound **11a** does not display any lyomesophase in binary mixtures with nonane, chloroform, or benzene. However, in the mixture **11a** with DMF the lyomesophase of the M-chromonic type

TABLE 8 Amphotropic Properties of Triphenylene Ethers **9**

Structural formula		X	n	Thermotropy	Lyotropy[b]
	**9a**	NO_2	1–2	–	–
			3–12	Col_h	+
	9b	NH_2	7	Col	+[a]
			10	Col	+[a]
	9c	$N=HC\text{-}C_6H_4\text{-}CH=N\text{-}$**9b**	7	Col	+

[a] The lyomesophase exists even at room temperature.

[b] The solvents used see the footnote to Table 7.

was induced. Whereas mesomorphic homologues **11b–c** in the mixtures with chloroform or benzene possess lyotropic polymorphism (N- and M-chromonic phases) (Table 9) [25].

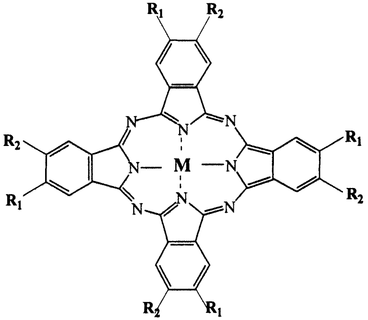
The next step in the investigation of amphotropic properties of phthalocyanine derivatives was connected with the studying of ***tetra***-substituted substances. It was already known that hydrophilic tetra-substituted phthalocyanines could show chromonic mesophases in aqueous solutions [8, 19]. Those lateral substituents were quite short, but nevertheless they displayed lyomesomorphism. We have already published the data concerning this subject [19]. In this paper we shall pay attention to hydrophobic copper (II) complexes of tetra(decylthio)-phthalocyanine **12** and series of tetra(alkoxycarbonyl)phthalocyanines **13** (Table 11).

The study of lyotropic properties of mesogenic tetra(decylthio)-substituted Pc complex **12** with linear alkanes, chloroform, benzene, cyclohexane or CCl_4 showed, that this compound could display lyotropic polymesomorphism: N- or M-chromonic phases (Table 11).

Among all the studied compounds of series **13** with the solvents indicated above the lyotropic mesomorphism was observed only for homologues **13d–k** (Table 11). The lyotropic mesomorphism depends on the number of carbon atoms in lateral substituents and the solvent nature. In systems with chloroform, benzene and nonane these Pc derivatives form both types of chromonic phases [28].

The comparison of the data on amphotropic properties of compounds **11** with tetra-alkoxycarbonyl analogues **13** has shown the decrease of thermotropic properties as well as of lyotropic ones for compounds **11**. Probably, alternation of carboxyl and alkoxycarbonyl groups is not

TABLE 9 Amphotropic properties of 2,3,9,10,16,17,23,24-octa-substituted Phthalocyanine and their Metal Complexes **10–11**

Structural formula	Compound	M	R_1	R_2	Thermotropy	Lyotropy*
	**10a**	$(2H^+)$	OC_8H_{17}	$R_2 = R_1$	Col_{ho}	N, M
	10b	Cu^{2+}	OC_8H_{17}	$R_2 = R_1$	Col_{ho}	N, M
	10c	Zn^{2+}	OC_8H_{17}	$R_2 = R_1$	Col_{ho}	N, M
	10d	Cu^{2+}	$OC_{12}H_{25}$	$R_2 = R_1$	Col_{ho}	N, M
	10e	Ni^{2+}	$OC_{12}H_{25}$	$R_2 = R_1$	Col_{hd}	N, M
	11a	Cu^{2+}	$COOC_4H_9$	COOH	–	M
	11b	Cu^{2+}	$COOC_9H_{19}$	COOH	Col	N, M
	11c	Cu^{2+}	$COOC_{11}H_{23}$	COOH	Col	N, M

[*] The detailed data on lyotropic mesomorphism of compounds **10a–c** see Table 10 or in the reference [22]; for **10c** – in [23], **10d–e** – in [24] and **11a–c** in – [25].

TABLE 10 Lyotropic Mesomorphism of Octa(octyloxy)phthalocyanine and its Metal Complexes with Linear Alkanes and some Cyclic Hydrocarbons (Based on the Contact Preparations), T = 100°C [23]

Solvents	**10a** ($2H^+$)	**10b** (Cu^{2+})	**10c** (Zn^{2+})
Pentane	–	–	–
Hexane	–	–	–
Heptane	$\boxed{\text{N}}$ M	$\boxed{\text{N}}$ M	$\boxed{\text{N}}$ M
Octane	$\boxed{\text{N}}$ M	$\boxed{\text{N}}$ M	$\boxed{\text{N}}$ M
Nonane	$\boxed{\text{N}}$ M	$\boxed{\text{N}}$ M	$\boxed{\text{N}}$ M
Decane	$\boxed{\text{N}}$ M	$\boxed{\text{N}}$ M	$\boxed{\text{N}}$ M
Undecane	$\boxed{\text{N}}$ M	$\boxed{\text{N}}$ M	$\boxed{\text{N}}$ M
Dodecane	$\boxed{\text{N}}$ M	$\boxed{\text{N}}$ M	$\boxed{\text{N}}$ M
Tridecane	$\boxed{\text{N}}$ M	$\boxed{\text{N}}$ M	$\boxed{\text{N}}$ M
Tetradecane	$\boxed{\text{N}}$ M	$\boxed{\text{N}}$ M	M
Pentadecane	M	$\boxed{\text{N}}$ M	M
Hexadecane	M	M	M
Heptadecane	M	M	M
Benzene	M	M	M
Cyclohexane	$\boxed{\text{(N)}}$ M	$\boxed{\text{N}}$ M	M
Cyclooctane	$\boxed{\text{(N)}}$ M	$\boxed{\text{N}}$ M	$\boxed{\text{N}}$ M

N – columnar nematic lyomesophase of chromonic type.
M – two dimensionally ordered lyomesophase of chromonic type.
☐ In such frames is shown induced N lyomesophase, [( ) – *monotropic*].

favourable for the space filling in the paraffin area and, therefore, increases the microsegregation within the columns.

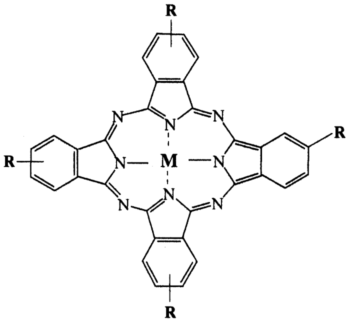
As for metal organyls their mesomorphism was described in detail in numerous articles, several of them are indicated in the list of references [29, 30, 37]. For this reason (as in the case of other compounds) we will only discuss the data, which can assist to answer the key-questions of this paper.

In the binary systems of *mono*-palladium organyl **14** with linear alkanes the formation of homeotropically oriented nematic phase and a *monotropic* lamellar phase (L) with spherulites and myelinic figures were observed. In contrast to the thermotropic phase behaviour of compound **14**, displaying the nematic phase in a narrow temperature range, the lyotropic nematic phase exists in a wide temperature area [29].

The *di*-palladium organyl **15a** does not form any lyomesophase in mixtures with linear alkanes (octane, decane, dodecane or pentadecane). Only dissolution of the substance (on heating) or crystallisation (on cooling) was observed. While **15b** and **15c** with the same solvents form one type of lyomesophase with myelinic figures and spherulites [29].

The occurrence of lamellar phase in the mixtures of **14** or **15b-c** with above mentioned organic solvents was connected with preservation of the

TABLE 11 Amphotropic Properties of Tetra-substituted Copper (II) Phthalocyanine Derivatives **12–13**

Structural formula	Compound	R	Thermotropy[a]	Lyotropy[b]
 M=Cu^{2+}	**12**	$SC_{10}H_{21}$	Col_{hd}	N,M
	13a	$COOCH_3$	–	–
	13b	$COOC_2H_5$	–	–
	13c	$COOC_3H_7$	Col_{ro}	–
	13d	$COOC_4H_9$	Col_{ro}	N,M
	13e	$COOC_6H_{13}$	Col_{ro}	N,M
	13f	$COOC_7H_{15}$	Col_{ro}	N,M
	13g	$COOC_9H_{19}$	Col_{ro}, Col_{ho}	N,M
	13h	$COOC_{10}H_{21}$	Col_{ho}	N,M
	13i	$COOC_{11}H_{23}$	Col_{ho}	N,M
	13k	$COOC_{16}H_{33}$	Col_{ho}	N,M

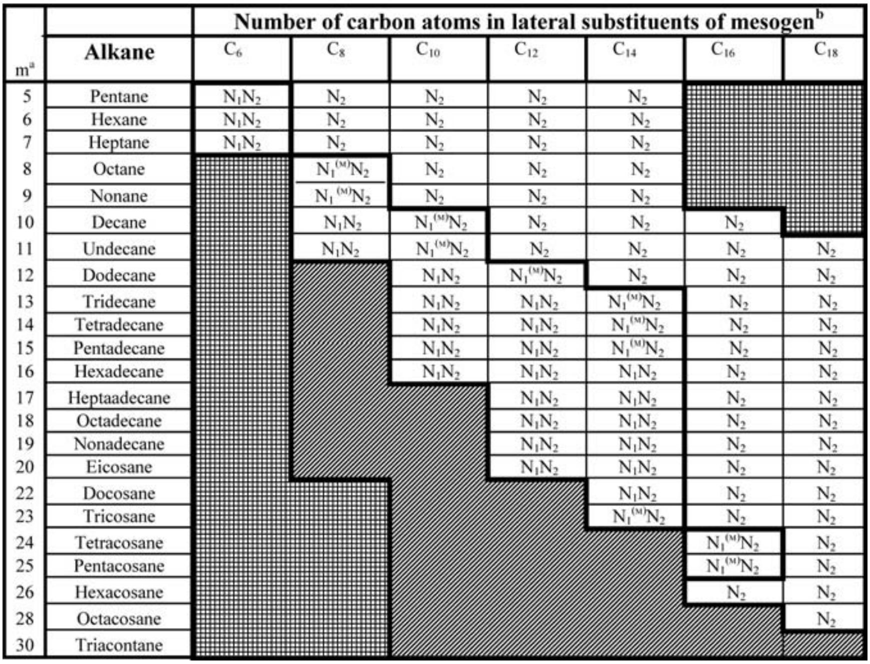
[a] The detail thermotopic and lyotropic data for **12** see in [26], for **13** – in [25, 28].

[b] The solvents used in this research: linear alkanes, cyclohexane, benzene, chloroform and CCl_4.

general symmetry of the layered structure of the thermotropic smectic phase also in lyotropic state. An expansion of the arrangement existing in the absence of solvent (swollen process) takes place in lyotropic systems [29].

As it has been established [30], all of the studied ***tetra***-nuclear organyls **17–18** also show induction/variation of lyomesomorphism in binary systems with linear alkanes (or chloroform). But the important features of tetra-ogranyls in comparison to all above mentioned studied disc-like compounds is the formation besides of M-chromonic phase of *two* columnar nematic lyomesophases (see Table 12), which differentiated by the type of intracolumnar arrangement of molecules [30f].

TABLE 12 The Influence of the Length of Lateral Substituents of Mesogen and Solvent Molecules on Nematic Polymorphism in the Tetra-nuclear Palladium Organyl/Linear Alkane Systems [30 h]



m^a		Number of carbon atoms in lateral substituents of mesogen[b]						
	Alkane	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}
5	Pentane	N_1N_2	N_2	N_2	N_2	N_2	▦	▦
6	Hexane	N_1N_2	N_2	N_2	N_2	N_2	▦	▦
7	Heptane	N_1N_2	N_2	N_2	N_2	N_2	▦	▦
8	Octane	▦	$N_1^{(M)}N_2$	N_2	N_2	N_2	▦	▦
9	Nonane	▦	$N_1^{(M)}N_2$	N_2	N_2	N_2	▦	▦
10	Decane	▦	N_1N_2	$N_1^{(M)}N_2$	N_2	N_2	N_2	▦
11	Undecane	▦	N_1N_2	$N_1^{(M)}N_2$	N_2	N_2	N_2	N_2
12	Dodecane	▦	▨	N_1N_2	$N_1^{(M)}N_2$	N_2	N_2	N_2
13	Tridecane	▦	▨	N_1N_2	N_1N_2	$N_1^{(M)}N_2$	N_2	N_2
14	Tetradecane	▦	▨	N_1N_2	N_1N_2	$N_1^{(M)}N_2$	N_2	N_2
15	Pentadecane	▦	▨	N_1N_2	N_1N_2	$N_1^{(M)}N_2$	N_2	N_2
16	Hexadecane	▦	▨	N_1N_2	N_1N_2	N_1N_2	N_2	N_2
17	Heptaadecane	▦	▨	▨	N_1N_2	N_1N_2	N_2	N_2
18	Octadecane	▦	▨	▨	N_1N_2	N_1N_2	N_2	N_2
19	Nonadecane	▦	▨	▨	N_1N_2	N_1N_2	N_2	N_2
20	Eicosane	▦	▨	▨	N_1N_2	N_1N_2	N_2	N_2
22	Docosane	▦	▦	▨	▨	N_1N_2	N_2	N_2
23	Tricosane	▦	▦	▨	▨	$N_1^{(M)}N_2$	N_2	N_2
24	Tetracosane	▦	▦	▨	▨	▨	$N_1^{(M)}N_2$	N_2
25	Pentacosane	▦	▦	▨	▨	▨	$N_1^{(M)}N_2$	N_2
26	Hexacosane	▦	▦	▨	▨	▨	N_2	N_2
28	Octacosane	▦	▦	▨	▨	▨	▨	N_2
30	Triacontane	▦	▦	▨	▨	▨	▨	▨

[a] number of carbon atoms in the molecule of linear alkane.

[b] $R = C_nH_{2n+1}$, n = number of even carbon atoms (from 6 to18) in lateral substituent of the mesogen molecule.

(M) – monotropic phase.

▦– the field of absence of lyotropic mesomorphism.

▨– the field of high viscous mesophase.

Thus, it has been shown that the lyotropic mesophases in the binary systems of mono-, di- and tetra-metal organyls **14–18** with linear alkanes (from pentane to pentadecane) can be formed. Similar to disc-like compounds with different central cores, which we discussed above, the ratio of the number of carbon atoms in lateral substituents of these palladium-organyls and in linear alkanes used as a solvent influences on the type of appearing lyomesophase as well as on their temperature range. Hence, organic solvents are the essential factor for induction/variation of lyomesomorphic state for these type of materials too.

Taking into account the possibility of formation of columnar nematic lyomesophases for these organyls, we successfully applied two ways of lyomesophase induction/variation: i) the using of chiral solvents (for example, (+)- or (−)-limonene) for induction of chiral nematic lyomesophases [29]; or ii) the formation of mesomorphic charge-transfer complexes with chiral electron acceptors (+)- or (−)-TAPA, which in the three-component mixtures with linear alkanes also formed chiral nematic lyomesophases [37].

It was interesting for us to apply an accumulated experience (on induction mesomorphic properties with the help of solvents) for other chemical classes of compounds, for example for disc-like materials having *no clearly expressed core*. For this goal 1,4,7-triazacyclononane derivatives **19** and poly(propylene imine) dendrimers **20** of various generations (from first to fifth), with different number of aliphatic chains in lateral substituents (see R in structural formulas **20**) were chosen as well as one analogue of the third generation, 100%-protonated with decylsulfonic acid (DSA).

The two first non-mesogenic homologues **19a–b** are *non-lyomesogenic* with any of the used solvents (*n*-hexane, cyclohexane, decane, decanol, DMF, DMSO, chloroform, THF). For *monotropic* homologue **19d** ($n = 6$) in binary systems with cyclohexane the *enantiotropic* lyomesophase has been obtained. The type of the original thermotropic mesophase of **19c** ($n = 5$) is kept in lyotropic state but the phase transition temperature into isotropic state has been lowered. For **19e** and **19f** in binary systems with the hydrocarbons mentioned above, an expansion of temperature diapason of the lyomesophase existence is observed: at cooling the lyomesophase remains the same up to room temperature. Besides, in contrast to thermotropic state, during cooling in lyotropic systems of **19c, d** and **e** the occurrence of several polymorphic modifications can be found. In a number of cases the formation of glass state is detected for compounds **19c–f** in mixtures with the solvents [38].

Dendrimers are superbranched synthetic macromolecules occupying intermediate space between low-molecular compounds and polymers. Despite the existence of a numerous variations of dendrimer structures in general, including those with mesomorphic properties, practically no

TABLE 13 Amphotropic Properties of Poly(Propylene Imine) Dendrimers **20**

Compound		Thermotropy [32]	Lyotropy [38]
20a	1K1[a]	–	+ (lyomesophase at room T)
20b	1K3	Col_{rd}	+ (polylyomesomorphism)
20c	3K2	Col_{hd}	+ (polylyomesomorphism)
20d	4K1	SmA [b]	+ (enantiotropic)
20e	5K2	[Cub] [c], Col_{hd}[d]	+ (polylyomesomorphism)
20f	3K2·14DSA	Mes_1, Mes_2	+ (polylyomesomorphism)

[a] The first number is a number of generation; K_1, K_2 or K_3 = lateral sustituent (R); DSA – decyl sulfonic acid.

[b] Liquid crystal phase is observed monotropically only at first cycle of heating (that is, it is *pseudoenantiotropic*).

[c] The mesophase was not determine by DSC. With the help of polarizing microscopy the decreasing of viscosity as well as of intensity and relaxation time of birefringence induced by the shearing deformation has been observed at ~50 ± 5°C.

[d] The mesophase appears only after a long stay at about 75°C.

[ ] – monotropic mesophase in the attitude to Col_{hd} phase, which has been found only at first heating and was not detected by DSC measurements.

attempt has been undertaken to study the properties of dendrimers with solvents from the mesophase induction point of view.

The data on lyotropic mesomorphism of dendrimers **20** are summarized in Table 13. The most important results obtained in our study of the influence of organic solvents on lyotropic mesomorphism of these dendrimers are [38]:

- induction of a lyomesophase in the case of ***non-mesomorphic*** dendrimer of the first generation **20a;**
- induction of an ***enantiotropic*** lyomesophase for monotropic mesomorphic dendrimer of the fourth generation **20d;**
- increasing of number of polymorphic lyotropic modifications for mesomorphic dendrimers **20b**, **20c**, **20e** and **20f**.

CONCLUSIONS

So, this work for the first time summarises the results of our investigations in the field of the research on lyotropic mesomorphism of disc-like compounds (benzene, scyllitol, benzenehexamine, triphenylene, phthalocyanine, triazacyclononane derivatives as well as dendrimers) in organic solvents. We answer a number of key-questions, connected with induction/variation of lyotropic liquid crystal properties of these mesomorphic and non-mesomorphic materials.

It has been shown that independent of the variation of the size, the rigidity and the chemical structure of central core of disc-like molecules or of the number of lateral substituents, it is common for the representatives of these compounds to form lyotropic phases in suitable solvents. In the choice of *linear hydrocarbons* as solvents the most important factor is the closeness of the number of carbon atoms in the solvent molecule and in lateral substituents of disc-like compound. The inducing ability of *cyclic hydrocarbons* is stronger than that of the linear ones. Due to chiral solvents or through the formation of charge transfer complexes with chiral electron acceptors in three component systems it is possible to form chiral nematic phases for non-chiral discotic compounds. Besides, the peculiarities of the structure of discotic compounds can lead to their quite new characteristics in lyomesophase: to the formation of two types of columnar nematic phases (tetra-palladium organyls) or to the appearance of chirality in lyomesophase for non-chiral compounds (benzenehexamine derivatives).

The peculiarities of intermolecular interaction of disc-like compounds inside the columns (ordered or disordered) influence the lyomesophase formation mainly for compounds with the *small central fragment* (benzene, scyllitol or benzenehexamine derivatives). The role of intracolumnar interactions between macrocyclic molecules with *large central fragment* is not displayed distinctly: the substances with both ordered and disordered packing can exhibit lyotropic mesomorphism.

The fulfilled summarising of the data is the basis for prediction of new lyotropic compositions with induction/variation of mesomorphic properties for non-mesomorphic and mesomorphic disc- and lath-like hydrophobic compounds. For example, using the described approach the successful results have been obtained for polycatenar alkoxystilbazole complexes of silver (I) with organic solvents [39].

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