Chem. Mater. **2006,** *18,* 59−68

Hydrogen-Bonded Polyphilic Block Mesogens with Semiperfluorinated Segments

Alexandra Kohlmeier and Dietmar Janietz*

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

Received July 13, 2005. Revised Manuscript Received October 4, 2005

Two 2,4-diamino-6-phenyl-1,3,5-triazines carrying either one or two alkoxy chains at the phenyl substituent have been investigated in binary mixtures with two-chain partially fluorinated benzoic acids. Equimolar compositions of the complementary molecular species form discrete hydrogen-bonded dimeric supermolecules. The dimers organize to infinite ribbons of parallel aligned H-bonded polar aromatic cores that are separated by mixed aliphatic/fluorinated regions. The cross-sectional shape of the ribbon aggregates and, therefore, the two-dimensional lattice symmetries of the ribbon phases, rectangular or oblique, are defined by the number of alkoxy chains of the triazine component. Docking of 2 or 3 equiv of the semiperfluorinated benzoic acids to the diaminotriazine core leads to H-bonded aggregates with a circular cross-sectional shape and, consequently, to the formation of columnar phases on a two-dimensional hexagonal lattice.

Introduction

Self-organization with the formation of thermotropic and lyotropic liquid-crystalline phases is mainly governed by the nanoscale segregation of incompatible molecular fragments.[1,2] Thermotropic liquid crystals most frequently are designed in such a way that flexible alkyl tails are attached to a rigid rod-shaped or disklike molecular block. The incompatible flexible segments segregate from the rigid molecular fragments into different subspaces. Thereby, calamitic mesogens preferentially organize to smectic layer structures,[3] whereas disk-shaped molecules prefer an arrangement in columnar mesophases.[4]

Increasing the number of aliphatic chains grafted to a rigid core or even to a nonanisometric but distinct polar molecular part leads to an increase in the volume fraction of the lipophilic aliphatic region. Nonlamellar mesophases such as columnar or cubic can result, as has been successfully demonstrated, e.g., for polycatenar[5] and swallow-tailed[6] mesogens, for taper-shaped polyhydroxy amphipiles,[7,8] and for cone-shaped dendrimers.[9]

Mesophase morphologies can be further tailored if a perhydrogenated chain is replaced by a perfluorinated segment. The main reasons are the incompatibility of the perfluorinated chains with aliphatic, aromatic, and polar molecular segments; their larger cross-sectional area compared to aliphatic chains; and their reduced conformational mobility.[10,11]

(Semi)perfluorinated molecular segments have been successfully introduced into calamitic,[12−16] discotic,[17,18] and polycatenar[1,19] mesogens as well as liquid crystals without a pronounced anisometric molecular geometry such as taper-shaped[20,21] and tetrahedral[22] compounds, and it was shown that the fluorophobic effect could lead to a significant stabilization and even to modifications of smectic, columnar, and cubic mesophases.

Aside from the fluorophobic effect, the distinct polar−nonpolar molecular gradient can be reinforced by introducing

---

* To whom correspondence should be addressed. E-mail: dietmar.janietz@iap.fhg.de.

(1) Kato, T. *Science* **2002**, *295*, 2414.
(2) Tschierske, C. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 69.
(3) Gray, G. W.; Goodby, J. W. *Smectic Liquid Crystals*; Leonard-Hill: London, 1984.
(4) Cammidge, A. N.; Bushby, R. J. In *Handbook of Liquid Crystals*; Demus, D., Goodby, J., Gray, G. W., Spiess, H.-W., Vill, V., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Vol. 2B, p 693.
(5) Nguyen, H.-T.; Destrade, C.; Malthête, J. *Adv. Mater.* **1997**, *9*, 375.
(6) Weissflog, W.; Letko, I.; Diele, S.; Pelzl, G. *Adv. Mater.* **1996**, *8*, 76.
(7) Borisch, K.; Diele, S.; Göring, P.; Kresse, H.; Tschierske, C. *J. Mater. Chem.* **1998**, *8*, 529.
(8) Lattermann, G.; Staufer, G.; Brezesinski, G. *Liq. Cryst.* **1991**, *10*, 169.
(9) Balagurusamy, V. S. K.; Ungar, G.; Percec, V.; Johansson, G. *J. Am. Chem. Soc.* **1997**, *119*, 1539.
(10) Smart, B. E. In *Organofluorine Chemistry: Principles and Commercial Applications*; Benks, R. E., Tatlow, J. C., Eds.; Plenum Press: New York, 1994; p 57.
(11) Lobko, T. A.; Ostrovskii, B. I.; Pavluchenko, A. I.; Sulianov, S. N. *Liq. Cryst.* **1993**, *15*, 361.
(12) Doi, T.; Sakurai, Y.; Tamatani, A.; Takenaka, S.; Kusabayashi, S.; Nishihata, Y.; Terauchi, H. *J. Mater. Chem.* **1991**, *1*, 169.
(13) Rieker, T. P.; Janulis, E. P. *Phys. Rev. E* **1995**, *52*, 2688.
(14) Guittard, F.; Taffin de Givenchy, E.; Geribaldi, S.; Cambon, A. *J. Fluorine Chem.* **1999**, *100*, 85.
(15) Pugh, C.; Small, A. C.; Helfer, C. A.; Mattice, W. L. *Liq. Cryst.* **2001**, *28*, 991.
(16) Pensec, S.; Tournilhae, F.-G.; Bassoul, P.; Durliat, C. *J. Phys. Chem. B* **1998**, *102*, 52.
(17) Dahn, U.; Erdelen, C.; Ringsdorf, H.; Festag, R.; Wendorff, J. H.; Heiney, P. A.; Maliszewskyi, N. C. *Liq. Cryst.* **1995**, *19*, 759.
(18) Terasawa, N.; Monobe, H.; Kiyohara, K.; Shimizu, Y. *Chem. Lett.* **2003**, *32*, 214.
(19) Pelzl, G.; Diele, S.; Lose, D.; Ostrovski, B. I.; Weissflog, W. *Cryst. Res. Technol.* **1997**, *32*, 99.
(20) Johansson, G.; Percec, V.; Ungar, G.; Zhou, J. P. *Macromolecules* **1996**, *29*, 646.
(21) Percec, V.; Johansson, G.; Ungar, G.; Zhou, J. *J. Am. Chem. Soc.* **1996**, *118*, 9855.
(22) Cheng, X. H.; Diele, S.; Tschierske, C. *Angew. Chem., Int. Ed.* **2000**, *39*, 592.

10.1021/cm0515193 CCC: $33.50

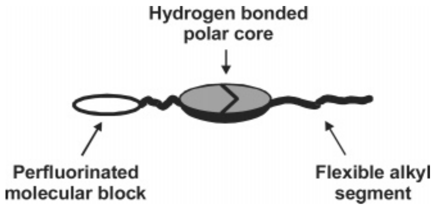


Figure 1. Hydrogen-bonded three-block supermolecules.

highly polar hydrogen bonds.[23] In this respect, we presented 2,4,6-triarylamino-1,3,5-triazines substituted with six long peripheral alkoxy chains.[24] These compounds exhibit columnar mesophases arising from microsegregation of the polar heterocyclic core from the lipophilic peripheral chains.[25]

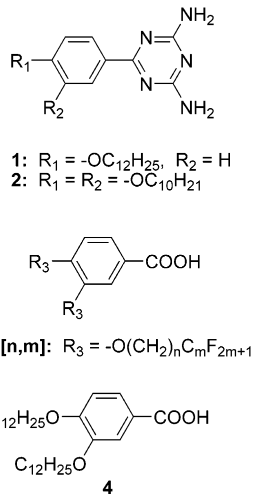
Hydrogen bonding of the columnar phase to form melamines with complementary alkoxy-substituted benzoic acids was reported by us to control the intercolumnar distances.[26] The number and positions of alkoxy chains of the benzoic acids defines the cross-sectional shape of cylindrical aggregates of the melamine−benzoic acid associates and, therefore, the two-dimensional lattice symmetries, hexagonal or rectangular.[27] Even a molecular-recognition-directed induction of a hexagonal columnar mesophase was found for a nonmesogenic three-fold alkoxy-substituted triarylmelamine mixed with a calamitic phase forming 4-alkoxybenzoic acid.[28]

However, reports regarding supramolecular mesogens combining hydrogen bonding and the fluorophobic effect are less frequent. Examples are semiperfluorinated amphiphilic polyhydroxy derivatives,[29,30] which form polymolecular aggregates with a dynamic network of intermolecular hydrogen bonds and dimers of semiperfluorinated benzoic acids.[20,21,29,31] Here, mesomorphic structure formation is due to the self-assembly of just a single molecular component.

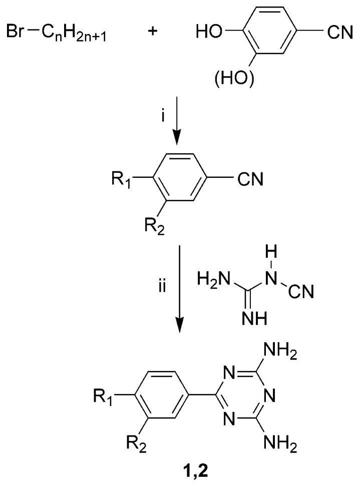
To our best knowledge, those mesomorphic H-bonded complexes derived from two complementary components and incorporating perfluorinated chains reported so far are restricted to mixtures of fluorinated acids and pyridine derivatives.[32−35]

We present here our efforts toward combining molecular recognition between two complementary species and fluorinated molecular blocks. The two components were designed such that one component incorporates semiperfluorinated fragments and the other, hydrocarbon chains (Figure 1).

Chart 1. Chemical Structures of the Compounds under Inverstigation



Scheme 1. Synthesis of the Two-Fold Amino-Substituted 1,3,5-Triazines 1 and 2[a]



[a] Reagents and conditions: (i) K_2CO_3, KI, acetone, Ar, 80 °C, 16 h; (ii) ethylene glycolmonomethyl ether, KOH, 130 °C, 5 h.

We report on the 2,4-diamino-6-phenyl-1,3,5-triazines 1 and **2** grafted with one or two alkoxy tails (Chart 1). The thermal behavior was investigated in mixtures with the semiperfluorinated benzoic acids **3**-[*n*,*m*]. Additionally, to elucidate the influence of the fluorinated segments, mixtures of the diaminotriazines with the nonfluorinated two-chain benzoic acid **4** were investigated.

Results and Discussion

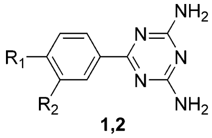
1. Synthesis. The synthesis of compounds **1** and **2** is shown in Scheme 1. Alkylation of hydroxy-substituted benzonitriles with dodecyl bromide and decyl bromide, respectively, in the presence of potassium carbonate as the base gave the appropriate alkoxybenzonitriles. Reaction of the alkoxybenzonitriles with dicyandiamide in the presence of KOH and ethylene glycolmonomethyl ether as the solvent yielded the two-fold amino-substituted alkoxyphenyl-1,3,5-triazines **1** and **2**.

Pd^0-catalyzed radical addition of 1-iodoperfluoroalkanes to ω-alken-1-ols, followed by reduction of the obtained

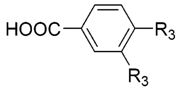
---

(23) Paleos, C. M.; Tsiourvas, D. *Angew. Chem.* **1995**, *107*, 215.
(24) Goldmann, D.; Janietz, D.; Festag, R.; Schmidt, C.; Wendorff, J. H. *Liq. Cryst.* **1996**, *21*, 619.
(25) Goldmann, D.; Janietz, D.; Schmidt, C.; Wendorff, J. H. *Angew. Chem.* **2000**, *112*, 1922.
(26) Goldmann, D.; Dietel, D.; Janietz, D.; Schmidt, C.; Wendorff, J. H. *Liq. Cryst.* **1998**, *24*, 407.
(27) Goldmann, D.; Janietz, D.; Schmidt, C.; Wendorff, J. H. *J. Mater. Chem.* **2004**, *14*, 1521.
(28) Janietz, D.; Goldmann, D.; Schmidt, C.; Wendorff, J. H. *Mol. Cryst. Liq. Cryst.* **1999**, *332*, 141.
(29) Cheng, X.; Das, M. K.; Diele, S.; Tschierske, C. *Langmuir* **2002**, *18*, 6521.
(30) Cheng, X.; Prehm, M.; Das, M. K.; Kain, J.; Baumeister, U.; Diele, S.; Leine, D.; Blume, A.; Tschierske, C. *J. Am. Chem. Soc.* **2003**, *125*, 10977.
(31) Schaz, A.; Valaityte, E.; Lattermann, G. *Liq. Cryst.* **2004**, *31*, 1311.
(32) Nishikawa, E.; Yamamoto, J. *Mol. Cryst. Liq. Cryst.* **2004**, *411*, 139.
(33) Nishikawa, E.; Yamamoto, J.; Yokoyama, H. *Chem. Lett.* **2001**, 454.
(34) Nishikawa, E.; Yamamoto, J.; Yokoyama, H. *Chem. Lett.* **2001**, 94.
(35) Bernhardt, H.; Weissflog, W.; Kresse, H. *Chem. Lett.* **1997**, 151.

Table 1. Phase Transition Temperatures (°C) of the Pure Compounds 1−4, DSC Second Heating at 10 K min^{-1}, Monotropic Phase Transitions[a] in Square Brackets, and Phase Transition Enthalpies (kJ mol^{-1}) in Parentheses



1,2

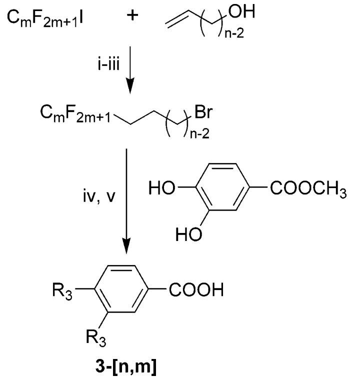


3-[n,m], 4

compd	R_1	R_2	R_3	phase transitions
1	$OC_{12}H_{25}$	H		Cr 157.7 (23.54) Iso
2	$OC_{10}H_{21}$	$OC_{10}H_{21}$		Cr 111.9 (21.67) Iso
3-[4,4]			$O(CH_2)_4C_4F_9$	Cr 103.0 (32.15) Iso
3-[6,4]			$O(CH_2)_6C_4F_9$	Cr 54.7 (14.21) [Col 53.1 (1.79)] Iso
3-[4,6]			$O(CH_2)_4C_6F_{13}$	Cr 115.7 (37.59) [Col 102.0 (1.57)] Iso
3-[6,6]			$O(CH_2)_6C_6F_{13}$	Cr 88.2 (20.04) [Col 75.3 (0.80)]) Iso
4			$OC_{12}H_{25}$	Cr 122.0 (50.65) Iso

[a] Obtained from the second DSC cooling scan. [b] Cr, crystalline; Col, columnar mesophase; Iso, isotropic liquid.

Scheme 2. Synthesis of the Semiperfluorinated Benzoic Acids 3-[*n*,*m*][a]



[a] Reagents and conditions: (i) $(Ph_3P)_4Pd(0)$, hexane, 0−20 °C, 36 h; (ii) Bu_4Sn, 80 °C, 30 min; (iii) Bu_4NHSO_4, HBr, H_2SO_4, 100 °C, 12 h; (iv) K_2CO_3, DMF, Ar, 65 °C, 2−4 h; (v) KOH, EtOH, 85 °C, 2 h.

Table 2. Phase Transition Data (°C) of Equimolar Compositions of the One-Chain Triazine 1 with the Benzoic Acids 3 and 4, DSC Second Heating at 10 K min^{-1}, and Phase Transition Enthalpies (kJ mol^{-1}) in Parentheses[a]

mixture	Cr		Col_r		Iso
1/**3**-[4,4]	•	111.1 (18.32)	•	129.9 (5.60)	•
1/**3**-[6,4]	•	103.3 (15.37)	•	130.3 (4.86)	•
1/**3**-[4,6]	•	128.6 (33.91)	•	154.6 (3.23)	•
1/**3**-[6,6]	•	106.7 (14.56)	•	132.7 (7.49)	•
1/**4**	•	116.4 (70.11)			•

[a] Cr, crystalline; Col_r, rectangular columnar; Iso, isotropic.

Table 3. Phase Transition Temperatures (°C) of Equimolar Mixtures of the Two-Chain Triazine 2 with the Benzoic Acids 3 and 4 and Corresponding Phase Transition Enthalpies (kJ mol^{-1}) in Parentheses, DSC Second Heating at 10 K min^{-1}

mixture	Cr		Col_{ob}		Iso
2/**3**-[4,4]	•	71.3 (17.90)	•	118.6 (1.21)	•
2/**3**-[6,4]	•	60.1 (15.67)	•	117.0 (2.48)	•
2/**3**-[4,6]	•	82.3 (28.86)	•	128.6 (1.74)	•
2/**3**-[6,6]	•	64.5 (15.08)	•	116.2 (3.85)	•
2/**4**	•	77.3 (28.93)			•

[a] Cr, crystalline; Col_{ob}, columnar, oblique lattice; Iso, isotropic.

iodides with tributyltinhydride resulted in semifluorinated alcohols (Scheme 2).[20,29] The semifluorinated alcohols were converted into the appropriate bromides[20,29] by bromination with 48% aqueous HBr in the presence of catalytic amounts of concentrated sulfuric acid and tetrabutylammonium hydrogensulfate. The semiperfluorinated benzoic acids **3**-[*n*,*m*] were finally obtained by etherification of methyl 3,4-dihydroxy benzoate with the bromides using potassium carbonate as the base and subsequent basic hydrolysis. The 3,4-bis(dodecyloxy)benzoic acid **4** was prepared by etherification of 3,4-dihydroxybenzoic acid methyl ester and alkaline ester cleavage according to standard procedures.[27,36]

2. Mesomorphic Properties. *2.1. General Trends.* The pure compounds and binary mixed systems were investigated by polarizing optical microscopy and differential scanning calorimetry. Additionally, selected mixtures were investigated by wide-angle X-ray scattering.

The pure alkoxy-substituted diamino-1,3,5-triazines **1** and **2** and the 3,4-bis(dodecyloxy)benzoic acid **4** are only crystalline compounds. Even the introduction of two short semiperfluorinated chains into the acid component does not give rise to mesomorphic behavior for the carboxylic acid **3**-[4,4]. Further elongation of the alkyl segment and/or the perfluoroalkyl part of the alkoxy tails leads to at least monotropic columnar mesophases for the semiperfluorinated benzoic acids **3**, as is evident from the spherulitic textures that develop upon cooling of the compounds from the isotropic melts. The columnar mesophases are related to the formation of discrete benzoic acid dimers via hydrogen bonding along with segregation of the polar central region from the surrounding semiperfluorinated chains.[29,31] The phase transition data of the pure compounds **1**−**4** are summarized in Table 1.

Contact preparations of the triazines **1** and **2** with the fluorinated acids **3** reveal that a mesophase is induced in the contact zone if the content of the acid reaches ca. 1 mol per mole of the triazine. This observation is confirmed by microscopic investigations on defined mixtures containing less than the stoichiometric amount of the semiperfluorinated acids **3**. These mixtures show miscibility of the two components but a direct transition from the crystalline state to the isotropic liquid.

The phase transition temperatures of equimolar compositions of the diaminotriazines **1** and **2** and the benzoic acids **3**-[*n*,*m*] and **4** are collected in Tables 2 and 3.

Each investigated binary 1:1 mixture of the triazines **1** and **2** with the semiperfluorinated benzoic acids **3**-[*n*,*m*] exhibits

---

(36) Staufer, G.; Schellhorn, M.; Lattermann, G. *Liq. Cryst.* **1995**, *18*, 519.

Table 4. Phase Transition Temperatures (°C) of Mixtures of Diaminotriazine 1 with Different Contents of the Benzoic Acid 3-[6,4] and Corresponding Phase Transition Enthalpies (kJ mol^{-1}) in Parentheses, DSC Second Heating at 10 K min^{-1}

mixture	Cr		Col		Iso
1:1 1/**3**-[6,4]	•	103.3 (15.37)	•	130.3 (4.86)	•
1:2 1/**3**-[6,4]	•	102.9 (18.90)	•	112.0 (3.71)	•
1:3 1/**3**-[6,4]	•	73.3 (22.4)	•	96.3 (3.27)	•

[a] Cr, crystalline; Col, columnar; Iso, isotropic.

an enantiotropic liquid-crystalline phase. The clearing temperatures are in excess of the melting temperatures of the appropriate pure carboxylic acids **3**-[*n*,*m*]. The melting and isotropization temperatures of the two-chain triazine **2** mixed with the acids **3** are lower than those of the 1:1 mixed **1**/**3** systems. 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, **2**/**3** mixtures show enlarged mesophase ranges in comparison to the 1:1 mixtures of the single-chain aminotriazine **1** with the acids **3**-[*n*,*m*].

The partially fluorinated chains of the benzoic acids **3**-[4,4], **3**-[6,4], and **3**-[6,6] do not have a significant influence on the clearing temperatures of the appropriate equimolar mixtures. Replacing the butyl spacer sequence of the acid component by six flexible methylene units leads to a decrease of the melting temperatures of the appropriate equimolar compositions. The mixtures **1**/**3**-[4,6] and **2**/**3**-[4,6] both display enhanced melting and clearing temperatures compared to the other investigated 1:1 mixtures of compounds **1** and **2** with the homologous partially fluorinated acids. Therefore, it seems that, by keeping constant all other molecular parameters, the mesophase stability can be increased if the number of fluorinated carbon atoms in the chains exceeds the number of nonfluorinated carbons.

The DSC traces of the respective equimolar mixtures of **1** and **2** with the nonfluorinated two-fold alkoxy-modified carboxylic acid **4** show a single melting transition below the melting points of the single compounds. However, we do not find evidence for mesomorphic properties of the mixed systems **1**/**4** and **2**/**4**.

Table 4 summarizes the phase transition data of 1:2 and 1:3 compositions of the diamino-1,3,5-triazine **1** with the partially fluorinated acid **3**-[6,4] in comparison to the appropriate 1:1 mixed system. The melting and clearing temperatures are lower and the mesophase range is reduced for the 1:2 complex. A further decrease of the phase transition temperatures is observed for the mixture containing 3 equiv of the acid **3**-[6,4].

Optical textures with spherulitic regions and pseudofocal conic fanlike regions are characteristic for equimolar mixtures of the single-chain diaminotriazine **1** with the partially fluorinated benzoic acids **3**-[*n*,*m*] (Figure 2a). Fernlike textures develop upon cooling of the 1:1 compositions of the two-chain triazine **2** and the acids **3** from the isotropic liquid, which coalesce to form spherulitic textures (Figure 2b). The textures of the 1:2 and 1:3 **1**/**3**-[6,4] complexes are characterized by regions with broken spherulites, mosaiclike regions, and pseudoisotropic areas containing birefringent lancets (Figure 2c).

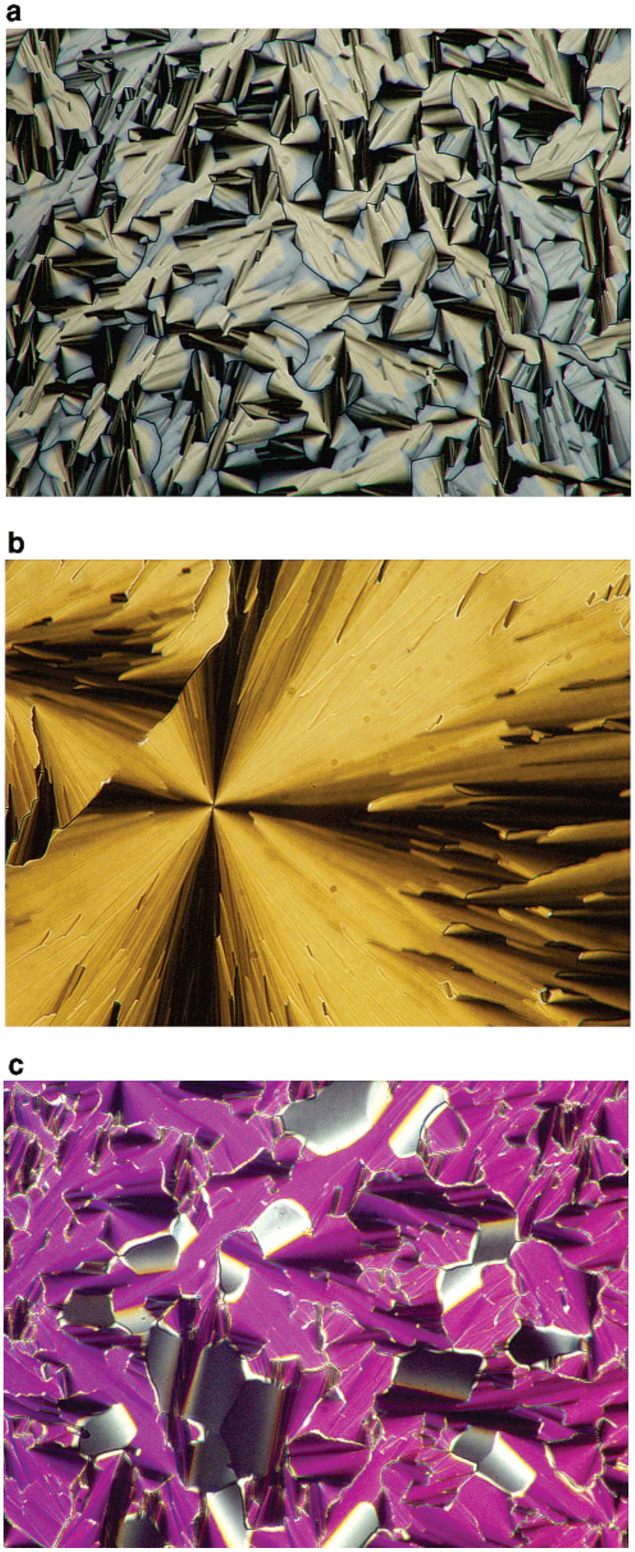


Figure 2. Optical micrographs of the columnar mesophases of (a) the equimolar **1**/**3**-[4,4] mixture at 119.8 °C, (b) the equimolar mixed **2**/**3**-[4,6] system at 124.6 °C, and (c) the 1:2 **1**/**3**-[6,4] mixture at 106.5 °C.

Therefore, it seems that the mixtures exhibit different mesophases depending on the number of alkoxy tails of the diaminotriazine component and the molar content of the semiperfluorinated acid.

2.2. Temperature-Dependent IR Spectroscopy. Temperature-dependent IR spectroscopy was performed to elucidate the nature of intermolecular interactions between the two-

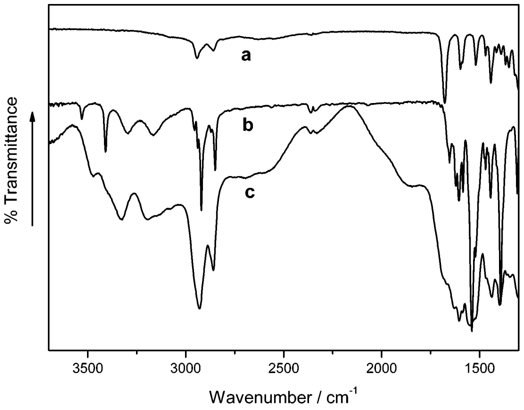


Figure 3. FTIR spectra of (a) the pure partially fluorinated benzoic acid **3**-[**6.6**], (b) the single-chain diamino-substituted 1,3,5-triazine **1** in its pure state, and (c) the equimolar composition **1**/**3**-[**6,6**] measured at 120 °C within the liquid-crstalline phase.

fold amino-substituted 1,3,5-triazines **1** and **2** and the partially fluorinated benzoic acids **3**. Figure 3 displays, as an example, the FTIR transmission spectrum of the equimolar 1/**3**-[6,6] mixture recorded at 120 °C within the mesophase, along with the spectra of the pure triazine **1** and the acid **3**-[6,6].

The two absorption bands at 3532 and 3296 cm^{-1} in the region of the NH$_2$-stretching vibrations[37] of the diaminotriazine **1** are shifted to 3470 and 3324 cm^{-1}, respectively, in the spectrum of the **1**/**3**-[6,6] mixture. The two bands of the pure aminotriazine **1** at 3410 and 3167 cm^{-1} are still present as shoulders in the spectrum of the thermally treated mixed system. A new absorption is visible at 3195 cm^{-1}, and two additional absorptions appear for the complex at 2570 and 1854 cm^{-1} that are attributed to a hydrogen bridge between the hydroxy group of the acid and the endocyclic nitrogen atom of the heterocycle.[38,39] The ν(C═O) absorption band of the carboxylic group at 1676 cm^{-1} for the pure benzoic acid **3**-[6,6] does not change its position in the mixture with the aminotriazine **1**. This behavior seems to be unsurprising if one considers that the hydrogen bonding of the acid dimers is replaced by a hydrogen bridge between the carboxylic group and an exocyclic amino group of the triazine.

Figure 4 shows the IR spectra of the equimolar 1/**3**-[6,6] mixture as a function of temperature, measured at room temperature, within the mesophase and in the isotropic state. The IR spectrum of the mixture before thermal treatment at room temperature reflects the characteristics of the spectra of the single compounds. However, the absorption band at 3324 cm^{-1} within the mesophase nearly completely disappears in the isotropic state, and the band at 3470 cm^{-1} is shifted to 3500 cm^{-1}. Furthermore, the carbonyl absorption band of the complementary mixture is shifted to 1695 cm^{-1} after isotropization and returns to 1676 cm^{-1} upon cooling of the mixture to the liquid-crystalline state. These results strongly suggest that the hydrogen-bonded complex breaks in the isotropic disordered state with the appearance of the two monomeric species.

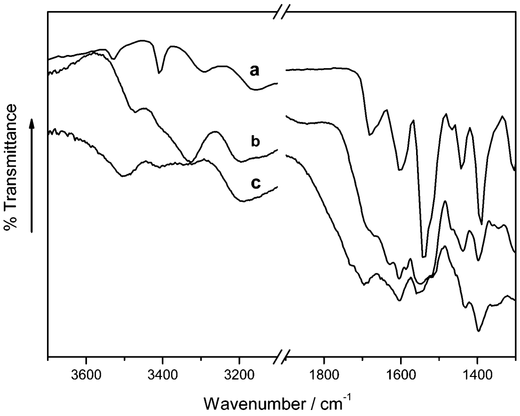


Figure 4. FTIR spectra of the equimolar **1**/**3**-[**6,6**] mixture recorded at (a) room temperature, (b) 120 °C within the liquid-crystalline phase, and (c) 160 °C in the isotropic phase.

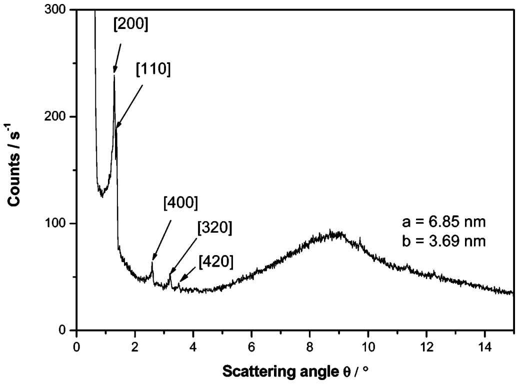


Figure 5. WAXS diffractogram for the rectangular columnar mesophase of the equimolar mixture of the single-chain triazine **1** with the semi-perfluorinated benzoic acid **3**-[**4,4**] at 115 °C (two-dimensional *p*2*gg* lattice).

From the IR investigations, it can be concluded that association of the complementary diaminotriazines **1** and **2** and the fluorinated benzoic acids **3** is related to double hydrogen bonding between the nitrogen heterocycle substituted with two exocyclic amino groups and the carboxylic group. Similar double hydrogen bonding has been reported for mesogenic complexes of triarylmelamines with alkoxy-substituted benzoic acids[26,27] and for mixtures of 2,6-diacylaminopyridines with 4-alkoxybenzoic acids.[40]

Hence, the affinity toward hydrogen bonding between the carboxylic groups and the diaminotriazine core prevents the dimerization of the fluorinated benzoic acids via H-bonds and, thus, the monotropic columnar phases formed by the acids in their pure state.

2.3. Equimolar Mixtures of the Single-Chain 1,3,5-Triazine 1 with the Semiperfluorinated Benzoic Acids 3. The WAXS diffractogram of the 1:1 mixture of **1**/**3**-[4,4] (Figure 5) shows a diffuse scattering in the wide-angle region that indicates a mesophase without long range order. A higher-ordered smectic phase can therefore be excluded. The small-angle reflections can be indexed on the basis of a two-dimensional rectangular unit cell. Because of the appearance of the (32) reflection, a centered cell can be excluded. This reflection can be explained by assuming a 2D noncentered *p*2*gg*

---

(37) Kurihara, K.; Ohto, K.; Honda, Y.; Kunitake, T. *J. Am. Chem. Soc.* **1991**, *113*, 5077.

(38) Kumar, U.; Frechet, J. M. J.; Kato, T.; Ujiie, S.; Iimura, K. *Angew. Chem.* **1992**, *104*, 1545.

(39) Kato, T.; Frechet, J. M. J.; Wilson, P. G.; Saito, T.; Uryu, T.; Fujishima, A.; Jin, C.; Kaneuchi, F. *Chem. Mater.* **1993**, *5*, 1094.

(40) Kato, T.; Kubata, Y.; Nakana, M.; Uryu, T. *Chem. Lett.* **1995**, 1127.

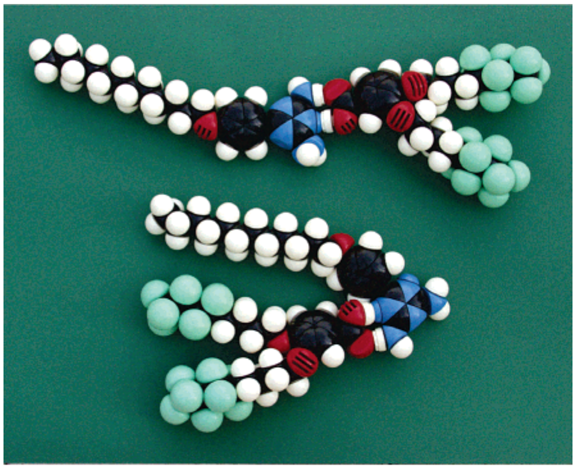


Figure 6. CPK models of a hydrogen-bonded dimeric supermolecule formed by the single-chain triazine **1** with the complementary two-chain fluorinated benzoic acid **3**-[**4,4**]. Upper part, rodlike shape of the H-bonded core; lower part, taperlike shape.

rectangular lattice. The lattice parameters amount to $a = 6.85$ nm and $b = 3.69$ nm. The diffuse halo in the wide-angle region is found around a Bragg angle of 8.9°. This value is between the values usually observed for pure aliphatic and perfluorinated chains[41,42] and points to a mixed arrangement of the aliphatic and fluorinated moieties.

We have to take into account the fact that self-organization with the formation of a liquid-crystalline phase occurs only if the mixtures contain no less than 1 equiv of the acid component. Therefore, it is most reasonable to suggest that, in equimolar compositions, the hydrogen bonding between the diaminotriazines **1** and **2** and the fluorinated acids **3** preferentially leads to discrete dimeric supermolecules.

The diamino-1,3,5-triazines are characterized by two exocyclic primary amino groups and three endocyclic nitrogen atoms, which means three molecular recognition sites for the docking of the complementary benzoic acids. Therefore, one could envisage two isomeric dimers differing with respect to their molecular topology as shown in Figure 6.

H-bonding involving one endocyclic nitrogen next nearest to the phenyl ring at the 6-position of the triazine would result in a dimer with a pronounced tapered molecular shape (lower part of Figure 6). It is well-established that the aggregation of taper-shaped molecules leads to the formation of hexagonal columnar (Col_h) and/or cubic mesophases.[43,44] As is evident from CPK models, four taper-shaped **1**/**3**-[4,4] dimers would fit two-dimensionally in space giving a superdisk with a diameter of 5.2 nm (Figure 7a). A hexagonal columnar organization should be strongly favored. This is not in agreement with the experimental finding from X-ray scattering. The alternative to a cyclic rosettelike arrangement[45] would be a tapelike motif[46] with antiparallel organization. However, CPK models (Figure 7b) reveal that a tapelike structure without steric demand preferentially should lead to a smectic layering, as was shown by Kato et al. for H-bonded V-shaped folic acid derivatives.[1,47] This is also not in agreement with the experimental results. For these reasons, a taper-shaped molecular geometry should be rather unlikely. Hydrogen bonding of the first equivalent of the benzoic acids **3** to a nitrogen next to the bulky phenyl ring of the triazines seems to be sterically less preferred. We conclude that predominantly dimeric supermolecules are formed by the triazines **1** and **2** with the acids **3** with a rodlike shape of the H-bonded core and with distinct lipophilic, polar, and fluorophilic molecular regions (upper part of Figure 6). This assumption is in line with the fact that double hydrogen

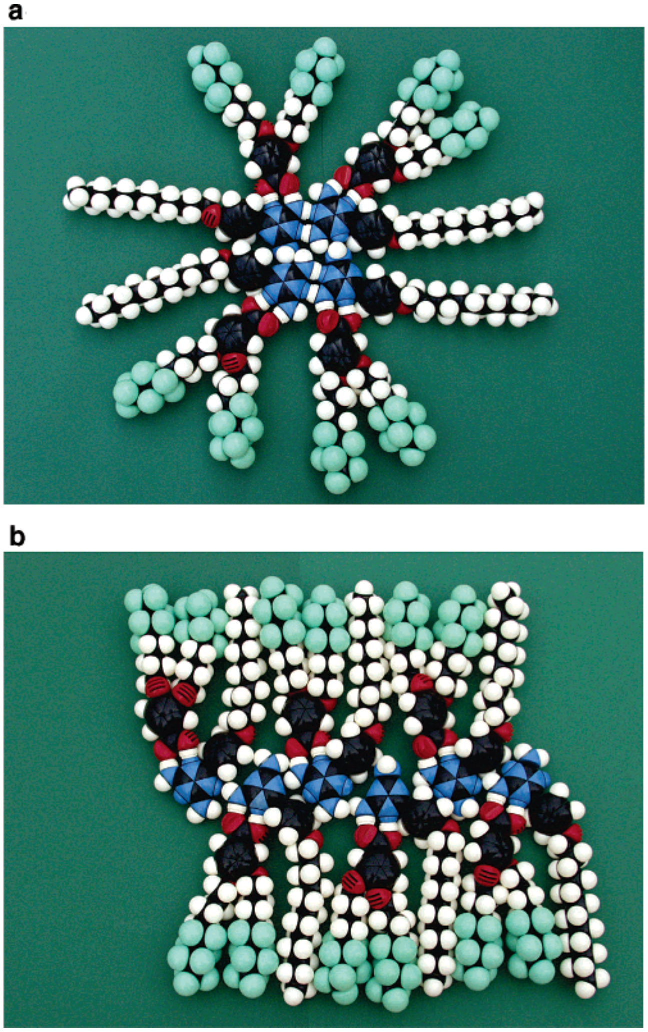


Figure 7. CPK models of the possible assemblies of taper-shaped H-bonded **1**/**3**-[**4,4**] dimers: (a) circular disklike arrangement, (b) smectic layer structure.

---

(41) Veber, M.; Sotta, P.; Davidson, P.; Levelut, A. M.; Jallabert, C.; Strzelecka, H. *J. Phys. Fr.* **1990**, *51*, 1283.

(42) Diele, S.; Lose, D.; Kruth, H.; Pelzl, G.; Guittard, F.; Cambon, A. *Liq. Cryst.* **1996**, *21*, 603.

(43) Percec, V.; Cho, W.-D.; Ungar, G. *J. Am. Chem. Soc.* **2000**, *122*, 10273.

(44) Tschierske, C. *J. Mater. Chem.* **1998**, *8*, 1485.

(45) Reviews of hydrogen-bonded rosettes: (a) Whitesides, G. M.; Simanek, E. E.; Mathias, J. P.; Seto, C. T.; Chin, D. N.; Mammen, M.; Gordon, D. M. *Acc. Chem. Res.* **1995**, *28*, 37. (b) Lawrence, D. S.; Jiang, T.; Levitt, M. *Chem. Rev.* **1995**, *95*, 5, 2229. (c) Prins, L. J.; Reinhoudt, D. N.; Timmermann, P. *Angew. Chem.* **2001**, *113*, 2447. (d) Timmermann, P.; Prins, L. J. *Eur. J. Org. Chem.* **2001**, 3191.

(46) (a) Zerkowski, J. A.; Mathias, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1994**, *116*, 4305. (b) Bielejewski, A. G.; Marjo, C. E.; Prins, L. J.; Timmermann, P.; de Jong, F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **2001**, *123*, 7518.

(47) (a) Kanie, K.; Yasuda, T.; Ujiie, S.; Kato, T. *Chem. Commun.* **2000**, 1899. (b) Kanie, K.; Nishii, M.; Yasuda, T.; Taki, T.; Ujiie, S.; Kato, T. *J. Mater. Chem.* **2001**, *11*, 2875.

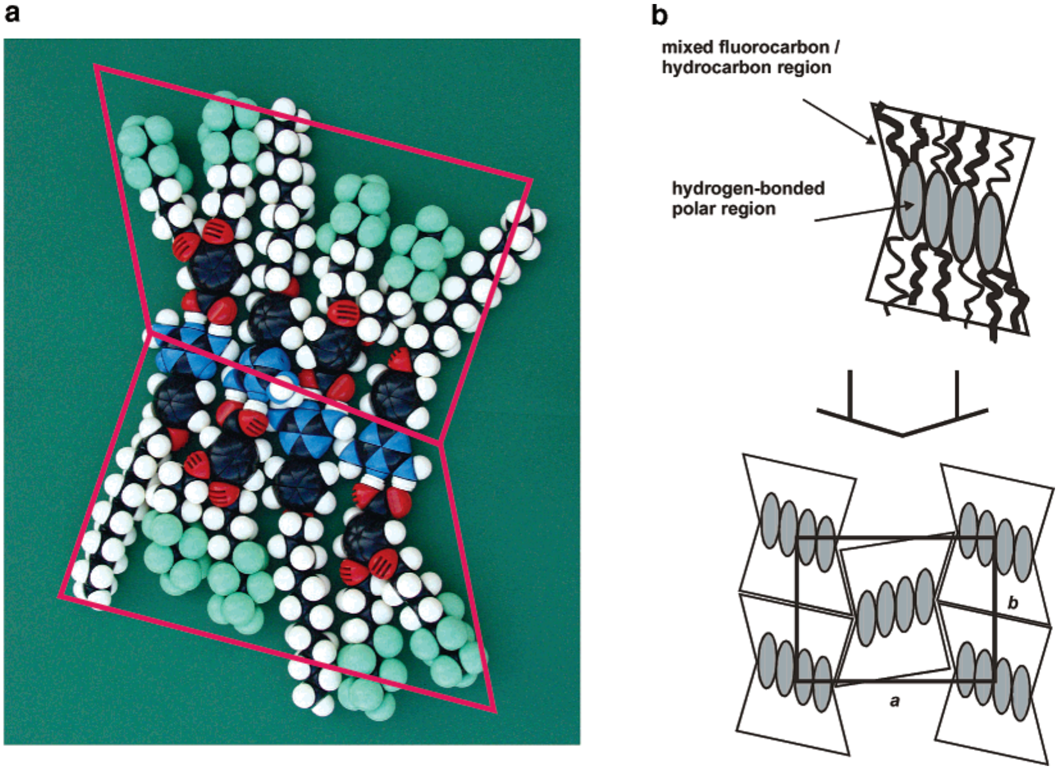


Figure 8. (a) CPK model showing an antiparallel arrangement of four **1**/**3**-[**4,4**] dimers; only more or less stretched conformations of the flexible alkyl chains are considered. (b) Schematic presentation of the ribbon phase of equimolar hydrogen-bonded complexes of the single chain triazine **1** with the fluorinated carboxylic acids **3**-[*n*,*m*] with a rectangular columnar (Col$_r$) organization (two-dimensional *p*2*gg* space group). Distortions of the rigid cores within the smectic C sublayers are not considered.

bonding of diamino-1,3,5-triazines with acids at a stoichiometric ratio occurs only at the sites that flank the smallest of the triazine substituents.[48]

To develop a structural model that coincides with the experimental findings from X-ray studies, the different cross-sectional areas of the perfluorinated chains (ca. 0.28 nm^2), of the aromatic parts (ca. 0.22 nm^2) and of the aliphatic moieties (ca. 0.18 nm^2)[49] of the molecules must be considered. The volume fraction of the two bulky semiperfluorinated chains is significantly larger than that of the single alkyl chain at the opposite position of the hydrogen-bonded central core. The result is a pronounced steric asymmetry that encourages an antiparallel packing of the molecules to achieve a favorable dense packing. An antiparallel correlation of molecules due to a steric dipole has been also reported, e.g., for partially fluorinated alkanes,[50] calamitic liquid crystals incorporating perfluorinated chains,[13] and semi-perfluorinated swallow-tailed mesogens.[51] Thus, the steric effects compete with the fluorophobic effect and frustrate the natural tendency of the three incompatible molecular parts to segregate into three different subspaces.

The number of dimeric **1**/**3**-[4,4] supermolecules in the rectangular unit cell was calculated according to $n = V_{\mathrm{cell}}/V_{\mathrm{mol}}$. The volume of the unit cell (V_{cell}) was calculated by assuming a height of 0.45 nm.[52] The molecular volume (V_{mol}) was calculated using volume increments.[53] The calculations yielded a value of approximately eight molecules per unit cell.

Figure 8a shows a possible antiparallel arrangement of four H-bonded dimers of the single-chain triazine **1** with the acid **3**-[4,4]. The hydrogen-bonded rodlike cores are parallel and close-packed. Thereby, the most efficient space filling arises for the aggregates if the rigid cores are shifted against each other. This arrangement corresponds to a smectic C layer structure of rod-shaped moieties that are tilted against the layer normal. The cross-sectional area of the terminal disordered mixed aliphatic/fluorinated regions still exceeds the cross section of the closely aligned H-bonded aromatic region. Therefore, we propose a ribbon structure for the mesophases formed by equimolar mixtures of the single-chain diaminotriazine **1** and the two-chain partially fluorinated benzoic acids **3** (Figure 8b).

The ribbons result from the breakup of the smectic layers due to the different space filling attributes of the mixed aliphatic/fluorinated and the polar aromatic regions. Ribbon phases have also been observed in the phase sequences of, for example, polar[54] or polycatenar[5] molecules.

It must, however, be noted that, for geometric reasons, the interruption of the smectic C layers with the formation

---

[48] (a) Paleos, C. M.; Tsiourvas, D.; Fillpakis, S.; Fillipaki, L. *Mol. Cryst. Liq. Cryst.* **1994**, *242*, 9. (b) Highfill, M. L.; Chandrasekaran, A.; Lynch, D. E.; Hamilton, D. G. *Cryst. Growth Design* **2002**, *2*, 15.

[49] Lose, D.; Diele, S.; Pelzl, G.; Dietzmann, E.; Weissflog, W. *Liq. Cryst.* **1998**, *24*, 707.

[50] Viney, C.; Twieg, R. J.; Russell, T. P.; Depero, L. E. *Liq. Cryst.* **1989**, *5*, 1783.

[51] Pelzl, G.; Diele, S.; Lose, D.; Ostrovski, B. I.; Weissflog, W. *Cryst. Res. Technol.* **1997**, *32*, 99.

[52] The value of 0.45 nm has also been used to calculate the number of semiperfluorinated calamitic bolaamphiphile molecules within the unit cell independent of the actual position of the maximum of the wide-angle scattering. See ref 30.

[53] Imirzi, A.; Perini, B. *Acta Crystallogr.* **1977**, *A33*, 216.

[54] Ostrovski, B. I. *Liq. Cryst.* **1993**, *14*, 131.

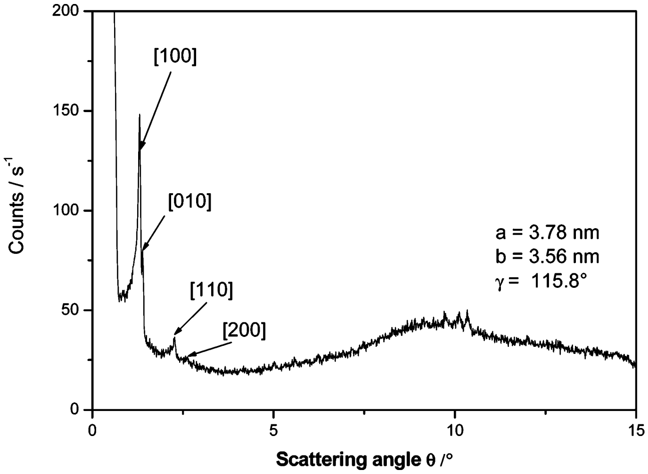


Figure 9. Wide-angle X-ray diffractogram for the columnar phase of the equimolar complementary mixture **2**/**3**-[**6,4**] measured at 90 °C.

of infinite ribbons of parallel aligned aromatic cores usually leads to columnar phases with a two-dimensional oblique lattice symmetry.[54]

According to the CPK model, at the outer sphere of the ribbons, 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 signifies a "second-order" steric asymmetry for the aggregates that can be compensated by an antiparallel arrangement of the ribbons, as shown schematically in Figure 8b. The assemblies of the rigid polar cores adopt an ellipsoidal shape. The ellipses within the rectangular unit cell are arranged in a herringbone manner, which is the geometrical requirement for a rectangular columnar phase with a 2D *p*2*gg* lattice symmetry.

The maximum molecular dimension of a **1**/**3**-[4,4] dimer amounts to approximately 4.2 nm, which is slightly larger than the lattice parameter *b* determined by X-ray diffraction. Hence, the lattice parameter *b* should correspond to the height of the ribbons taking into account the fluid character of the flexible molecular segments. The lattice parameter *a* matches nearly twice the lateral dimensions of the ribbons assuming an average of four dimers arranged within one ribbon.

The structural model with mixed hydrocarbon and fluorocarbon tails is further confirmed by the wide-angle halo in the X-ray diffraction, which is shifted to a lower angle compared to a pure alkyl halo. Thus, these considerations can explain the experimental findings quite well.

2.4. Equimolar Mixed Systems of the Two-Chain Triazine 2 with the Partially Fluorinated Acids **3**. Figure 9 shows the wide-angle X-ray diffractogram obtained for the mesophase of the equimolar **2**/**3**-[6,4] mixture. The small-angle reflections fit best by assuming a columnar structure with a two-dimensional oblique lattice (Col_{ob}). The resulting lattice parameters are $a = 3.78$ nm, $b = 3.56$ nm, and $\gamma = 116°$. A tentative explanation for the three low-intensity reflections in the wide-angle region might be a partial crystallization of the side chains during the time of the X-ray measurement.

Dimers of the two-chain triazine **2** and the fluorinated acids **3** with a rod-shaped H-bonded core resemble the structure of tetracatenar molecules[5] whereby the cross section of the semiperfluorinated chains still exceeds the cross-sectional area of the two alkyl chains. Therefore, it seems likely that the dimers within the mesophase are, on average, arranged in an antiparallel manner.

The number of hydrogen-bonded dimers of the triazine **2** with the benzoic acid **3**-[6,4] within the cross section of the oblique unit cell was calculated to be about three. One possible arrangement of the dimers with an antiparallel organization is shown in Figure 10a. The closest packing again arises for a parallel alignment of the rod-shaped cores in a smectic C manner.

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 to the complementary dimers of the single-chain triazine **1** with the acids **3**, compensates for a steric dipol of the aggregates. Therefore, the collapse of the smectic C layers results in a ribbon phase on a two-dimensional oblique lattice as expected (Figure 10b).

The single melting transition of equimolar compositions of the triazines **1** and **2** with the nonfluorinated two-fold alkoxy-substituted benzoic acid **4** can be regarded as a hint that the aminotriazines **1** and **2** and the acid **4** do not act as single molecular species, but that association of the two components occurs.

The polar nature of hydrogen-bonded cores of the triazines **1** and **2** with the acid **4** should be of the same order of magnitude as in the case of the apparent mesomorphic 1:1 mixtures with the fluorinated acids **3**. Obviously, three or even four alkyl tails are not sufficient for a balanced intramolecular contrast[44] to force mesomorphic structure formation.

Thus, the nonappearance of mesomorphic behavior for the mixtures **1**/**4** and **2**/**4** very distinctly illustrates the enhanced structure formation tendencies obtained by replacing the alkyl groups of the benzoic acid component by semiperfluorinated chains.

Thereby, it has to be emphasized that the fluorophobic effect is in competition with steric effects because of the different sizes of the hydrocarbon and fluorocarbon chains, leading to an antiparallel pairing of the H-bonded dimers. Simply tilting the aromatic cores with respect to the layer normal cannot sufficiently reduce the steric frustration. The smectic layers break up into ribbonlike aggregates that consist of segregated polar aromatic and mixed fluoroaliphatic regions. The ribbons organize into columnar mesophases.

2.5. Mixtures of the Single-Chain Triazine 1 with Two and Three Equivalents of the Fluorinated Acids **3**. The investigations of defined mixtures of the triazines with 2 and 3 equiv of the two-chain partially fluorinated benzoic acids revealed that mesomorphic structure formation is not restricted to equimolar complementary compositions.

The 1:2 mixture of **1**/**3**-[6,4] was investigated by X-ray scattering. 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 $a_{hex} = 3.95$ nm.

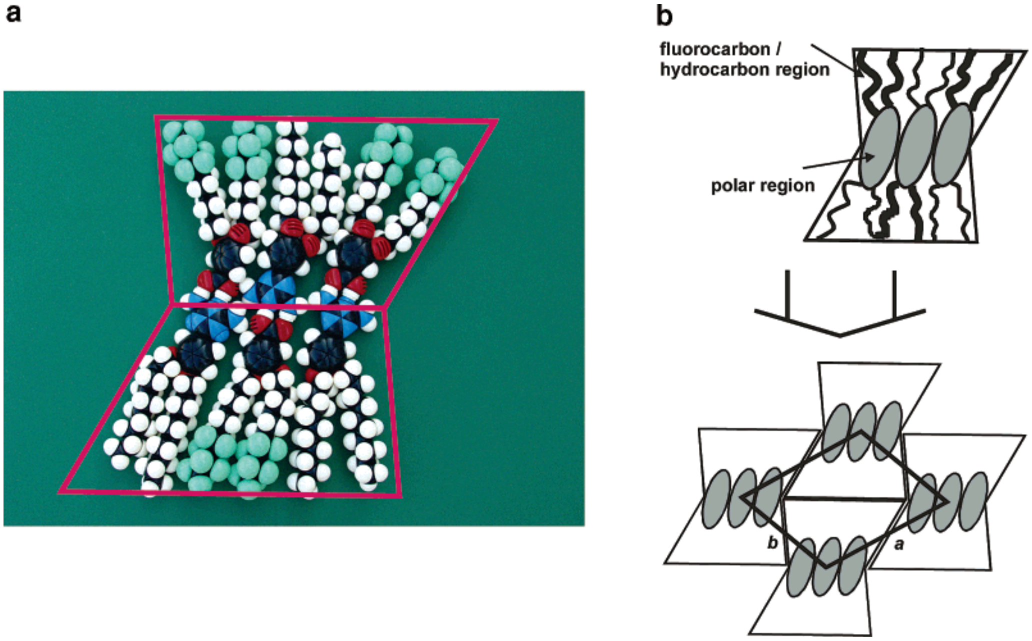


Figure 10. (a) CPK model showing three **2**/**3**-[**6,4**] dimers. The hydrogen-bonded rod-shaped cores are closely packed side-by-side and form a smectic C sublayer. (b) Model for the molecular arrangement of the equimolar H-bonded supermolecules of the two-chain triazine **2** with the benzoic acids **3**-[*n*,*m*] in the columnar mesophases with two-dimensional oblique lattice symmetry ($\mathrm{Col_{ob}}$).

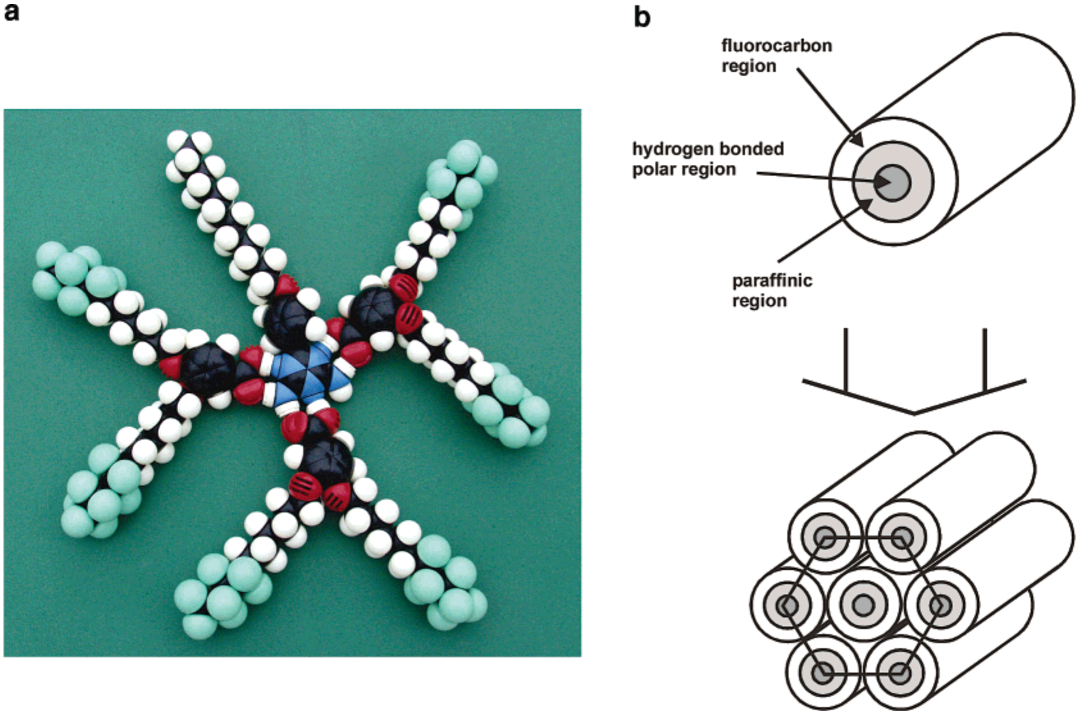


Figure 11. (a) CPK model of the single-chain triazine **1** associated with 3 equiv of the partially fluorinated benzoic acid **3**-[**6,4**] via hydrogen bonding. (b) Hexagonal columnar mesophase of the diaminotriazine **1** in mixtures with 2 or 3 equiv of the fluorinated benzoic acids **3**-[*n*,*m*] through hydrogen bonding and nanosegregation.

CPK models (Figure 11a) reveal a pronounced circular shape for H-bonded associations of the triazine **1** with 2 or 3 equiv of the acids **3**. The flexible lipophilic segments lead to a random distribution of the peripheral groups around the polar hydrogen-bonded core. Cylindrical aggregates are formed that are composed of three distinct molecular regions, the polar hydrogen-bonded aromatic region in the center surrounded by the lipophilic alkyl segments and finally by a shell of the fluorinated moieties. The parallel alignment of these aggregates gives rise to the two-dimensional hexagonal lattice symmetry (Figure 11b). The diameter of the (1:2) mixture of the triazine **1** and the acid **3**-[6,4], for example, evaluated from the CPK model amounts to ca. 4.4 nm. This value is in excellent agreement with the hexagonal lattice constant (3.95 nm) determined by X-ray diffraction.

The hydrogen bonding of the diaminotriazine with up to three acid molecules enhances the polarity of the core region. Simultaneously, the nonpolar and fluorophilic nature of the molecular periphery is enhanced by increasing the number of semiperfluorinated chains. The polar/nonpolar balance as the main driving force for the formation of the hexagonal columnar mesophases is not disturbed.

In case of both 1:1 and 1:2 aggregates of the triazine **1** with the acids **3**, H-donor groups as well as H-acceptor groups are still present. Therefore, additional (dynamic) hydrogen bonding should take place within the ribbons and/or along the column axis. This assumption is in line with the decrease of mesophase stability of the 1:3 complexes, as here, only one N−H function remains uncomplexed by the acid component and additional H-bonding of this function might be sterically hindered.

Conclusions

The diamino-substituted nitrogen heterocycle of the 1,3,5-triazines investigated here allows for hydrogen bonding with complementary two-chain semiperfluorinated benzoic acids. We suggest that, in equimolar mixtures of the complementary components, predominantly descrete dimeric supermolecules are formed. The shape of the dimers introduces a steric molecular dipole that encourages an antiparallel alignment of the supermolecules with a close packing of the aromatic cores. However, the different cross sections of the aliphatic/fluorinated and aromatic regions lead to a frustration of the organization in layers. The H-bonded aromatic sublayers break up into infinite ribbons of parallel aligned polar aromatic cores that are separated by mixed lipophilic/fluorinated regions. The aromatic−aliphatic/fluorinated interface curvature and, thus, the two-dimensional lattice type of the ribbon phases are determined by the number of alkoxy tails grafted to the aminotriazine component.

Docking of 2 or 3 equiv of the acid component to the diaminotriazine core significantly increases the volume fraction of the semiperfluorinated segments. Cylinders with a circular shape are formed that organize into hexagonal columnar mesophases.

Hence, the competitive combination of polar−nonpolar microsegregation through molecular recognition along with tailoring of the molecular topology by the space requirement of lipophilic and fluorinated segments determine the mesophase morphologies of the hydrogen-bonded diaminotriazine−benzoic acid supermolecules.

Acknowledgment. This work was suported by the Land Brandenburg, Germany. We are grateful to L. Torre-Lorente and G. Lattermann for their kind support in performing X-ray measurements at Bayreuth University, Bayreuth, Germany.

Supporting Information Available: Experimental procedures and analytical data (NMR). This material is available free of charge via the Internet at http://pubs.acs.org.

CM0515193