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Dietmar Janietz[a]; Alexandra Kohlmeier[a]
[a] Fraunhofer Institute for Applied Polymer Research, Potsdam-Golm, Germany

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INVITED ARTICLE

Nanoscale segregation, molecular recognition and fluorophobic effect – from molecular design towards complex mesophase morphologies

Dietmar Janietz* and Alexandra Kohlmeier

Fraunhofer Institute for Applied Polymer Research, Geiselbergstr. 69, D-14476 Potsdam-Golm, Germany

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Mesomorphic structure formation of hydrogen-bonded complexes of amino substituted 1,3,5-triazines with complementary (semiperfluoro)alkoxybenzoic acids is presented. The substitution pattern of both components was modified systematically in order to elucidate the influence of molecular parameters on the mesophase morphologies of the binary mixed systems. The phase sequence of the triazines, and of their associates with the acids, spans the range from smectic layer structures to discontinuous cubic phases composed of closed inverted micelles. Columnar phases with various two-dimensional lattice symmetries and bicontinuous cubic phases were found as intermediates. The mesophase morphologies are discussed in terms of the microsegregation of rigid polar, lipophilic and fluorinated molecular blocks in different sub-spaces along with tailoring the shape of (curved) aggregates by the space requirement of incompatible molecular fragments.

Keywords: hydrogen bonding; fluorophobic effect; nanosegregation 1,3,5-triazines

1. Introduction

Mesogenic self-assembly is mainly affected by the segregation of incompatible molecular sub-units in space into distinct microdomains (*1, 2*). Thereby, the mesophase morphologies are essentially governed by the space requirement of the competing molecular blocks. If the volume fractions of the incompatible parts are almost equal, non-curved aggregates are formed, which organise into lamellar (smectic) mesophases. Increasing the average lateral area of one molecular component leads to aggregates with a finite mean interface curvature. Consequently, the phase sequence bicontinuous cubic (Cub_V), columnar (Col) and, finally, spheroidic cubic (micellar; Cub_I) can be found by successively increasing the size of one segment of incompatible sub-units, as reported for the sequence of thermotropic mesophases of polyhydroxy amphiphiles in (*3*).

As the simplest case of low molecular mass diblock mesogens with amphiphilic segments, one can imagine the classical amphiphiles composed of a polar head group and a lipophilic flexible alkyl tail, which are capable of forming lyotropic as well as thermotropic mesophases. However, besides the well-explored hydrophilic/lipophilic intramolecular contrast, in a more general context amphiphilicity describes any chemical or structural contrast within a molecule (*2*). One such orthogonal set of incompatibilities arises from rigid/flexible amphiphilicity (Figure 1(a)), whereby rigid molecular parts may introduce specific molecular topologies (*4*).

Hydrogen-bonded mesomorphic complexes (*5*) arising from complementary molecular entities fitted with lipophilic chain segments can be regarded as non-covalent analogues of amphiphilic diblock molecules. Thereby, the introduction of hydrogen bonding reinforces the intramolecular polarity gradient and may contribute to an increased stiffness of the polar core region. A remarkable feature is that the single components need not necessarily be mesogenic by themselves.

Certain different hydrogen bonding motifs were reported. The single hydrogen bonding between carboxylic acids and pyridine fragments was exploited to induce and/or stabilise calamitic thermotropic mesophases (*6–8*). Heterodimers emerging from double-hydrogen bonding of 2,6-diacylaminopyridines with aromatic carboxylic acids display smectic and columnar phases (*9, 10*). Triple-hydrogen bonding between 2,6-diacylaminopyridines and uracil derivatives was utilised to design columnar phase forming complexes (*11, 12*).

An alternative approach towards increasing the intramolecular contrast arises from replacing a perhydrogenated chain with a perfluorinated segment. The main reasons are the incompatibility of perfluorinated chains with aliphatic, aromatic and polar molecular segments, their larger cross-sectional area compared with aliphatic chains and their reduced conformational mobility (*13*).

The simplest examples are smectic liquid crystalline phase-forming diblock molecules combining

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*Corresponding author. Email: dietmar.janietz@iap.fraunhofer.de

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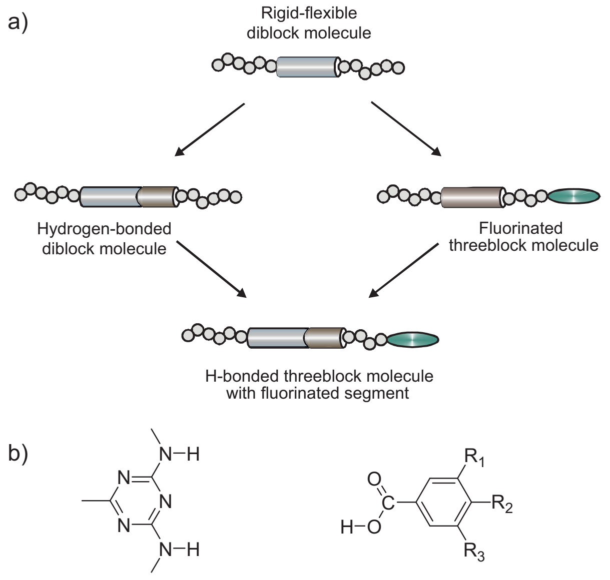


Figure 1. (a) Covalent and non-covalent approaches towards polyphilic block mesogens. (b) Molecular components suitable for intermolecular hydrogen bonding: amino substituted nitrogen heterocycles based on a 1,3,5-triazine core and complementary aromatic carboxylic acids.

hydrocarbon and fluorocarbon chains (*14, 15*). Moreover, (semi)perfluorinated alkyl chains have been successfully incorporated into mesogens with a rigid core (*16–20*) as well as into liquid crystals without a pronounced anisometric shape (*21–23*). It could be shown that the fluorophobic effect may lead to stabilisation, as well as to modifications of smectic, columnar and cubic mesophases.

Strong cohesive forces emerging from hydrogen bonding between complementary molecules, along with the simultaneous introduction of (partially) fluorinated structural units, may lead to non-covalently associated three-block molecules with distinct regions of a polar H-bonded (rigid) core, lipophilic alkyl chain segments and fluorinated building blocks as depicted in Figure 1(a). Thereby, the cooperative interplay of enhanced polar–non-polar microsegregation and tailoring the space requirement of lipophilic and fluorinated segments should provide a very suitable approach towards tailoring thermotropic mesophase morphologies.

None the less, appropriate examples so far are rather limited. A few mesogenic complexes have been reported, derived from fluorinated acids and pyridine derivatives, which exhibit smectic or columnar phases depending on the number of fluoroalkyl chains of the acid component (*24–28*).

We present here an overview regarding our efforts towards combining molecular recognition between two complementary species and the fluorophobic effect. As the two components we chose amino substituted 1,3,5-triazine derivatives and aromatic carboxylic acids (Figure 1(b)).

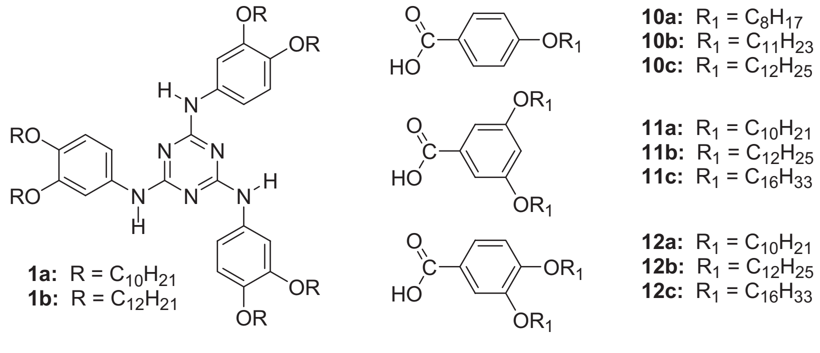
A major advantage of the concept we follow here is that it enables a diversity of systematic structural modifications, i.e., by incorporation of lipophilic and/or fluorophilic chain segments selectively into one or both of the components.

2. Alkoxy substituted triarylmelamines

2.1 Thermal properties of the pure melamine derivatives

One suitable approach towards functionalised 1,3,5-triazine derivatives consists in grafting three phenyl moieties to the central heterocyclic core via secondary amino groups as was realised with the triarylmelamines **1** bearing six lipophilic side chains (Scheme 1).

The pure 2,4,6-triarylamino-1,3,5-triazines **1** exhibit a hexagonal columnar mesophase with an aperiodic intracolumnar stacking of the molecules (*29*). Due to the ability of the phenyl rings to perform rotational motions around the C–N single bonds it is not only the flexible alkyl side chains, but also the core region of



Scheme 1. Chemical structure of the 2,4,6-triarylamino-1,3,5-triazines **1** fitted with six peripheral lipophilic tails and of complementary alkoxy substituted benzoic acids **10–12**.

the molecules that can adopt certain different conformations. The result is a lack of inherent molecular planarity. No specific anisometric geometry is provided by the central part of the molecules. Therefore, the hexagonal columnar mesophases formed by the triazines in their pure state cannot be explained in a conventional sense as resulting from a rigid disc-like molecular geometry.

The hexagonal lattice constants obtained from the X-ray amounts to 30.2 Å for compound **1a** and 32.8 Å for **1b** (*29*). The values are somewhat smaller than the molecular diameter of radial two-dimensional conformers of **1a,b** in the most extended form (Figure 2). Hence, the columns are piled up from the polar triphenylaminotriazine cores, preferably exhibiting flat radial conformations, with a two-dimensional random distribution of the flexible side chains (*30*). The main driving force for liquid crystallinity of the triarylmelamines is thus a micro-segregation of the polar central molecular part from the non-polar aliphatic chains in such a way that cylindrical aggregates are formed, with the polar groups of the molecules located in the centre surrounded by a continuum of the lipophilic chains. The parallel alignment of these aggregates gives rise to the observed two-dimensional hexagonal lattice symmetry.

2.2 Hydrogen-bonded complexes with benzoic acids bearing aliphatic tails

The thermal properties of the compounds **1** were investigated in binary mixtures with the alkoxy-substituted benzoic acids **10–12** (Scheme 1) (*31, 32*). The acid components were systematically modified with respect to the number, the positions and the chain lengths of the alkoxy substituents.

Figure 2. CPK model showing a two-dimensional radial conformer of the six-fold decyloxy substituted triarylmelamine **1a** with a pronounced circular shape. Only more or less all-*trans* arrangements of the peripheral flexible chains are considered.

The 4-alkoxybenzoic acids **10a–c** display a smectic C mesophase and a nematic phase in their pure state (*33*) due to a dimerisation via hydrogen bonds. In contrast, the pure two-fold alkoxy substituted acids **11** and **12** are non-mesomorphic.

Mixed systems of the melamines **1a,b** with the aromatic acids **10–12** show an enantiotropic mesophase. Mesomorphic behaviour is restricted to equimolar compositions of the components. The binary 1:1 mixtures of the melamines **1** with the single-chain aromatic acids **10** and with the 3,5-dialkoxy substituted benzoic acids **11** exhibit a hexagonal columnar (Col_h) phase. For the mixed systems with the triazine **1a** an increase of the intercolumnar distances is observed as a function of increasing alkoxy chain lengths of the benzoic acids. Thus, the number of methylene groups of the benzoic acids allows control over the spacings between the hexagonally arranged columns. Contrary to this, the intercolumnar distances of the 1:1 mixtures **1b/10** and of the pure melamine **1b** are of the same order of magnitude.

The 3,4-dialkoxy substitution pattern of the benzoic acid component gives rise to a change of the columnar mesophase structure of the melamine **1a** from a hexagonal to a rectangular lattice in mixtures with the aromatic acids **12**. The small angle reflections could be indexed on the basis of a simple non-centred rectangular unit cell with *P2m* lattice symmetry (*32*).

Infrared (IR)-spectroscopic investigations (*31*) confirmed that the association of the complementary benzoic acid and the melamine molecules is due to double-hydrogen bonding between the carboxylic group and the nitrogen heterocycle, substituted with secondary exocyclic amino groups leading to discrete heterodimers (Figure 3).

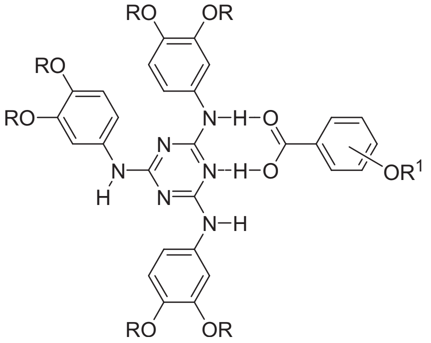


Figure 3. Hetero-dimeric supermolecules with double-hydrogen bonding between the amino substituted nitrogen heterocycle of the triarylmelamines **1**, bearing six alkoxy tails and the complementary benzoic acids **10–12**.

CPK models (Figures 4(a), 5(a)) reveal that docking of the acid component to the inner functional core region of the aminotriazines gives rise to a more or less flat hydrogen-bonded aggregate if the six-fold alkoxy substituted triphenylaminotriazine core adopts a non-symmetric conformation. Two molecular recognition sites remain uncomplexed due to steric hindrance (*32*). Thereby, a pronounced circular molecular geometry results for heterodimers involving the one-chain acids **10** and the benzoic acids **11** fitted with two alkoxy tails at the 3,5-positions of the phenyl ring (Figure 4(a)). Cylindrical aggregates are formed with the polar groups located in the centre, randomly surrounded by the lipophilic chains. The parallel alignment of these aggregates gives rise to the two-dimensional hexagonal lattice symmetry (Figure 4(b)).

A 3,4-dialkoxy substitution pattern reduces the symmetry of the acid component. Obviously, the symmetry break is transferred to the heterodimers **1/12**. The result is an unequal distribution of the alkyl chains around the hydrogen-bonded core, which leads to an ellipsoidal cross-sectional shape of the supermolecules (Figure 5(a)). The majority of the flexible chains segregate in layers, whereas in the perpendicular direction the density of alkyl chains is reduced. Consequently, columnar phases on a two-dimensional rectangular lattice are formed (Figure 5(b)).

The rectangular columnar mesophases of the equimolar compositions **1a/12** can be considered as a lamellar arrangement of parallel-aligned columns with a positional and orientational correlation of the columns in neighbouring layers. The $\mathrm{Col_r}$ phase is intermediate in the transition from hexagonal columnar to lamellar organisation, where only the individual molecules are organised in layers (*4*).

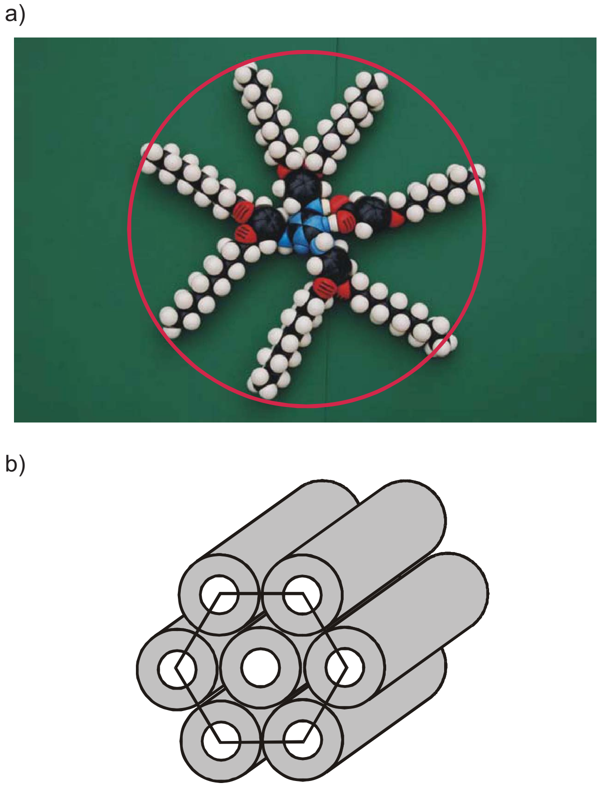


Figure 4. (a) CPK model of a hydrogen-bonded heterodimer of the six-fold decyloxy substituted triarylmelamine **1a** and the 4-octyloxybenzoic acid **10a** with circular shape. (b) Hexagonal columnar organisation of the equimolar mixtures of the triarylmelamines **1** and the benzoic acids **10** and **11** through hydrogen bonding and nanoscale segregation.

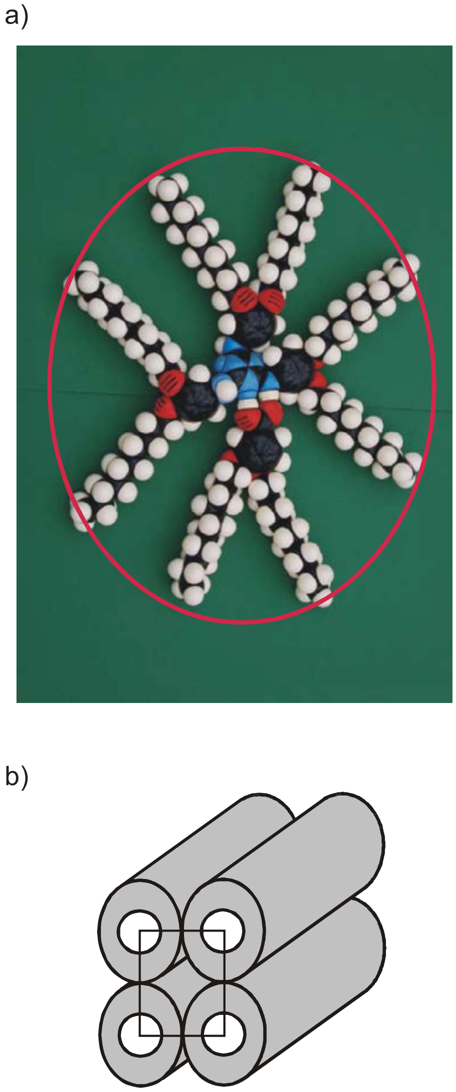


Figure 5. (a) CPK model showing an ellipsoidal aggregate of the melamine **1a** with the two-fold decyloxy substituted benzoic acid **12a**. (b) Possible arrangement of the hydrogen-bonded 1:1 complexes **1/12** in their columnar mesophases with two-dimensional *P2m* lattice symmetry.

2.3 Mixed systems with semiperfluorinated benzoic acids

In the next step, we replaced the alkyl tails of the acid by semiperfluorinated chains. As the melamine component, the 1,3,5-triazines **1a** and **2** were chosen as they differ with respect to the number of alkoxy chains grafted onto the molecular periphery (Scheme 2).

The pure triazine **2**, with only three peripheral alkoxy groups, shows no mesomorphic behaviour (*34*). Obviously, the three alkyl tails at the melamine core are insufficient for a balanced intramolecular contrast to force mesomorphic structure formation. The partially fluorinated carboxylic acids display a $\mathrm{Col_h}$ phase in their pure states (*35*).

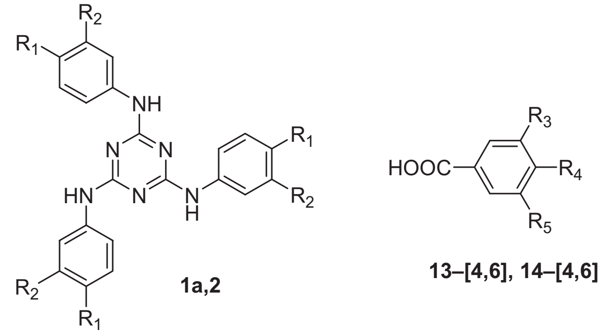
1:1 associates of the melamines **1a** and **2** with the fluorinated acids **13** and **14** (*36*) have significantly enhanced mesophase regions and exceptionally higher clearing temperatures compared with heterodimeric hydrocarbon analogues **1/10–12** (Figure 6). It shows that the mesophases of H-bonded melamine/benzoic acid dimers can be stabilised by enhancing the intramolecular contrast through the incorporation of fluorinated molecular fragments into the acid component.

The optical textures of all investigated melamine/benzoic acid complexes **1a,2/13,14** are characterised by regions with broken spherulites, mosaic like domains and pseudoisotropic areas containing birefringent filaments (Figure 7). These textures are typical for a hexagonal columnar ($\mathrm{Col_h}$) mesophase. The phase assignment was confirmed by X-ray diffraction.

The number of dimeric **1a/13-[4,6]** and **1a/14-[4,6]** supermolecules in the unit cell was calculated to be just one (*36*). Basically, the molecular arrangement of one hydrogen-bonded heterodimer of the six-chain triarylmelamine **1a**, with the fluoroalkyl modified carboxylic acids **13** and **14** within one slice of the hexagonally aligned columns, is quite similar to that of the respective 1:1 mixtures with the alkoxybenzoic acids **10** and **11** (see Figure 4(a)). The six alkoxy tails of the triazine component **1a**, along with the two or three partially fluorinated chains of the complementary benzoic acids **13** and **14**, respectively, are sufficient to form circular dimers with optimum peripheral space filling. These dimers build up columnar stacks with a cylindrical shape, which organise to hexagonal columnar liquid crystalline phases.

However, a remarkable feature of the X-ray diffractograms of the mixed systems **1a/13,14** is that they show an additional reflection in the small angle region (*36*). The additional reflection corresponds to a *d*-spacing nearly twice as large as that for the (100) reflection and points towards a superstructural ordering of the liquid crystalline phase. The new unit cell has at least one lattice dimension that is approximately twice as large as the intercolumnar distance. Considering that demixing of the lipophilic aliphatic and fluorinated side chain regions occurs, the superstructure can be realised if three (or even two) fluorinated segments point to each other within the hexagonal array (Figure 8).

The segregation of the chemically incompatible aliphatic and fluorinated parts in space along the column axis with formation of a superlattice was confirmed by analysing the wide-angle regions of the WAXS diffractograms (*36*). The diffuse wide-angle scattering



1a,2

13–[4,6], 14–[4,6]

Compound	R_1	R_2	R_3	R_4	R_5
1a	$OC_{10}H_{21}$	$OC_{10}H_{21}$			
2	$OC_{12}H_{25}$	H			
13–[4,6]			$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$	H
14–[4,6]			$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$

Scheme 2. Six-chain and three-chain substituted triarylmelamines **1a** and **2** and complementary semiperfluorinated benzoic acids **13** and **14**.

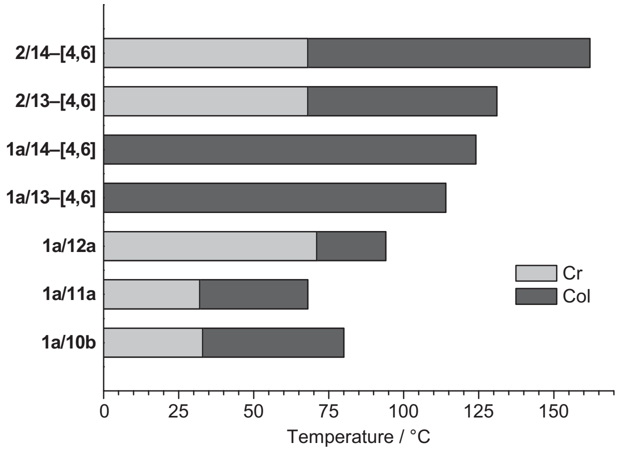


Figure 6. Influence of the fluorinated chain segments attached to the acid component onto the thermodynamic mesophase stability of hydrogen-bonded triarylmelamine/ benzoic acid heterodimers.

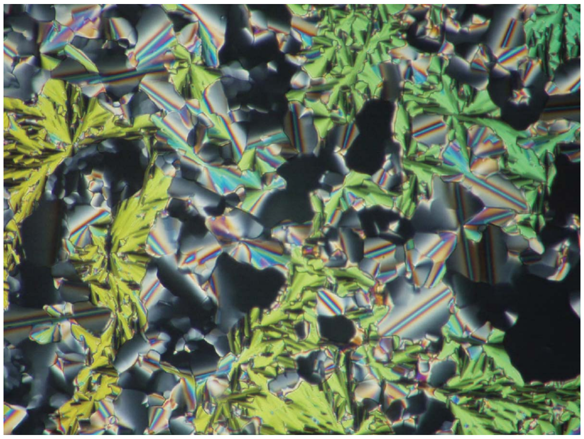


Figure 7. Optical microphotograph of the $\mathrm{Col_h}$ mesophase of the equimolar mixed system **2/14-[4,6]** at 115°C.

consists of two maxima that can be assigned to perfluorinated segments and fluid aliphatic regions, respectively.

The number of hydrogen-bonded dimers of the melamine **2** with the benzoic acids **13** and **14** within the cross-section of the hexagonal unit cell was calculated to be about two. Reducing the number of alkoxy chains of the melamine component to a total of three no longer promotes a sufficient space filling around the polar core of the H-bonded dimers. Instead, the dimers may turn to a molecular conformation, which enables additional attractive interactions between the triarylaminotriazines at hydrogen bonding sites not complexed by the acid component. In case of the hydrogen bonded complexes of the six-fold alkoxy modified triarylmelamine **1a** with the benzoic acids **13** and **14**, such a pairing of dimers seems to not be favoured for steric reasons, due to the bulkiness of the six flexible peripheral alkoxy moieties.

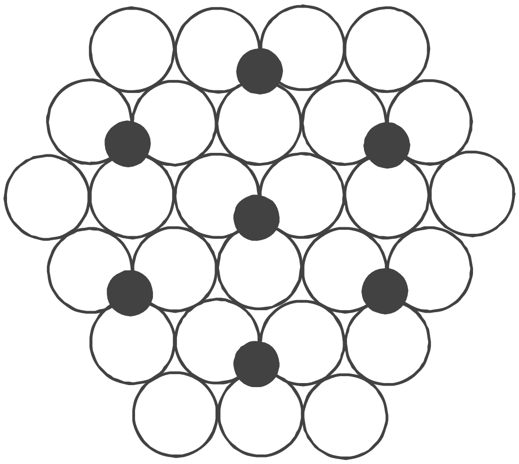


Figure 8. One possible model for the superstructure within the hexagonal columnar mesophases of the hydrogen-bonded dimers of the six-fold alkoxy substituted triarylaminotriazine **1a** with the partially fluorinated acids **13** and **14**. The black circles represent the fluorinated regions separated from the aliphatic molecular periphery.

Figure 9 presents a CPK model of one possible arrangement of pairs of hydrogen-bonded dimers **2/13-[4,6]** with a circular shape. The maximum diameter of the discs (47 Å) is slightly larger then the measured intercolumnar distance within the hexagonal columnar mesophase (40.3 Å). In reality, the alkyl segments are not in all-*trans* conformations, but will exhibit several *gauche* defects. Therefore, the hexagonal lattice constants agree quite well

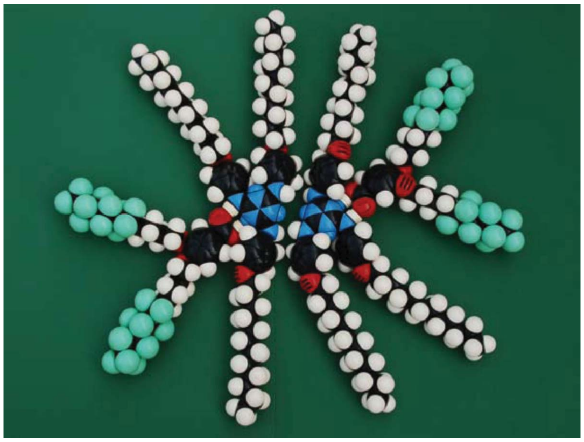


Figure 9. CPK model of one possible molecular arrangement of pairs of dimers of the melamine/benzoic acid complexes **2/13-[4,6]** with circular cross-sectional shape giving rise to columnar mesophases on a two-dimensional hexagonal lattice.

with our model that the $\mathrm{Col_h}$ phases of the 1:1 mixtures of the melamine **2** with the benzoic acids **13,14** are built up by columns of paired dimers with flat hydrogen-bonded central polar cores surrounded by a shell of the alkyl segments.

No hint regarding an additional periodical superstructure within the hexagonal lattice is evident from the small angle region of the X-ray diffractograms. However, the double halo that appears in the wide-angle region again points to segregated regions of lipophilic and fluorinated fragments, due to the fluorophobic effect introduced by the benzoic acid component.

3. Melamine derivative incorporating a single alkoxyphenyl group

In order to evaluate structural modifications of the triazine component on self-organisation of H-bonded associates with fluorinated acids, we changed the number of alkoxyphenyl groups linked to the nitrogen heterocycle. Compound **3** is characterised by two primary amino functions and just one alkoxyphenyl unit fitted to the triazine core via a secondary amino moiety (Scheme 3). The melamine **3** is a rather high melting solid without mesomorphic properties.

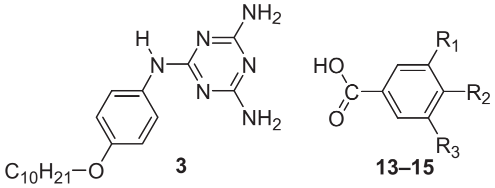
Contrary to the threefold phenyl modified melamines **1** and **2,** the appearance of a thermotropic liquid crystalline phase is not restricted to an equimolar ratio of the triazine/acid components (*37*). The mesomorphic properties of selected binary mixtures of the triazine **3** with one, two and three equivalents of the two-chain benzoic acids **13** and **15**, respectively, are shown in Figure 10. The mesophase stability decreases with increasing content of the acid. Furthermore, the phase stability is governed by the position of the two semiperfluorinated chains of the acid. Mixtures of the melamine **3** with the benzoic acid **13-[6,4]** with the two partially fluorinated chains in the 3,4-position have significantly higher clearing temperatures in comparison to mixed systems with the isomeric 3,5-disubstituted acid **15-[6,4]**, both having the same number of fluorinated and non-fluorinated methylene groups.

On cooling of the 1:1 mixtures comprising the two-chain acids from the isotropic liquid state, spherulitic textures can be observed between crossed polarisers. These features are indicative for columnar mesophases. As a typical example, the texture of the **3/15** mixed system is shown in Figure 11.

The X-ray diffractogram pattern obtained for the mesophase of the equimolar **3/15-[6,4]** mixture shows only reflections with $h + k = 2n$ in the small angle region. These reflections can be assigned to a columnar phase with a centred rectangular lattice (*C2mm*). The lattice parameters amount to $a = 65$ Å and $b = 71$ Å.

Docking of just one equivalent of the benzoic acid **15** to the melamine heterocycle **3** preferentially occurs opposite the bulky phenyl group for steric reasons, leading to heterodimeric supermolecules **3/15-[6,4]** with pronounced rod-like core geometry (*37*). An efficient space filling within the mesophase is accomplished by a close side-by-side organisation of the elongated aromatic units. The length of H-bonded dimers **3/15** amounts to approximately 45 Å, considering almost stretched conformations of the flexible alkyl segments. The lattice parameter *b* matches nearly twice the molecular length. Therefore, it is most likely that hydrogen-bonded bilayer aggregates are present in the rectangular lattice.

Figure 12 shows a CPK model of a possible bilayer organisation of closely packed supermolecules **3/15.** The cross-sectional area of the terminal semiperfluorinated chains exceeds the cross-section of the closely aligned central H-bonded aromatic and the lipophilic



3 **13–15**

Compound	R_1	R_2	R_3
13–[6,4]	$O(CH_2)_6C_4F_9$	$O(CH_2)_6C_4F_9$	H
13–[4,6]	$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$	H
14–[4,6]	$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$
15–[6,4]	$O(CH_2)_6C_4F_9$	H	$O(CH_2)_6C_4F_9$

Scheme 3. Decyloxyphenyl substituted melamine **3** investigated in binary mixtures with the two-chain and three-chain partially fluorinated aromatic acids **13–15**.

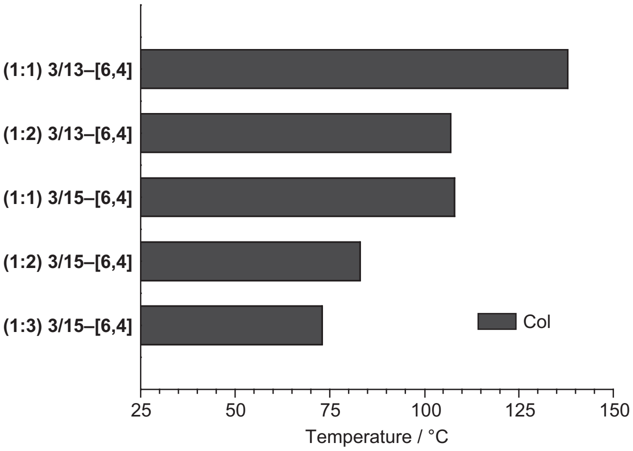


Figure 10. Influence of the chain positions and the molar content of the two-chain fluorinated benzoic acids **13** and **15** on the liquid crystalline behaviour of binary mixtures with the decyloxyphenylmelamine **3**.

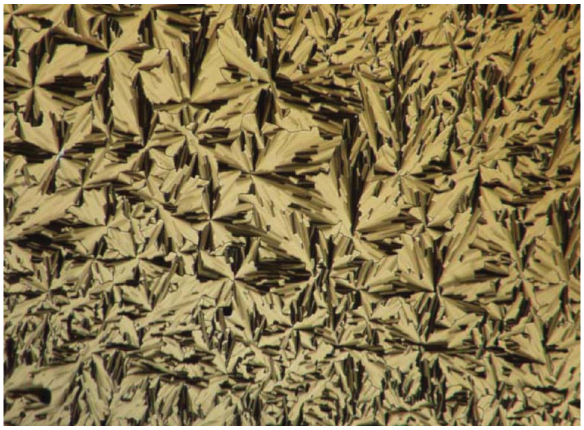


Figure 11. Optical texture of the rectangular columnar mesophase of the 1:1 mixture **3/15** as obtained by cooling from the isotropic melt (crossed polarisers) at 80°C.

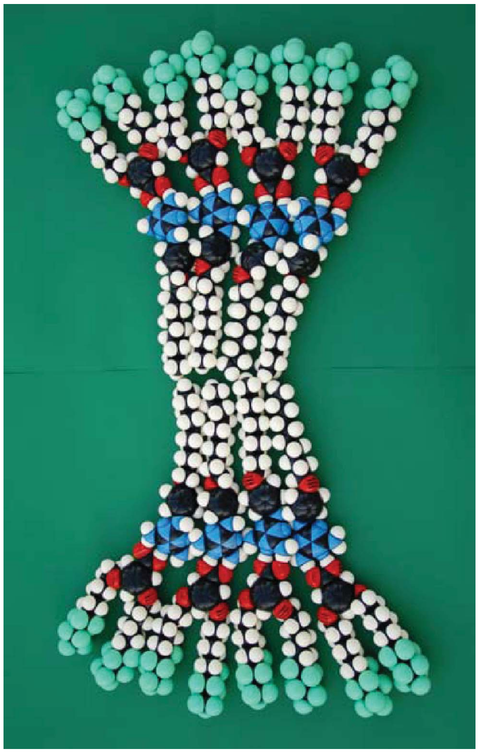


Figure 12. CPK model showing a possible bilayer arrangement of eight hydrogen-bonded **3/15-[6,4]** dimers. Only more or less stretched conformations of the flexible alkyl chains are considered.

regions. The resulting different space filling within the segregated domains gives rise to a frustration within the layers, which causes their collapse with the formation of bilayer ribbons arranged in a rectangular *c2mm* lattice (Figure 13(a)). The ribbons can be regarded as small band-like segments of the layers.

The lattice parameter *b* corresponds to the height of the bilayer ribbons considering the fluid nature of the flexible alkyl chains, whereas the lattice constant *a* is in accordance with the lateral dimension of the ribbons by assuming, on average, four neighbouring dimers within one ribbon.

A major structural change takes place on changing the positions of the partially fluorinated alkoxy chains of the acid component. The X-ray diffractogram of the equimolar mixture of the triazine **3** with the 3,4-disubstituted benzoic acid **13-[6,4]** displays a set of reflections in the small angle region, which can be indexed on the basis of a two-dimensional oblique lattice (Col_{ob}). The lattice parameters of the Col_{ob} phase of the equimolar **3/13-[6,4]** complex amount to $a = 53$ Å, $b = 43$ Å and $\gamma = 70.7°$ (*37*).

The molecular organisation of the elongated H-bonded heterodimers **3/13** within the oblique unit cell resembles a bilayer arrangement. However, fixing the two semiperfluorinated tails at the 3,4-positions of the benzoic acid changes the symmetry of the acid component. As a consequence, the H-bonded heterodimers **3/15** and **3/13** differ with respect to their molecular topology.

It follows from CPK models that shifting of the rigid rod-like cores of the **3/13** dimers against each other leads to a more efficient space filling compared to the heterodimers **3/15**. However, the cross-section of the segregated semiperfluorinated chains still exceeds the cross-sectional area of the alkyl chain regions. Solely tilting the molecules cannot sufficiently compensate for the resulting steric frustration. The smectic layers break up into ribbon-like segments with curved interfaces, due to the different space filling of the fluorinated and lipophilic regions. The ribbon-like aggregates organise to columnar mesophases on a two-dimensional oblique lattice (Figure 13(b)).

The X-ray diffractogram obtained for the mesophase of the alkoxyphenylmelamine **3**, with the three-chain partially fluorinated benzoic acid **14-[4,6]** at an equimolar ratio of the components, is characterised by (100) and (110) reflections in the small angle region with a reciprocal spacing ratio of $1{:}\sqrt{3}$. This is unambiguously typical for a hexagonal columnar mesophase. The hexagonal lattice constant amounts to a_{hex} = 67.5 Å. The length of the hydrogen-bonded supermolecules **3/14** in their most extended conformation is $L = 44$ Å. The ratio a_{hex}/L amounts to 1.53. This value is of the same order of magnitude as those found for the Col$_\text{h}$ phases of taper-shaped mesogens. (*3, 38, 39*)

The incorporation of a third semiperfluorinated chain into the acid component increases the wedge-shaped character of the H-bonded melamine/acid heterodimers. Hence, the hexagonal columnar phase of the equimolar associates **3/14** should consist of extended columnar aggregates built up by a distinct lipophilic region of strongly coiled fluid alkyl chains in the centre, surrounded by the polar aromatic segments arranged side-by-side and, finally, by a shell of the fluorinated moieties (Figure 13(c)). The number of dimers **3/14** arranged in a single slice of the columns was estimated to be approximately ten. Due to the elongated rigid hydrogen-bonded aromatic units, this value is larger than that found for other wedge shaped compounds (*3, 39, 40*).

Upon heating, the hexagonal columnar mesophase of the binary equimolar mixture of the melamine **3** with the three-chain semiperfluorinated benzoic acid **14-[4,6]** transforms into a highly viscous optically isotropic cubic phase. Taking into account the increased molecular mobility at more elevated temperatures, the aggregates forming the cubic phase should be more strongly curved than cylindrical aggregates in the Col$_\text{h}$ phase of the 1:1 mixture **3/14**. Therefore, the cubic mesophase should be a discontinuous cubic (Cub$_\text{I}$) phase built up by closed micelles with an inner lipophilic core and an outer spheroidic region of the fluorinated tails. The transition from a hexagonal columnar phase composed of aggregates with an average circular cross-sectional shape to a micellar cubic phase upon heating has so far been reported, i.e., for amphiphilic taper shaped polyhydroxy derivatives (*3*). Hence, this columnar–cubic dimorphism further supports our structural model for the Col$_\text{h}$ phase of the 1:1 mixture **3/14** given schematically in Figure 13(c).

The structures of the columnar mesophases of the hydrogen-bonded 1:1 complexes **3/13–15** are shown schematically in Figure 13. Accordingly, the hexagonal columnar phase of the H-bonded heterodimers **3/14** should be characterised by an average cylindrical

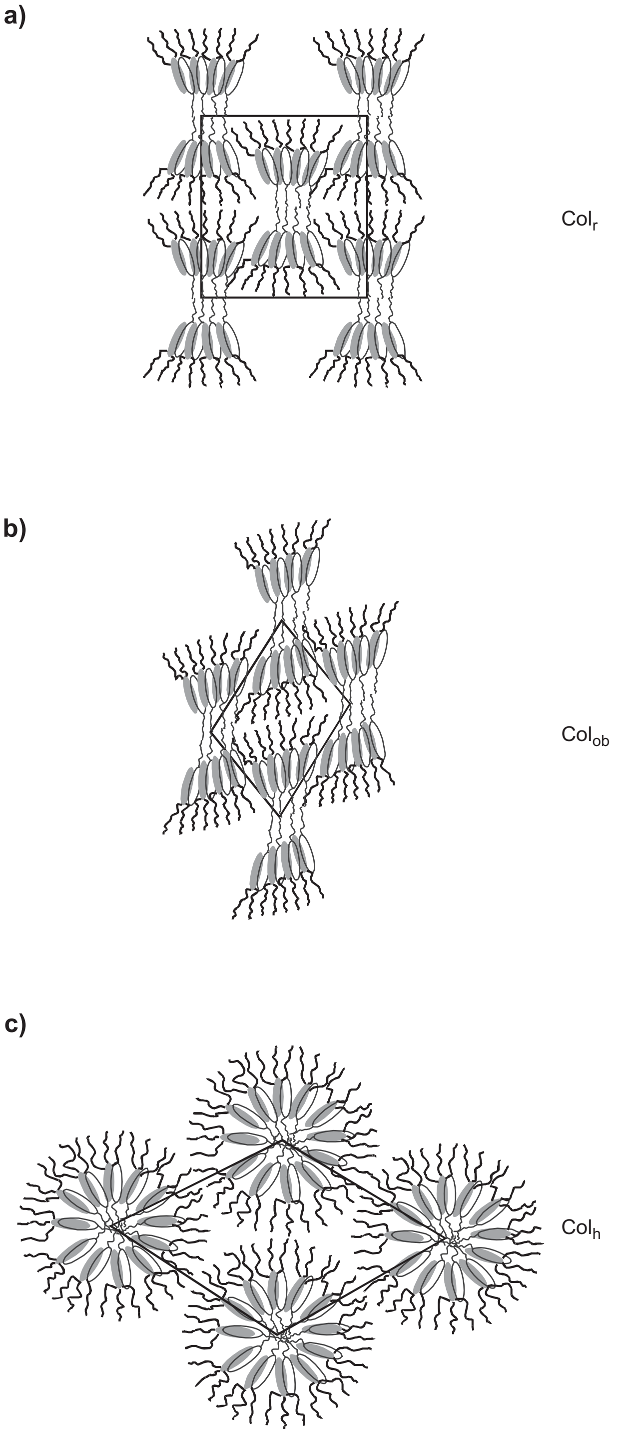


Figure 13. Schematic presentation of the molecular arrangements of the H-bonded heterodimers **3/13–15** in their columnar mesophases depending on the positions and the number of semiperfluorinated chains of the acid component. (a) Rectangular columnar organisation (Col$_\text{r}$) (two-dimensional *c2mm* space group) with the two-chain semiperfluorinated benzoic acid **15-[6,4]**. (b) Columnar mesophases with two-dimensional oblique lattice symmetry (Col$_\text{ob}$) of the H-bonded supermolecules **3/13**. (c) Hexagonal columnar (Col$_\text{h}$) phase with the three-chain semiperfluorinated benzoic acid **14**.

diameter of the columns, whereas the Col_r and Col_{ob} phases of equimolar compositions **3/13** and **3/15** involving the respective two-chain semiperfluorinated benzoic acids represent ribbon phases, which are built up by ribbon-like segments of a collapsed smectic layer structure.

The structures of the columnar and of the micellar phases of the equimolar melamine/benzoic acid compositions **3/13–15** are special, as aliphatic and semiperfluorinated segments are separated by the H-bonded aromatic cores. In this respect, the novel hydrogen-bonded heterodimers cannot be regarded as belonging to either a normal or a reversed phase type forming mesogen. In reversed phases (type 2; negative curvature of the polar/apolar interface) the stronger cohesive forces, such as hydrogen bonding, are located inside the aggregates. In normal phases (type 1) they are located in the outer sphere surrounding the aggregates (*38*).

The X-ray diffraction pattern obtained for the mesophases of the investigated (1:2) and (1:3) compositions of the triazine **3** with the two-chain acids **13** and **15** are characterised by scatterings in the small angle region with a ratio of their positions $1 : 3^{1/2}$, which confirms a hexagonal columnar organisation (Col_h).

CPK models reveal that docking of two or three molecules of the semiperfluorinated benzoic acids at the melamine core leads to H-bonded associates with a pronounced circular geometry (Figure 14(a)).

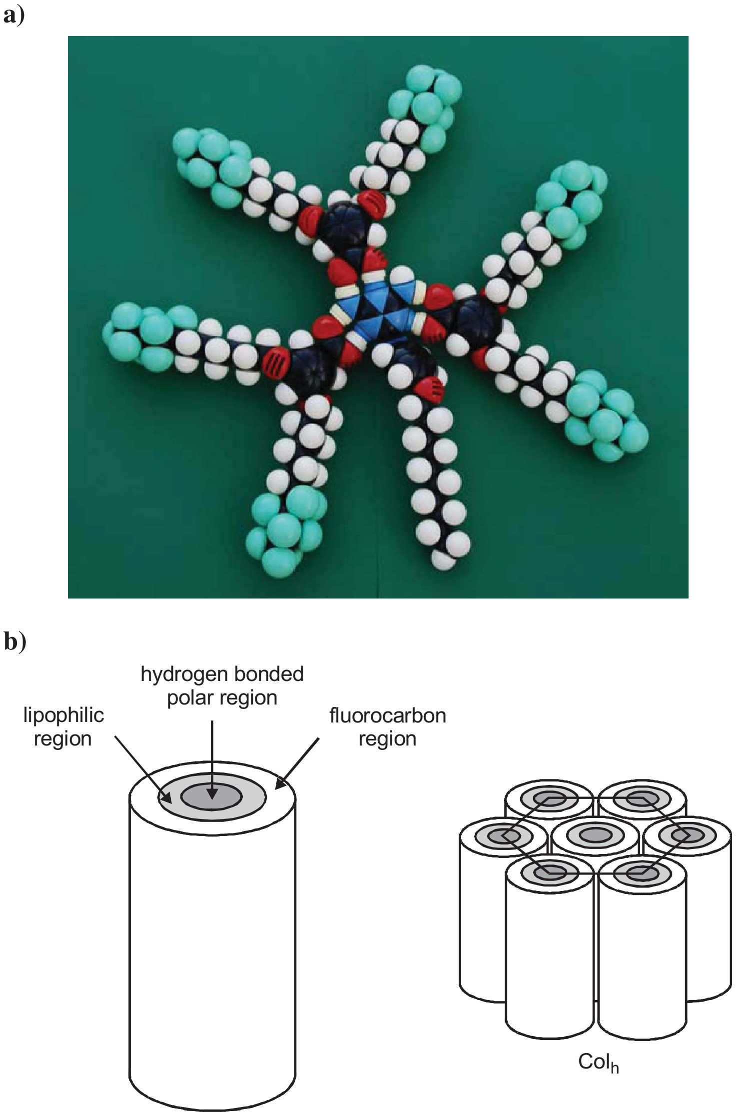


Figure 14. (a) CPK model of the hydrogen-bonded (1:3) complex of the melamine **3** with the two-chain semiperfluorinated benzoic acid **15-[6,4]**. (b) Core-shell model for the hexagonal columnar organisation of the melamine **3** in mixtures with two or three equivalents of the two-chain fluorinated benzoic acids **13** and **15**.

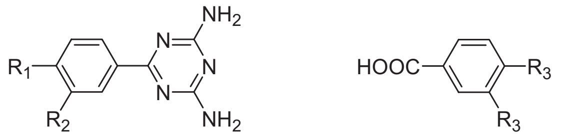
Extended cylindrical aggregates are formed, which consist of three distinct molecular regions, the polar hydrogen-bonded aromatic region located in the centre surrounded by the lipophilic alkyl segments and, finally, the fluorinated blocks distributed around the cylindrical core region. These cylinders organise into a hexagonal two-dimensional lattice, which allows the most efficient space filling (Figure 14(b)).

The hexagonal lattice constants of the 1:2 and 1:3 compositions **3/13,15** are considerably smaller compared with the intercolumnar distance obtained for the Col_h phase of the equimolar mixture **1/14**. For example, the hexagonal lattice parameter determined for the (1:3) mixture of the melamine **3** and the acid **15-[6,4]** amounts to 40 Å. This value corresponds well with the diameter of the disc-like (1:3) associate with all-*trans* conformations of the alkyl segments (44 Å) shown in Figure 14(a), if one takes into account the molten disordered state of the alkyl chains and the possibility of interdigitation of neighbouring molecules in the liquid crystalline state.

4. Two-fold amino substituted alkoxyphenyl-1,3,5-triazines

In a next step we omitted the secondary amino linking group between the triazine nucleus and the alkoxyphenyl moiety. The pure alkoxyphenyl substituted diamino-1,3,5-triazines **4** and **5** are only crystalline compounds. The thermal behaviour of the triazines **4** and **5** was investigated in mixtures with the two-chain semiperfluorinated benzoic acids **13-[n,m]** (Scheme 4) (*41*).

Again, at least a stoichiometric amount of the acids **13** is necessary to induce a thermotropic mesophase in binary mixtures with the triazines **4** and **5**. In Figure 15 the equimolar mixed systems of the triazines **4** and **5** with the benzoic acids **13-[6,4]** and **13-[4,6]** and the appropriate 1:1 complexes involving the decyloxyphenylmelamine **3** are compared.



4,5 **13–[n,m]**

Compound	R_1	R_2	R_3
4	$OC_{12}H_{25}$	H	
5	$OC_{10}H_{21}$	$OC_{10}H_{21}$	
13–[4,4]			$O(CH_2)_4C_4F_9$
13–[6,4]			$O(CH_2)_6C_4F_9$
13–[4,6]			$O(CH_2)_4C_6F_{13}$
13–[6,6]			$O(CH_2)_6C_6F_{13}$

Scheme 4. Alkoxyphenyl substituted diamino-1,3,5-triazines **4** and **5** investigated in mixtures with the two-chain partially fluorinated carboxylic acids **13-[n,m]**.

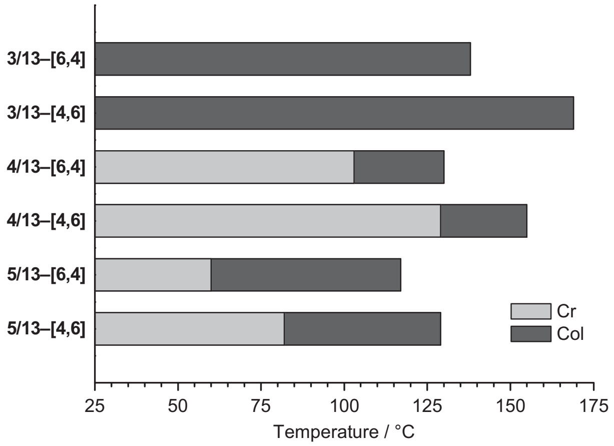


Figure 15. Comparison of the mesomorphic properties of 1:1 mixtures of the semiperfluorinated carboxylic acids **13-[6,4]** and **13-[4,6]** with the triazines **4** and **5** and with the melamine derivative **3**.

The direct coupling of the phenyl substituent to the triazine core leads to a remarkable decrease of the isotropisation temperatures. The tendency towards recrystallisation strongly increases and the mesophase ranges are reduced. It seems that this decrease in thermodynamic mesophase stability is associated with a gradual reduction of the intramolecular polarity gradient by removing the secondary amino group of the triazine component.

Furthermore, the melting and isotropisation temperatures of the two-chain triazine **5** mixed with the acids **13** are lower than those of the mixed 1:1 systems **4/13**. Obviously, grafting a second alkoxy chain to the triazine component increases the flexibility of the triazine/acid associates, leading to a decrease of the phase transition temperatures. On the other hand, the mixtures **5/13** show enlarged mesophase ranges in comparison with the 1:1 mixtures of the single-chain aminotriazine **4** with the acids **13-[n,m]**.

Chain variations of the homologous benzoic acids **13-[4,4]**, **13-[6,4]** and **13-[6,6]**, respectively, do not have a significant influence on the clearing temperatures of the appropriate equimolar mixtures. A considerable increase in mesophase stability can be achieved if the number of fluorinated carbon atoms of the chains exceeds the number of non-fluorinated carbons. The mixtures **4/13-[4,6]** and **5/13-[4,6]** both display enhanced melting and clearing temperatures compared with the other investigated 1:1 mixtures of compounds **4** and **5** with the partially fluorinated acids.

The equimolar mixtures **4/13-[4,4]** and **5/13-[6,4]** were investigated by X-ray diffraction (*41*). The

WAXS diffractogram of the 1:1 mixture **4/13-[4,4]** is characterised by a diffuse scattering in the wide-angle region around a Bragg angle of 8.9°. This value is between the values usually observed for pure aliphatic and perfluorinated chains (*42*, *43*) and indicates a mixed arrangement of the aliphatic and fluorinated moieties. The small angle reflections can be indexed on the basis of a two-dimensional rectangular unit cell with non-centred *p2gg* lattice symmetry. The lattice parameters amount to a = 68.5 Å and b = 36.9 Å.

The lattice constant b is slightly less than the maximum molecular length of heterodimers **4/13-[4,4]** with a rod-shaped H-bonded central core. The dimeric supermolecules **4/13** resemble the structure of tricatenar mesogens bearing two bulky fluorocarbon chains at one end and one slim alkyl chain at the other end of the calamitic core (*44*). The steric dipole arising from the pronounced taper shape is obviously strong enough to inhibit the segregation of the incompatible end groups and leads to antiparallel packing of the molecules with a sequence of aromatic and mixed fluoroaliphatic sub-layers (Figure 16(a)).

Interestingly, this antiparallel correlation of molecules is quite different from the molecular organisation of heterodimers of the structurally similar alkoxyphenylmelamine **3** with semiperfluorinated benzoic acids mentioned in the previous section. In that case, steric effects do not override the segregation of the different end-chains into different subspaces. Probably, additional hydrogen bonding, embracing the secondary amino function of the melamine and molecular recognition sites of the nitrogen heterocycle not involved in association with the acid components, contributes to the parallel arrangement of neighbouring melamine/acid heterodimers **3/13–15**.

Favourable dense packing arises for the aggregates **4/13** if the parallel-aligned rigid cores are shifted against each other. This arrangement corresponds to a smectic layer structure of the rod-shaped moieties, which are tilted against the normal layer. The mean lateral area of the terminal disordered mixed aliphatic/fluorinated regions is larger than that of the polar hydrogen-bonded regions, which causes the collapse of the smectic layers with formation of a ribbon phase.

It must, however, be noted that for geometric reasons the interruption of tilted smectic layers with the formation of infinite ribbons of parallel-aligned aromatic cores usually leads to columnar phases with a two-dimensional oblique lattice symmetry (*45*). A more detailed inspection of the molecular models reveals that the semiperfluorinated chains at the meta-position of the benzoic acid component are tilted by about 50° with respect to the long axis of the H-bonded rod-shaped cores. The outer p-alkoxy chains at the opposite position of the dimer form a tilt angle of about 20°. This imposes a steric asymmetry for the aggregates, which can be compensated for by an antiparallel arrangement of the ribbons that assemble to a rectangular columnar phase with two-dimensional *p2gg* lattice symmetry (Figure 16(b)).

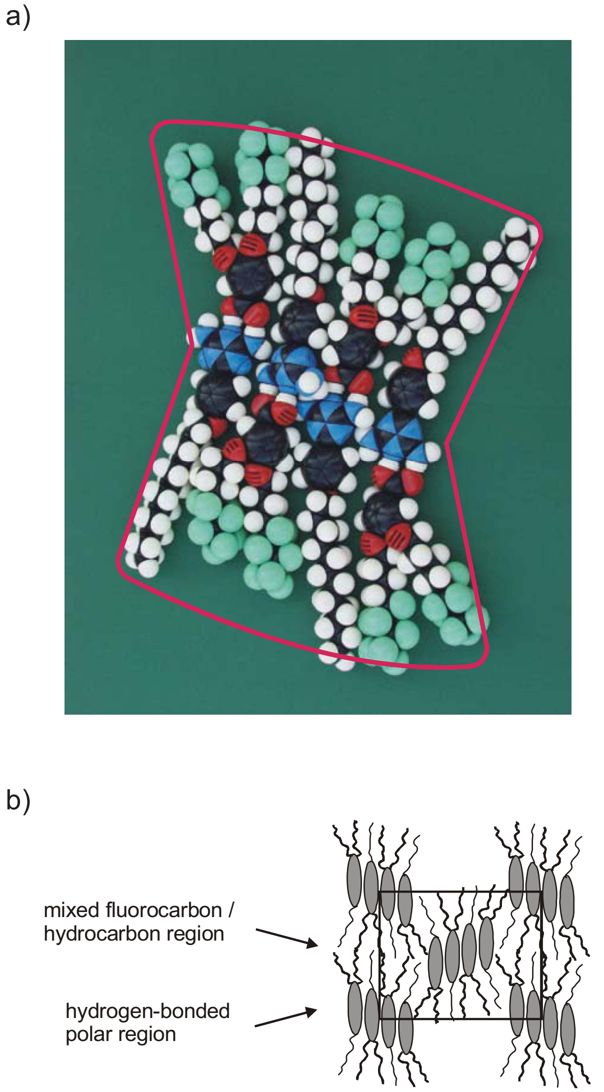


Figure 16. (a) CPK model showing an antiparallel arrangement of four dimers **4/13-[4,4]**. (b) Schematic presentation of the ribbon phase of equimolar hydrogen bonded complexes of the single chain triazine **4** with the fluorinated carboxylic acids **13-[n,m]** with a rectangular columnar (Col_r) organisation (two-dimensional *p2gg* space group). Distortions of the rigid cores within the smectic sub-layers are not considered.

The small angle reflections of the X-ray diffractogram obtained for the mesophase of the equimolar mixture **5/13-[6,4]** fit best by assuming a columnar structure with a two-dimensional oblique lattice (Col_{ob}). The resulting lattice parameters are a = 37.8 Å, b = 35.6 Å and γ = 116°. The wide-angle halo in the

X-ray diffraction is shifted to a lower angle compared with a pure alkyl halo, which confirms a mixing of the hydrocarbon and fluorocarbon tails.

One possible arrangement of heterodimers of the two-chain triazine **5** and the fluorinated acid **13-[6,4]** with an antiparallel organisation is shown in Figure 17(a). The closest packing again arises for a parallel alignment of the rod-shaped cores in a tilted smectic manner, whereby the cross-section of the semiperfluorinated chains still exceeds the cross-section area of the two alkyl chains. The incorporation of a second flexible alkyl tail into the aminotriazine component further increases the curvature of the terminal mixed alkyl/fluoroalkyl regions and, compared with the complementary dimers of the single-chain triazine **4** with the acids **13**, compensates for a steric dipole of the aggregates. Therefore, the collapse of the smectic layers results in a ribbon phase on a two-dimensional oblique lattice, as would be expected (Figure 17(b)).

Thus, it has to be emphasised that, independent of the number of alkoxy tails for heterodimers of both triazines **4** and **5**, the fluorophobic effect is in competition with steric effects due to the different size of the hydrocarbon and fluorocarbon chains leading to an antiparallel pairing of the H-bonded dimers. Tilting of the aromatic cores with respect to the normal layer cannot sufficiently reduce the steric frustration. The smectic layers break up into ribbon-like aggregates, which consist of segregated polar aromatic and mixed fluoroaliphatic regions. The ribbons organise to columnar mesophases.

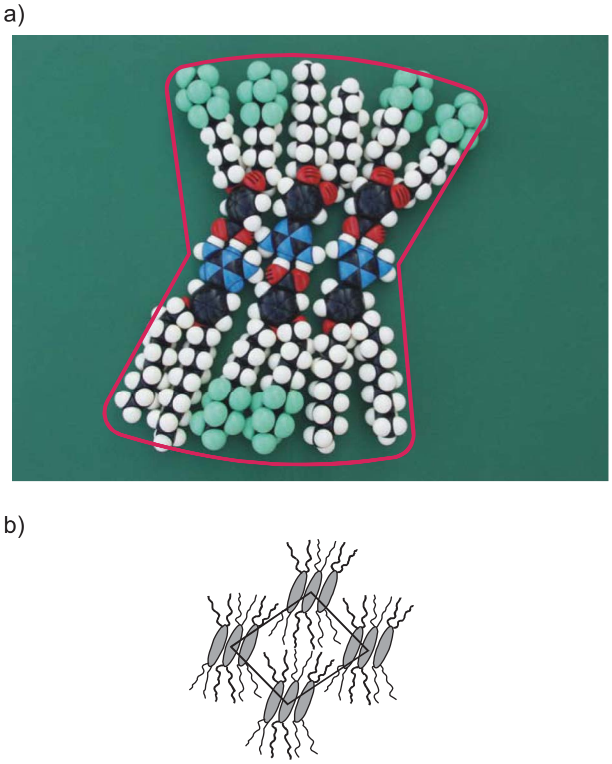


Figure 17. (a) CPK model showing three dimers **5/13-[6,4]**. The hydrogen-bonded rod-shaped cores are closely packed side-by-side and form a tilted smectic sub-layer. (b) Model for the molecular arrangement of the equimolar H-bonded supermolecules of the two-chain triazine **5** with the benzoic acids **13** in the columnar mesophases with two-dimensional oblique lattice symmetry (Col$_{ob}$).

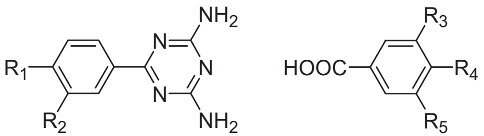
Even though the triazines **4** and **5** incorporate just two exocyclic amino groups, the functionalised nitrogen heterocycle allows for docking of up to three molecules of the acid component. The investigations of defined mixtures of the triazine **4** with two and three equivalents of the two-chain partially fluorinated benzoic acids **13** revealed that mesomorphic structure formation is not restricted to equimolar complementary compositions.

The 1:2 mixture **4/13-[6,4]** was investigated by X-ray scattering (*41*). The X-ray diffractogram displays (100) and (110) reflections in the small angle region with the ratio of the lattice spacings $d_{100}:d_{110} = 1:3^{1/2}$. This diffraction pattern is typical for a hexagonal columnar phase. The hexagonal lattice constant amounts to a_{hex} = 39.5 Å. This value is in good agreement with the maximum diameter (44 Å) of (1:2) aggregates with a circular geometry evaluated from CPK models. The triazine **1**, thus, forms H-bonded associations with two or three equivalents of the acids **13** with a pronounced circular shape. This means that the molecular topology is quite similar to that of apparent (1:2) and (1:3) aggregates of the melamine **3** with semiperfluorinated benzoic acids. The peripheral groups are randomly distributed around the polar hydrogen-bonded core, giving rise to radial symmetrical cylinders that form a columnar phase with two-dimensional hexagonal lattice symmetry.

5. Semiperfluorinated 1,3,5-triazine derivatives

In order to increase the intramolecular polarity gradient, we replaced the lipophilic alkyl groups of the diaminotriazine component by partially fluorinated chains. The one-chain and two-chain semiperfluorinated diamino-1,3,5-triazines **6** and **7** (Scheme 5) can be regarded as polyphilic three-block molecules composed of a polar amino substituted (hetero)aromatic rod-like core, a flexible lipophilic molecular segment and a fluorinated block.

The pure one-chain compounds **6-[4,4]** and **6-[6,4]**, incorporating the shorter fluorinated segment, exhibit a monotropic liquid crystalline phase. Elongation of the perfluoroalkyl chain length enhances the thermodynamic mesophase stability, and the diaminotriazines **6-[4,6]** and **6-[6,6]** form an enantiotropic phase



6,7 **13–16**

compound	R_1	R_2	R_3	R_4	R_5
6–[n,m]	$O(CH_2)_nC_mF_{2m+1}$	H			
7–[n,m]	$O(CH_2)_nC_mF_{2m+1}$	$O(CH_2)_nC_mF_{2m+1}$			
13–[n,m]			$O(CH_2)_nC_mF_{2m+1}$	$O(CH_2)_nC_mF_{2m+1}$	H
14–[n,m]			$O(CH_2)_nC_mF_{2m+1}$	$O(CH_2)_nC_mF_{2m+1}$	$O(CH_2)_nC_mF_{2m+1}$
15–[n,m]			$O(CH_2)_nC_mF_{2m+1}$	H	$O(CH_2)_nC_mF_{2m+1}$
16–[n,m]			H	$O(CH_2)_nC_mF_{2m+1}$	H

Scheme 5. Semiperfluorinated diamino-1,3,5-triazines **6** and **7** and complementary partially fluorinated benzoic acids **13–16**.

(*46*). X-ray scattering confirms a lamellar (SmA_d) phase for the single-chain triazines. The molecules are antiparallelly aligned and shifted against each other so that the polar aromatic parts are interdigitated. The perfluorinated chains build up a separate sub-layer.

The two-chain semiperfluorinated triazine compound **7-[4,4]** forms a highly viscous optically isotropic cubic phase above the melting point. Mixing of structurally related compounds, which form different mesophase morphologies as pure compounds, provides a powerful tool to distinguish between different types of cubic mesophases (*3*, *35*). We applied this method to binary mixtures consisting of the two-chain triazine **7-[4,4]** and the partially fluorinated one-chain compound **6-[4,6]**.

A new birefringent mesophase is induced within a broad concentration range between the SmA phase and the cubic phase of the pure compounds **6-[4,6]** and **7-[4,4]**, respectively. The optical textures are typical for a hexagonal columnar (Col_h) liquid crystalline phase built up of cylindrical aggregates. An additional optically isotropic phase appears in regions with a high concentration of compound **6-[4,6]**. The high viscosity again points to a cubic mesophase.

The polar/apolar interface curvature becomes increasingly negative on increasing the content of the two-chain semiperfluorinated triazine **7-[4,4]**. Since the induced cubic phase occurs as an intermediate between the SmA phase and the induced inverted hexagonal columnar (Col_{h2}) mesophase, in analogy to lyotropic systems (*47*), this cubic phase is a reversed bicontinuous cubic phase (Cub_{V2}) consisting of two interwoven, but non-connected networks of branched cylinders formed by the polar regions within the apolar continuum of the semiperfluorinated chains.

The aggregates forming the cubic phase of **7-[4,4]** must be more strongly curved than the cylindrical aggregates in the induced columnar phase. The cubic mesophase of the pure compound **7-[4,4]**, therefore, is a reverse discontinuous micellar cubic phase (type-2-phase; Cub_{I2}), built up by closed spheroidic inverted micelles of the polar parts surrounded by the non-polar fluorinated chains.

The phase sequence and structure of the thermotropic mesophase morphologies found for the binary mixtures **6-[4,6]/7-[4,4]** are shown schematically in Figure 18. The phase sequence covers the whole range of inverted lyotropic mesophases found for

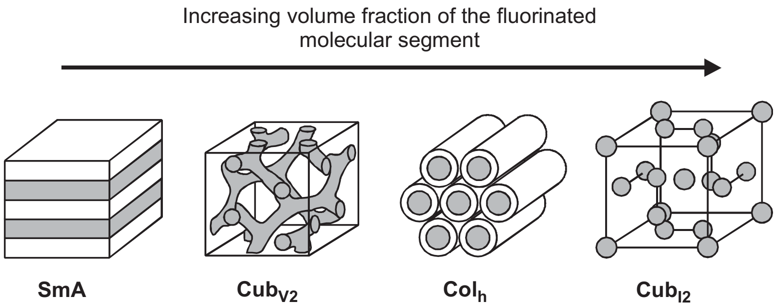


Figure 18. Schematic presentation of the sequence of mesophase morphologies of binary mixed systems **6/7** depending on the volume fractions of the semiperfluorinated molecular segments.

amphiphile/solvent systems depending on the solvent content and temperature. It is realised here without any solvent by mixing of two structurally related low molar mass molecules, which exhibit different mesophase morphologies as pure compounds, hence by gradually changing the average volume fractions of incompatible molecular fragments.

The thermal properties of the diaminotriazines **6** and **7** were investigated in mixtures with the semiperfluorinated benzoic acids **13–16** (Scheme 5). The number and the positions of the fluorinated chains of the carboxylic acids were systematically modified.

Surprisingly, equimolar mixed systems of the one-chain triazines **6** with the 4-fluoroalkoxybenzoic acids **16** are non-mesomorphic. The investigated complexes **6/16** show a direct transition to the isotropic liquid at temperatures quite different from the phase transition temperatures of the single components. On the one hand, the SmA phases of the triazines **6**, as well as the SmC phases of the pure benzoic acids **16**, disappear due to heterodimerisation of the molecules via hydrogen bonding. On the other hand, it seems that the intramolecular contrast of the heterodimers **6/16** is not sufficient to force mesomorphic structure formation.

Incorporation of at least a second partially fluorinated fragment into one of the complementary molecular species produces liquid crystallinity. The phase transition temperatures of the selected appropriate 1:1 compositions are given in Table 1.

As evident from X-ray investigations, equimolar mixtures of the single-chain triazines **6** with the two-fold semiperfluorinated acids **13** and, conversely, of the two-chain triazine **7** with the p-fluoroalkoxybenzoic acids **16**, display a rectangular columnar phase with a centred *c2mm* lattice symmetry.

Obviously, the average molecular topology of the three-chain H-bonded supermolecules is the same independent of whether the two fluorinated tails are grafted to the 3,4-positions of the phenyl ring of the triazine or the benzoic acid component. One can envisage that this is similar for dimers comprising the structurally related non-fluorinated one-chain triazine **4**. Favourable dense packing within the mesophase is achieved by an antiparallel assembly with close alignment of the rod-shaped (hetero)aromatic cores (Figure 19). The antagonisting parts of the molecules segregate in different sub-layers. The bulkiness of the fluorinated end-chains inhibits a lamellar arrangement and the layer fragments organise to a columnar phase composed of ribbons.

Thereby, the replacement of an alkoxy chain of the heterodimers by a partially fluorinated segment equalises the outer sphere of the ribbons. In this way, increasing the symmetry of the ribbon shape gives rise to a change of the two-dimensional space group from *p2gg* (see heterodimers with the alkoxyphenyltriazine **4**) to *c2mm*.

Equimolar compositions of the single-chain triazine **6** with benzoic acids **14** and **15** display a columnar mesophase with oblique two-dimensional lattice symmetry (Table 1). Attaching two fluorinated tails at the 3,5-positions of the benzoic acid, as well as the incorporation of a third semiperfluorinated chain into the acid component, leads to an increase of the space requirement of the fluorinated region at one terminus of the H-bonded heterodimers. The enlarged cross-sectional area of the terminal fluorinated blocks of antiparallel oriented dimers resulting from the change of the substitution pattern of the acid component is balanced by a change of the two-dimensional lattice symmetry from rectangular to oblique.

As a next step towards modifying the molecular shape of the triazine/acid dimers, we attached a second partially-fluorinated chain to the triazine component. The interface curvature is further increased in the case of (1:1) mixtures of the semiperfluorinated triazine **7**

Table 1. Phase transition temperatures (°C) and lattice parameters (Å) of selected equimolar mixtures of the phenyl-modified diaminotriazines **6** and **7** with the semiperfluorinated benzoic acid **13–16**.

Mixture	Cr		Phase type		Iso	a	b	γ
6-[4,6]/13-[4,6]	•	79.5 (5.9)	Col_r	161.5 (2.8)	•	66.6	44.6	
6-[4,6]/13-[6,6]	•	101.1 (11.2)	Col_r	170.9 (1.9)	•	59.2	48.6	
6-[6,4]/13-[6,4]	•	133.4 (6.6)	Col_r	150.4 (2.3)	•	59.0	42.5	
7-[4,4]/16-[4,4]	•	78.5 (5.8)	Col_r	142.5 (2.6)	•	58.1	42.8	
7-[4,4]/16-[4,6]	•	86.4 (10.4)	Col_r	164.1 (2.8)	•	56.9	44.1	
6-[4,6]/14-[4,6]	•	43.1 (1.7)	Col_{ob}	129.8 (2.3)	•	47.8	36.4	67.6
6-[6,4]/15-[4,6]	•	72.2 (2.2)	Col_{ob}	143.6 (3.2)	•	48.3	40.4	68.4
7-[4,4]/13-[6,4]	–		Cub	80.3 (1.4)	•			
7-[4,4]/13-[4,6]	–		Cub	123.7 (0.5)	•			
7-[4,4]/15-[6,4]	–		Cub	81.1 (1.9)	•			
7-[4,4]/14-[4,6]	–		Cub	104.8 (0.6)	•			

Cr: crystalline; Col_r: rectangular columnar; Col_{ob}: columnar, oblique lattice; Cub: cubic; Iso: isotropic.

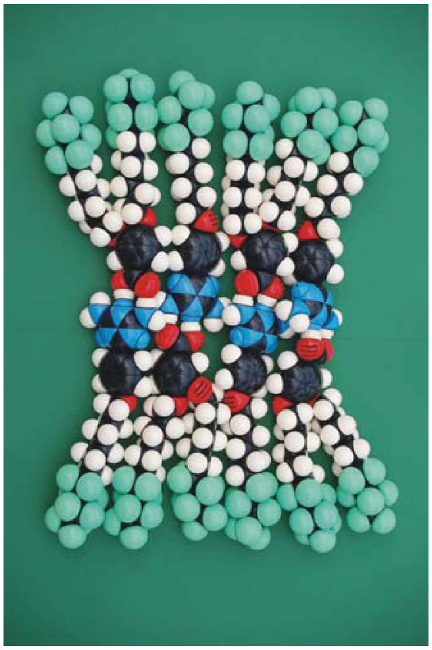


Figure 19. CPK model of four hydrogen-bonded dimers **6-[6,4]/13-[6,4]** with antiparallel alignment of the rod-shaped central polar cores.

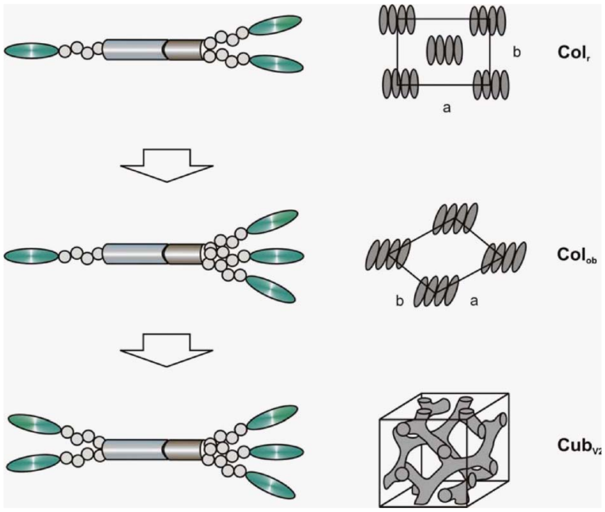


Figure 20. Mesophase morphologies of hydrogen-bonded heterodimers of phenyltriazines **6** and **7** with fluorinated benzoic acids depending on the space requirement of the partially fluorinated molecular fragments.

with the two-chain and three-chain acids **13–15**. As a consequence, heterodimers **7** with the benzoic acids **13–15** exhibit a cubic phase. If one considers that the rectangular columnar phases of the 1:1 complexes **6/13** and **7/16** and the Col$_{ob}$ phases of **6/14,15** are ribbon phases, consisting of fragments of layers, and in strong analogy to polycatenar mesogens (*48*), the cubic phases should have a bicontinuous interwoven network structure (Cub$_{V2}$), probably built up by ribbons.

Figure 20 sketches the mesophase structures of equimolar mixtures of the triazines **6** and **7**, with the benzoic acids **13–16**, as a function of the number of terminal fluorinated tails attached to the polar heterodimeric rod-like core.

6. Biphenyl substituted diamino-1,3,5-triazines

In the next step we elongated the rod-shaped aromatic core of the amino substituted aryltriazine component to further increase the intramolecular contrast of incompatible counterparts. The mesomorphic properties of the two-fold amino-substituted 1,3,5-triazines **8** and **9**, grafted with either one semiperfluorinated alkoxy segment or with two lipophilic alkoxy tails to the heterocyclic core via a biphenyl moiety, were investigated in mixtures with the two-chain and three-chain partially fluorinated benzoic acids **13-[4,6]** and **14-[4,6]** (Scheme 6) (*49*).

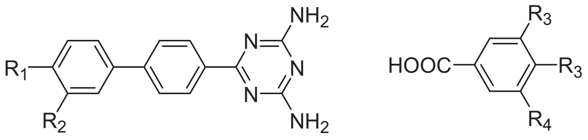
The 1,3,5-triazine **8**, fitted with one fluoroalkoxy segment at the terminus of the biphenyl moiety, displays an enantiotropic smectic A mesophase. Interestingly, the phenyl substituted analogue **6-[4,4]** with the same semiperfluoroalkoxy chain forms only a monotropic SmA phase (*46*). A bilayer structure with intercalation of the polar aromatic cores was proposed (*49*), which is similar to the lamellar SmA$_d$ phases formed by the structurally related semiperfluorinated aminotriazines **6-[n,m]** involving just a single phenyl ring.

The two-chain decyloxy modified triazine **9** was reported to exhibit a hexagonal columnar (Col$_h$) mesophase (*50*). This behaviour was discussed in terms of the formation of hydrogen-bonded hexameric rosettes with a disc-like shape, which assemble to parallel aligned columns on a hexagonal two-dimensional lattice.

Hence, the incorporation of a second phenyl fragment at the heterocyclic triazine nucleus influences the balance of intramolecular contrast, such that a mesophase stabilisation (compound **8**) and even mesophase induction (compound **9**) results compared with the chemically familiar diaminotriazines **6** and **5**, respectively, with shorter only phenyl substituted rigid aromatic core.

The investigated 1:1 mixtures of the triazines **8** and **9** with the partially fluorinated benzoic acid **13-[4,6]** display a thermotropic mesophase. The isotropisation temperatures are significantly higher than for equimolar mixed systems of the structurally related phenyl modified diaminotriazines **6** and **5** with the carboxylic acids **13**, which again confirms the stabilising effect of the biphenyl moiety.

A rectangular columnar phase with a centred *c2mm* plain group was confirmed for the 1:1 mixture



8,9

13,14

Compound	R_1	R_2	R_3	R_4	R_5
8	$O(CH_2)_4C_4F_9$	H			
9	$OC_{10}H_{21}$	$OC_{10}H_{21}$			
13–[4,6]			$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$	H
14–[4,6]			$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$

Scheme 6. Biphenyl substituted diamino-1,3,5-triazines **8** and **9** investigated in mixtures with the two-chain and three-chain semiperfluorinated benzoic acids **13-[4,6]** and **14-[4,6]**.

of the semiperfluorinated triazine **8** with the two-chain benzoic acid **13** by X-ray scattering. The lattice parameters are a = 53.8 Å and b = 35.5 Å. The $\mathrm{Col_r}$ phase results from the collapse of a smectic layer structure into ribbons (*49*). Thus, replacing the phenyl ring of the semiperfluorinated triazine component by a rod-like biphenyl unit does not essentially effect the molecular organisation of appropriate heterodimers with 3,4-difluoroalkoxy benzoic acids.

The melting and clearing temperatures of 1:3 mixtures of compounds **8** and **9** with the semiperfluorinated benzoic acids **13** and **14** are lower in comparison to the appropriate 1:1 mixed systems. The optical textures of the (1:3) complexes with the two-chain partially fluorinated carboxylic acid **13** are typical for a columnar mesophase.

The X-ray diffraction pattern of the (1:3) binary mixture of the fluorinated diaminotriazine **8** with the two-chain acid **13** gives evidence for a columnar mesophase with a simple non-centred rectangular unit cell with *P2m* symmetry. This $\mathrm{Col_r}$ phase type is the same as that found for heterodimers of the six-fold alkoxy substituted triarylmelamines **1** with the 3,4-dialkoxybenzoic acids **12** (see Scheme 1). In the case of triazine **8**, however, the elongated biphenyl core substituted with a single semiperfluorinated chain should mainly contribute to a non-circular shape of the hydrogen-bonded central core of the 1:3 associates **8/13**, turning the partially fluorinated peripheral tails towards an unequal distribution around the core region. The resulting ellipsoidal aggregates build up the columnar phase with the *P2m* space group.

The wide angle X-ray diffractogram obtained for the mesophase of the (1:3) complex **9/13-[4,6]** displays (100) and (110) reflections in the small angle region, with a reciprocal spacing ratio of $1{:}\sqrt{2}$, which confirms a columnar phase with a square lattice (*p4mm*). All further small angle reflections of higher order can be indexed accordingly (*49*).

Replacing the single partially fluorinated segment at the biphenyl fragment of the triazine component by two lipophilic alkyl tails partly compensates for the asymmetric shape of the central H-bonded core region of the 1:3 aggregates with the two-chain acid **13**. The cross-sectional shape of the H-bonded 1:3 complex between the triazine **9** and the two-chain partially fluorinated benzoic acid **13** should be a square with rounded corners (*51*) (Figure 21). Therefore, the columns in the $\mathrm{Col_{sq}}$ phase have a more pronounced square-like shape instead of an elliptical cross-sectional shape. This enhances the symmetry and gives rise to the change in the lattice type. Hence, the $\mathrm{Col_{sq}}$ phase of the (1:3) mixed system **9/13** can be regarded as an intermediate stage in the transition from a rectangular to a hexagonal two-dimensional lattice.

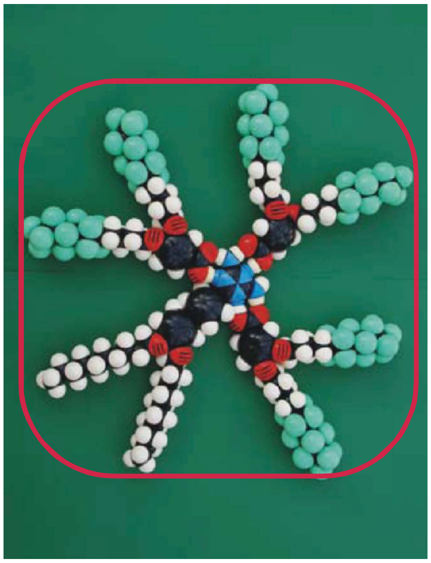


Figure 21. CPK model of alkoxy substituted biphenyltriazine **9** associated with three equivalents of the two-chain partially fluorinated benzoic acid **13-[4,6]** via hydrogen bonding.

Considering the almost stretched conformations of the alkyl segments as shown in Figure 21, the length of each side of the square is ca. 45 Å. This value is very close to the measured lattice parameter of 43.7 Å.

The binary 1:3 mixtures of the amino substituted triazines **8** and **9** with the three-chain semiperfluorinated benzoic acid **14-[4,6]** exhibit a cubic phase, as is evident from optical polarising microscopy and calorimetric investigations. Increasing the number of semiperfluorinated chains of the acid component increases the interfacial curvature. Therefore, the cubic phases of the 1:3 compositions **8,9/14** should be inverse discontinuous cubic phases.

The phase sequence and structure of the thermotropic mesophase morphologies found for binary mixed systems of the biphenyl substituted diaminotriazines **8** and **9**, with the semiperfluorinated benzoic acids **13-[4,6]** and **14-[4,6]** at 1:1 and 1:3 molar ratios, are shown schematically in Figure 22. The phase sequence is the consequence of the onset and successive increase of the aromatic-(fluoro)aliphatic interface curvature by increasing the volume fraction of the (semiperfluorinated) alkyl chains.

7. Conclusions

Complex mesophase morphologies were obtained by careful molecular design. This was achieved with non-covalently associated three-block molecules comprising distinct polar, lipophilic and fluorinated fragments.

The amino functionalised nitrogen heterocycle of the 1,3,5-triazines presented here allows for molecular recognition with complementary benzoic acids. Thereby, the mesomorphic structures can be tailored by the cooperative interplay of various effects. The molar content of the two components defines the molecular geometry of the H-bonded polar central core. The interface curvature of the assembled aggregates is controlled by the volume fractions of peripheral (semiperfluorinated) tails. As a third molecular component, the substitution pattern of the triazines (i.e., the number of aryl moieties and the topology of connection) accounts for the tailoring mesophase

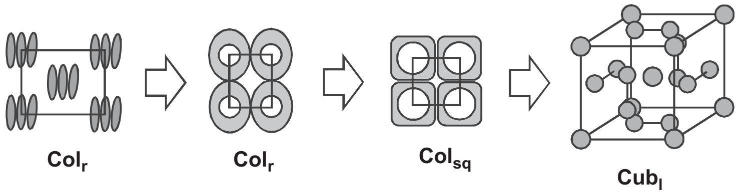


Figure 22. Mesophase morphologies of the H-bonded complexes of triazines **8** and **9** with the partially fluorinated benzoic acids **13** and **14** depending on the volume fractions of the pendant (semiperfluorinated) alkoxy tails.

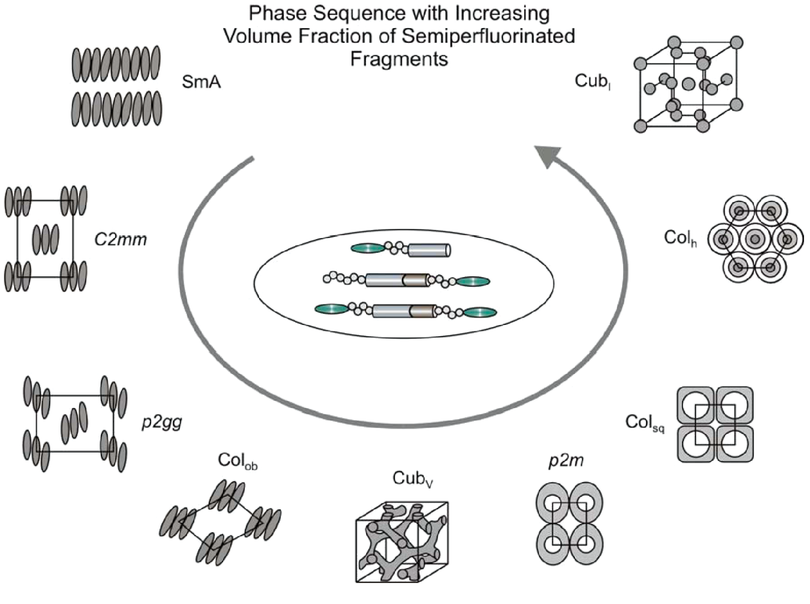


Figure 23. Liquid crystalline phases formed by amino substituted 1,3,5-triazines and by their hydrogen bonded complexes with complementary benzoic acids with respect to the cross-sectional area of peripheral (semiperfluorinated) chains.

morphologies of the binary complementary mixed systems. Thereby, in certain cases, a suitable substitution pattern provides an intramolecular contrast that is sufficient to generate liquid crystallinity for the triazines by themselves.

Thus, as shown in Figure 23, the phase sequence of the triazines, and their H-bonded associates with benzoic acids, covers the complete range from lamellar to micellar cubic. The transition occurs via columnar phases with various two-dimensional lattices as well as, in certain cases, additionally comprising an intermediary three-dimensional bicontinuous cubic phase.

Hence, the competitive combination of polar–non-polar microsegregation through molecular recognition, along with adjusting the molecular topology by the space requirement of lipophilic and fluorinated segments, provides an exciting and powerful approach towards tailoring thermotropic mesophase morphologies.

Acknowledgement

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