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Mesomorphic complexes through hydrogen bonding between alkoxy-substituted triarylmelamines and semiperfluorinated benzoic acids

Alexandra Kohlmeier[a]; Dietmar Janietz[a]
[a] Fraunhofer Institute for Applied Polymer Research, D-14476 Potsdam-Golm, Germany

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Mesomorphic complexes through hydrogen bonding between alkoxy-substituted triarylmelamines and semiperfluorinated benzoic acids

ALEXANDRA KOHLMEIER and DIETMAR JANIETZ*
Fraunhofer Institute for Applied Polymer Research, Geiselberstr. 69, D-14476 Potsdam-Golm, Germany

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The thermal behaviour of two 2,4,6-triarylamino-1,3,5-triazines carrying either three or six peripheral alkoxy chains have been investigated in binary mixtures with two-chain and three- chain partially fluorinated benzoic acids by means of polarizing microscopy, differential scanning calorimetry and X-ray scattering. The melamines form hydrogen-bonded aggregates with the complementary carboxylic acids. Each investigated equimolar mixture exhibits a hexagonal columnar mesophase. In the case of the six-fold alkoxy-modified triazine the individual columns are built up by descrete hetero-dimers with a circular cross-sectional shape. The segregation of fluorinated from lipophilic side chain regions leads to a superstructure within the hexagonal lattice. The hexagonal columnar phases of 1:1 compositions of the triazine, incorporating just three aliphatic chains with the semiperfluorinated benzoic acids, are formed by pairs of H-bonded dimeric supermolecules.

1. Introduction

The formation of thermotropic and lyotropic liquid crystalline phases results mainly from nanoscale segregation of incompatible moleculer segments [1, 2]. Thereby, the mesophase morphologies (lamellar, columnar or cubic) are predominantly determined by the volume fractions of the chemically distinct molecular fragments, such as rigid/flexible or polar/non-polar, which separate into different subspaces.

The molecular polarity gradient can be reinforced by introducing highly polar hydrogen bonding between complementary molecular species [3]. Thermotropic mesophases may result, even if the constituent components are non-mesomorphic alone [4–6].

We describe six-fold alkoxy substituted 2,4,6-triarylamino-1,3,5-triazines which organize into columnar stacks of molecules [7]. The mesomorphic structure formation arises from the microsegregation of the polar triphenylmelamine cores from the peripheral lipophilic chains, along with a flat conformation of the core region that becomes favoured during the process of self-organization [8]. The columnar mesophases of the triarylmelamines can be controlled by hydrogen bonding with alkoxy-substituted benzoic acids [9, 10]. The number and position of the alkoxy chains of the acid component defines the cross-sectional shape of cylindrical aggregates of the aminotriazine – benzoic acid complexes and, therefore, the two-dimensional lattice symmetry, hexagonal or rectangular.

A further approach towards increasing the intramolecular polarity gradient arises from replacing hydrocarbon chains by semiperfluorinated segments. (Semi) perfluorinated molecular fragments have been successfully introduced into calamitic [11], columnar [12] and polycatenar [13] mesogens as well as in liquid crystals without a pronounced anisometric molecular shape [14, 15]. It was shown that the fluorophobic effect may lead to a significant stabilization and even to modifications of smectic, columnar and cubic mesophases.

Reports regarding supramolecular mesogens combining hydrogen bonding between two different components and a fluorophobic effect are rather limited. Mixed systems of single-chain fluorinated acids with pyridine derivatives were reported to exhibit smectic or cubic mesophases [16–20]. Incorporation of a second semiperfluorinated chain into the acid component leads to the formation of columnar phases [20].

Recently we described supramolecular mesogens with double hydrogen bonding between alkoxy substituted 2,4-diamino-6-phenyl-1,3,5-triazines and two-chain semiperfluorinated benzoic acids. The H-bonded complexes organize into columnar phases with rectangular, oblique or hexagonal lattice symmetry, depending on the number of alkoxy chains of the triazine and on the molar content of the complementary components [21].

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

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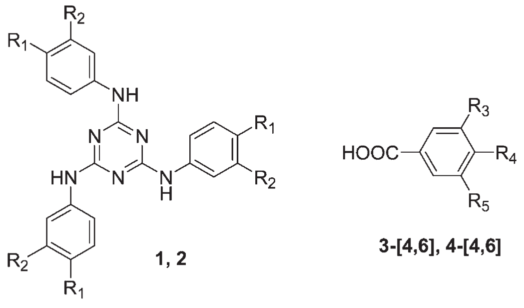

1, 2

3-[4,6], 4-[4,6]

Compound	R_1	R_2	R_3	R_4	R_5
1	$OC_{10}H_{21}$	$OC_{10}H_{21}$			
2	$OC_{12}H_{25}$	H			
3-[4,6]			$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$	H
4-[4,6]			$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$	$O(CH_2)_4C_6F_{13}$

Scheme 1. Chemical structures of the 2,4,6-triarylamino-1,3,5-triazines **1** and **2** and of the complementary semiperfluorinated benzoic acids **3** and **4**.

In this paper we report mesomorphic structure formation in the triarylmelamines **1** and **2**, differing with respect to the number of alkoxy chains grafted onto the molecular periphery, in mixtures with the two-chain and three-chain partially fluorinated benzoic acids **3** and **4** (Scheme 1).

2. Materials and methods

The 2,4,6-triarylamino-1,3,5-triazines **1** and **2** were obtained by reaction of cyanuric chloride with the appropriate alkoxy-substituted anilines as described previously [7, 22]. The semiperfluorinated benzoic acids **3** and **4** were prepared by etherification of the respective ethyl hydroxybenzoates with 1-bromo-1H,1H,2H,2H,3H,3H,4H,4H-perfluorodecane using potassium carbonate as the base followed by basic ester cleavage [23]. The mixtures of the triazines **1**, and **2** with the benzoic acids **3** and **4** were prepared by dissolving the components separately in THF, mixing the solutions and evaporating the solvent. Further investigations were performed after annealing the residues in the isotropic state. Texture observations were made using an Olympus BHS polarizing microscope in conjunction with a Linkam TMH/S 600 hot stage and a Linkam TP 92 control unit. Photomicrographs were obtained with an Olympus E20 digital mirror reflex camera. Calorimetric investigations were performed with a Netzsch DSC 200. Wide angle X-ray scattering (CuK_α) was carried out with a Nenius PDS 120 (Bruker) equipped with a detector from Inel.

3. Results and discussion

The six-fold alkoxy substituted triarylmelamine **1** exhibits an enantiotropic hexagonal columnar (Col_h) mesophase [7]. The hexagonal lattice constant a_{hex} amounts to 30.2 Å. The triazine **2** with only three peripheral alkoxy chains is non-mesomorphic in its pure state. The two-chain semiperfluorinated carboxylic acid **3** forms a monotropic hexagonal columnar phase. The benzoic acid **4** grafted with three partially fluorinated chains displays an enantiotropic Col_h phase. The columnar phases are related to the formation of descrete benzoic acid dimers via hydrogen bonding [23]. The phase transition temperatures of the pure compounds **1**–**4** are summarized in table 1.

Binary mixtures of both triarylaminotriazines **1** and **2** with either of the semiperfluorinated carboxylic acids **3** and **4**, show complete miscibility with the formation of an enantiotropic liquid crystalline phase at an equimolar content of the two complementary components. The phase transition temperatures of the respective mixtures are given in table 2.

All the investigated equimolar mixtures show enlarged mesophase ranges compared with the pure compounds, and a significant increase in the isotropization temperature. The clearing temperatures of the

Table 1. Phase transition data of the pure compounds **1**–**4** from DSC, second heating at 10 K min^{-1}; phase transition enthalpies (kJ mol^{-1}) in parentheses. Cr=crystalline; Col_h= hexagonal columnar; I=isotropic.

Compound	Cr		Col		I
1	•	73.2 (92.3)[a]	•	89.8 (2.9)	•
2	•	105.2 (57.2)			•
3	•	115.7 (37.6)	•	[102.0 (1.6)][b]	•
4	•	51.0 (7.1)	•	81.1 (2.7)	•

[a] Strong tendency to supercool; values obtained from 1st heating scan. [b] Monotropic phase transition.

Table 2. Phase transition temperatures (°C) of equimolar compositions of the alkoxy-substituted triarylmelamines **1** and **2** with the semiperfluorinated benzoic acids **3** and **4** from DSC, second heating at 10 K min^{-1}; phase transition enthalpies (kJ mol^{-1}) in parentheses. Cr=crystalline; Col$_h$= hexagonal columnar; I=isotropic.

Mixture	Cr		Col$_h$		I	a_{hex}
1/3-[4,6]	—		•	114.0 (3.5)	•	36.4 Å
1/4-[4,6]	—		•	124.4 (8.3)	•	36.0 Å
2/3-[4,6]	•	68.0 (20.8)	•	131.0 (5.7)	•	40.3 Å
2/4-[4,6]	•	67.5 (17.6)	•	162.1 (9.8)	•	39.8 Å

six-chain triazine **1** mixed with the acids **3** and **4** are lower than those of the 1:1 mixed **2/3**,**4** systems. Clearly, an increase in the number of alkoxy tails in the triazine component increases the flexibility of the triazine/acid associates, leading to a decrease in the phase transition temperatures.

On the other hand, the mixed systems of the melamines **1** and **2** with the three-chain benzoic acid **4** show higher isotropization temperatures in comparison with the 1:1 mixtures with the two-chain semiperfluorinated carboxylic acid **3**. Thus, an increase in the number of fluorinated chains of the acid component leads to an enhanced thermodynamic mesophase stability of the triazine/benzoic acid systems.

No crystallization is observed for the 1:1 compositions involving the triazine **1** grafted with six alkoxy chains, while the equivalent complexes of the three-fold dodecyloxy-substituted melamine **2** with the partially fluorinated carboxylic acids show a pronounced tendency towards crystallization.

The optical textures of all the investigated melamine/benzoic acid complexes are characterized by regions with broken spherulites, mosaic-like domains and pseudoisotropic areas containing birefringent filaments (figure 1). These textures are typical for a hexagonal columnar (Col$_h$) mesophase.

Figure 2 shows the X-ray diffractogram obtained for the mesophase of the equimolar complex of the triazine **1**, bearing six terminal chains, with the three-chain benzoic acid **4-[4,6]**. The X-ray pattern is characterized by the appearance of a set of reflections in the small angle region. The maxima can be assigned to (1 0 0), (1 1 0), (2 0 0), (2 1 0) and (3 0 0) reflections with a reciprocal spacing ratio of $1{:}\sqrt{3}{:}2{:}\sqrt{7}{:}3$. This is unambiguously characteristic for a hexagonal columnar phase, which is in accordance with the phase assignment made by polarizing microscopy.

IR-spectroscopic investigations have shown that association of complementary benzoic acids and six-fold alkoxy-modified triarylmelamine molecules is related to double-hydrogen bonding between the carboxylic group and the nitrogen heterocycle substituted with secondary amino groups, leading to descrete hetero-dimers [9] (figure 3).

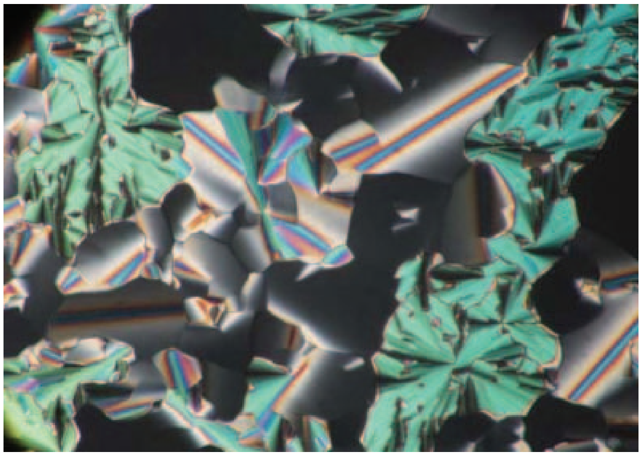

Figure 1. Optical photomicrograph of the Col$_h$ mesophase of the equimolar mixed system **2/4-[4,6]** at 115°C.

The number of dimeric **1-3[4,6]** and **1-4[4,6]** supermolecules in the unit cell was evaluated according to $n = V_{cell}/V_{mol}$. The cell volume (V_{cell}) was calculated by considering the hexagonal lattice constants obtained from X-ray observations (table 2) and by assuming a height of 4.5 Å [21, 24]. The molecular volume (V_{mol}) was obtained by using volume increments [25]. The calculations clearly give evidence that there is one dimeric supermolecule per unit cell.

Figure 4 shows a CPK model of the H-bonded 1:1 complex between the melamine **1** and the three-chain partially fluorinated carboxylic acid **4-[4,6]** with a pronounced flat and circular molecular geometry. As evident from the CPK model, the maximum diameter of the dimer is approximately 40 Å. This value is in quite

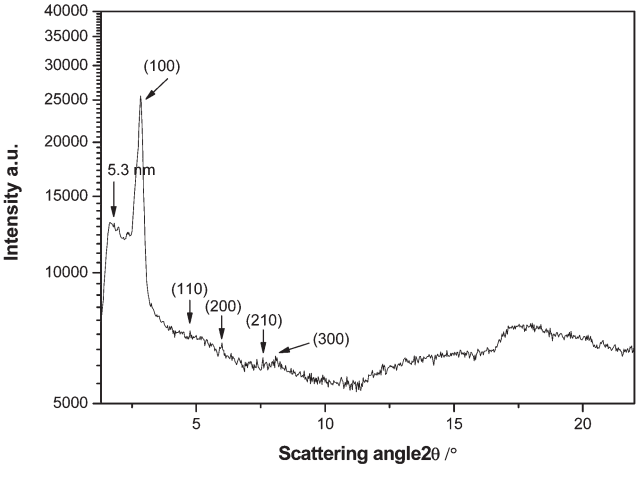

Figure 2. Wide angle X-ray diffractogram for the hexagonal columnar mesophase of the 1:1 mixture **1/4-[4,6]** at 80°C.

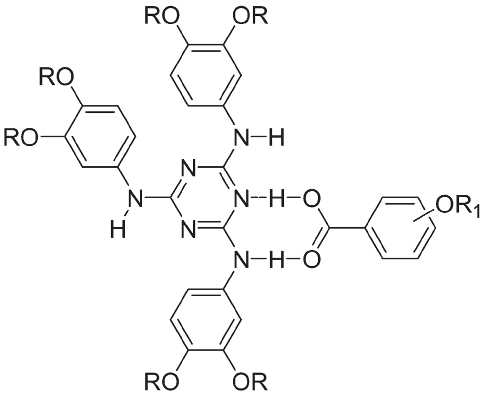

Figure 3. Hetero-dimeric supermolecule with double-hydrogen bonding between the amino substituted nitrogen heterocycle of the triarylmelamine **1** bearing six alkoxy tails and the complementary semiperfluorinated benzoic acids **3** and **4**.

reasonable agreement with the hexagonal lattice constants obtained by X-ray if one considers the fluid nature of the flexible alkyl segments within the mesophase. It follows that the six alkoxy tails of the triazine component **1**, along with the two or three partially fluorinated chains of the complementary benzoic acids **3** and **4**, are sufficient to form circular dimers with optimum peripheral space filling. These dimers build up columnar stacks of cylindrical shape, which organize to hexagonal columnar liquid crystalline phases.

A remarkable feature of the X-ray diffractograms of the mixed systems **1/3,4** is that they show an additional reflection at about $2\theta=1.6^\circ$. The additional reflection corresponds to a *d*-spacing nearly double as that for the (1 0 0) reflection, and points towards a superstructural ordering of the liquid crystalline phase. The new unit cell must have at least one lattice dimension that is approximately double as the intercolumnar distance. We assume that demixing of the lipophilic aliphatic and fluorinated side chain regions occurs. The superstructure could be realized if three (or even two) fluorinated segments point to each other within the hexagonal array (figure 5).

The diffuse scattering in the wide angle region of the WAXS diffractograms of the mixed systems **1/3,4** exhibit an asymmetric profile which has been analysed as consisting of two maxima at $2\theta=17.7^\circ$ and 19.6° (figure 6). The first value can be attributed to the perfluorinated segments, whereas the second is commonly observed for fluid aliphatic regions [26]. This result further supports the proposal that the chemically incompatible aliphatic and fluorinated segments segregate in space along the column axis with formation of a superlattice. Similar supermolecular arrangements within a hexagonal columnar phase have been reported for alkoxytriphenylenes assymetrically incorporating

Figure 4. CPK model of the hydrogen-bonded dimeric supermolecule **1/4-[4,6]** with circular shape. Only more or less *trans*-conformations of the flexible alkyl segments are considered.

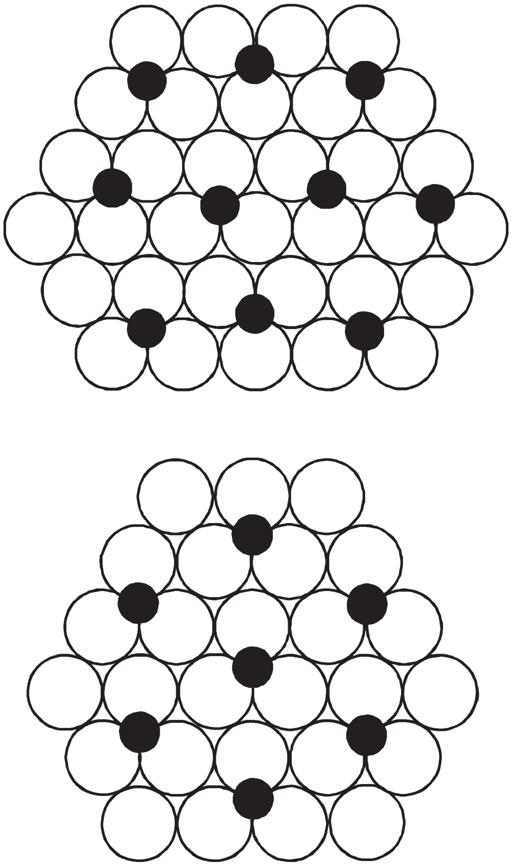

Figure 5. Possible models for the superstructure within the hexagonal columnar mesophases of the hydrogen-bonded dimers of the six-fold alkoxy substituted triarylaminotriazine **1** with the partially fluorinated acids **3** and **4**. The black circles represent fluorinated regions separated from the aliphatic molecular periphery.

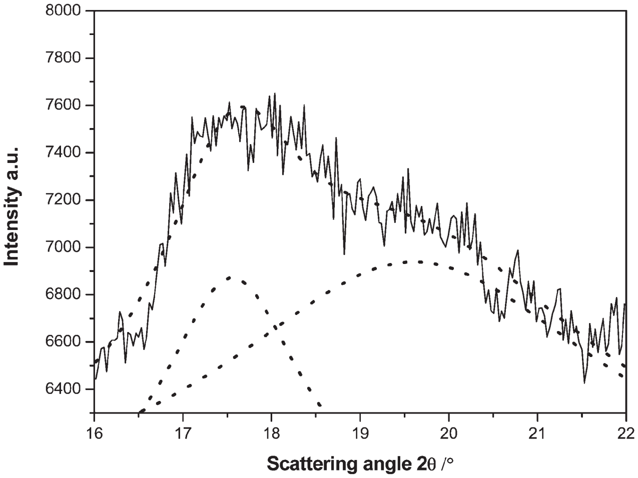

Figure 6. Profile of wide angle scattering in the hexagonal columnar phase of the mixed system **1/4-[4,6]** with splitting into two maxima.

one terminal bulky substituent [27] and for a 1,3,5-benzenetrisamide with three pendant hexaalkoxytriphenylene groups [28].

The wide angle X-ray diffractograms obtained for the mesophases of the triazine **2** mixed with the fluorinated acids **3** and **4** display the characteristics for common $\mathrm{Col_h}$ phases with a ratio of the lattice spacings d_{100}:d_{110}=1:$3^{1/2}$ (figure 7) which again is in accordance with the optical investigations. The diffuse scattering that appears in the wide angle region can be attributed to liquid-like ordering of the flexible alkyl moieties. Thus, no periodic ordering is present within the columns.

The hexagonal lattice constants are larger than those of the equivalent equimolar mixed systems of the acids **3,4** with the six-chain triazine **1** (table 2). The larger values might, at first glance, be attributed to the elongation of the alkoxy chains of the dodecyloxy modified triazine **2** in comparison with the six-fold decyloxy-substituted triarylmelamine **1**. However, the number of hydrogen-bonded dimers of melamine **2** with benzoic acids **3** and **4** within the cross-section of the hexagonal unit cell was calculated to be about two.

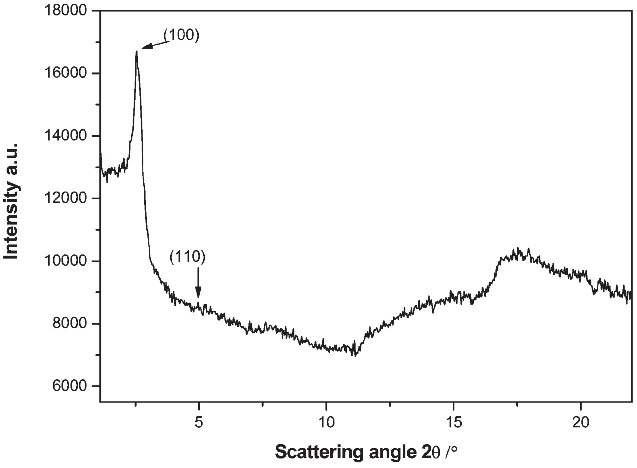

Figure 7. Wide angle X-ray diffractogram for the hexagonal columnar mesophase of the triarylmelamine **2** in equimolar mixture with the three-chain partially fluorinated benzoic acid **4-[4,6]** at 120°C.

It seems reasonable to suggest that reducing the number of alkoxy chains of the melamine component to a total of three no longer promotes sufficient space filling around the polar core of the H-bonded dimers. Instead, the dimers may turn to a molecular conformation that enables additional attractive interactions between the triarylaminotriazines at hydrogen bonding sites not complexed by the acid component (figure 8). In the case of the hydrogen-bonded complexes of the six-fold alkoxy modified triarylmelamine **1** with the benzoic acids **3** and **4** such a pairing of dimers seems not to be favoured for steric reasons due to the bulkyness of the six flexible peripheral alkoxy moieties.

Figure 9 presents a CPK model of one possible arrangement of pairs of hydrogen-bonded dimers **2/3-[4,6]** with a circular shape. The maximum diameter of the discs is approximatly 47 Å. This value is slightly larger then the measured intercolumnar distances within the hexagonal columnar mesophases. 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 with our proposal that the $\mathrm{Col_h}$ phases of the 1:1 mixtures of the melamine **2** with the benzoic acids **3,4** are built up by columns of paired dimers with flat hydrogen-bonded central polar cores surrounded by a shell of the alkyl segments.

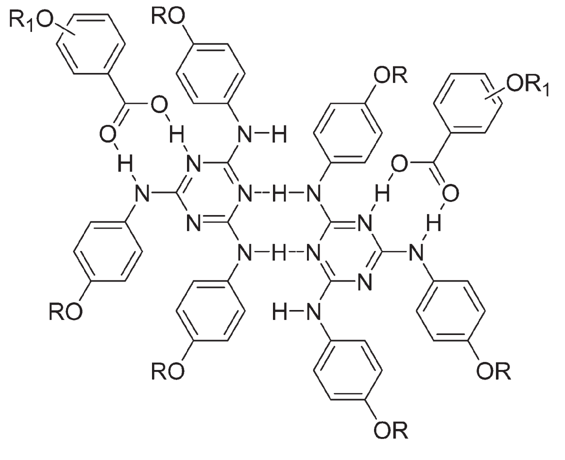

Figure 8. Schematic presentation of paired hydrogen-bonded hetero-dimers of the three-chain triarylamino-1,3,5-triazine **2** with the semiperfluorinated benzoic acids **3** and **4**.

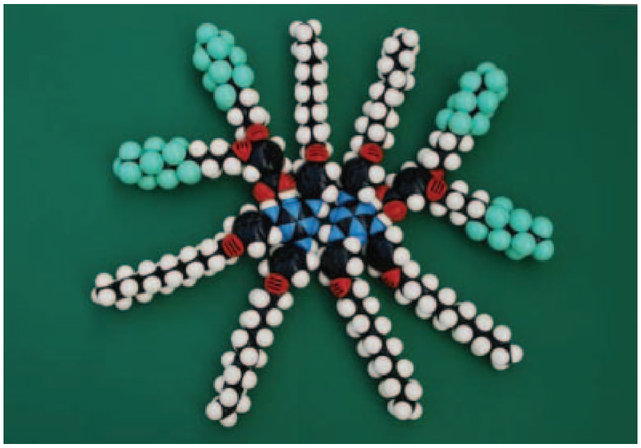

Figure 9. CPK model of one possible molecular arrangement of pairs of dimers of the melamine/benzoic acid complexes **2/3-[4,6]** with circular cross-sectional shape giving rise to columnar mesophases on a two-dimensional hexagonal lattice.

No hint regarding an additionl 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.

4. Conclusions

The amino-substituted nitrogen heterocycle of the investigated triarylmelamines promotes hydrogen bonding with semiperfluorinated benzoic acids. Thereby, molecular recognition between the complementary molecular species frustrates the natural tendency of the aromatic acids to form dimers. We suggest that predominantly H-bonded dimers are formed in equimolar mixed systems. Micro-segregation of the polar core region from the non-polar molecular periphery leads to cylindrical aggregates which align parallel with the formation of columnar mesophases on a two-dimensional hexagonal lattice. The fluorophobic effect introduced by the semiperfluorinated chains of the acid component generates a 'second order' of nano-segregation, giving rise to a superstructure within the hexagonal lattice of the six-chain triazine mixed with the benzoic acids. In the case of hetero-dimers involving the three-chain melamine, the loss of peripheral space filling by reducing the number of alkoxy chains is compensated for by the formation of circular pairs of dimers which organize into columnar stacks with 2D hexagonal lattice symmetry.

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