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Structural Study on Columnar Mesophases Consisting of H-Bonded Supramolecules

Joaquín Barberá, Laura Puig, José Luis Serrano,* and Teresa Sierra

Química Orgánica, Facultad de Ciencias, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

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The use of complementary 2,4,6-triarylamino-1,3,5-triazines and benzoic acids has allowed the preparation of a variety of disklike supramolecules with different substitution patterns around an H-bonded aromatic core. Most of the complexes obtained show columnar mesomorphism promoted by an efficient columnar packing of the aromatic cores surrounded by a minimum of six peripheral tails. The steric requeriments for the appearance of mesomorphic behavior in these supramolecular complexes have been established by X-ray diffraction studies and density calculations based on the parameters of the liquid crystalline organization.

Introduction

Hydrogen bonding, one of the most important of the inter- and intramolecular interactions in natural molecular organizations, is an important driving force in the control of supramolecular organizations based on the mesomorphic state. Several reviews have clearly described the importance of this type of noncovalent interaction in the construction of new liquid crystalline materials.[1] Supramolecules as well as supramolecular polymers have been prepared from components that are appropriately substituted with functional H-donor and H-acceptor groups. Such systems are able to self-organize into mesophases, even though they are not necessarily mesogenic in their own right. These complexes present the same types of mesophases as covalently built mesogenic molecules. However, the resulting organizations may rely on some additional features derived from the dynamic character of the H-bond.

Several disklike supramolecules built through hydrogen bonding have been reported to display columnar mesomorphism. Owing to the importance of this type of liquid crystalline architecture, for applications such as (semi)conducting and photoconducting materials and chemical sensors,[2] we considered it of interest to undertake an exhaustive structural study of columnar mesophases formed from disklike supermolecules. In this respect, 2,4,6-triarylamino-1,3,5-triazines have already been reported as useful components for mesogenic H-bonded complexes with carboxylic acids.[3] For example, it has already been reported that 2,4,6-triarylamino-1,3,5-triazines form heterodimeric complexes with benzoic acid derivatives and that the resulting materials show columnar mesomorphism. We took this type of complex as a model and prepared several modified molecular structures that formed the basis of a study, based mainly on X-ray diffraction and density calculations, aimed at understanding the requirements of these supramolecular complexes for mesophase formation and how they are accommodated within a given columnar mesophase. Five types of 2,4,6-triarylamino-1,3,5-triazine (T1−T5 in Chart 1) with different substitution patterns in the aromatic ring were prepared and complexed with the polycatenar benzoic acids (A1−A6 in Chart 2).

Results

Synthesis. The 2,4,6-triarylamino-1,3,5-triazines (T1−T5) were prepared by reaction of the corresponding alkyl(alkoxy)-substituted anilines with cyanuric chloride using potassium carbonate as a base and 2-butanone as a solvent.[4] The synthesis initially involved the preparation of alkoxy-substituted anilines by reduction of the corresponding nitro compounds with 20% $Pd(OH)_2/C$ in ethanol in the presence of cyclohexene as a hydrogen donor. The alkyl-substituted anilines were commercially available.

The benzoic acid derivatives A1−A4 were prepared by Williamson etherification of the corresponding methyl hydroxybenzoate with the appropriate alkyl bromide, followed by alkaline ester cleavage according to methods

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* To whom correspondence should be addressed. E-mail: joseluis@unizar.es.

(1) For reviews see: (a) Paleos, C. M.; Tsiourvas, D. *Angew. Chem., Int. Ed. Eng.* **1995**, *34*, 1696−1711. (b) Kato, T.; Mizoshita, N.; Kanie, K. *Macromol. Rapid Commun.* **2001**, *22*, 797−814. (c) Beginn, U. *Prog. Polym. Sci.* **2003**, *28*, 1049−1105.

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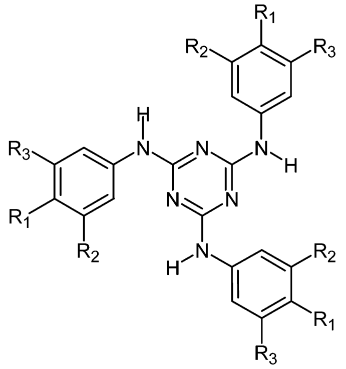
10.1021/cm049738w CCC: $27.50

Chart 1



Triazine	R_1	R_2	R_3
T1	$C_{10}H_{21}$	H	H
T2	$C_{12}H_{25}$	H	H
T3	$OC_{10}H_{21}$	H	H
T4	$OC_{10}H_{21}$	$OC_{10}H_{21}$	H
T5	$OC_{10}H_{21}$	$OC_{10}H_{21}$	$OC_{10}H_{21}$

described elsewhere.[5] The acid A5 was synthesized by Williamson etherification of methyl 3,4,5-trihydroxybenzoate with 4-*n*-dodecyloxybenzyl chloride, followed by alkaline ester cleavage according to the method described in detail elsewhere.[6] The acid A6 was prepared by esterification of benzyl 3,5-dihydroxybenzoate with 3,4,5-tridodecyloxybenzoyl chloride by the procedure described elsewhere.[7]

When a solution of equimolar amounts of both a triazine (T1−T5) and one of the benzoic acids (A1−A6) was evaporated and the material heated to the isotropic state, a dimeric complex consisting of both species linked through H-bonding was obtained. All the mixtures gave rise to homogeneous materials, providing evidence for the formation of a complex, except for triazine T5 with the bulky acids A5 and A6. Steric hindrance is the most likely reason for the separation of the two components on cooling from the melt.

The formation of the mixed complex is readily deduced from infrared spectra. The infrared spectra of the separate components, triazine and acid, and that of the corresponding mixture were recorded from KBr pellets. As a representative example, the infrared spectra of T3, A5, and their complex T3:A5 are shown in Figure 1. A clear change in the characteristic carbonyl bands is observed between the acid and the mixture. Two $C{=}O$ stretching bands appear in the acid and these correspond to the dimeric form (1668 cm^{-1}) and to the nonassociated form (1733 cm^{-1}). After H-bonding association with the triazine, however, these bands merge to give a single peak at 1680 cm^{-1}, which corresponds to the associated triazine−carboxylic acid. Changes in the region corresponding to the N−H stretching band are also significant. A sharp peak (3392 cm^{-1}) and a broad band (3250 cm^{-1}) that could be assigned to nonassociated and H-bonded N−H bonds, respectively, are observed in the mixture, which gives a much simpler spectrum than the triazine alone. Indeed, triazine T3 shows several bands within this region and these are thought to correspond to different conformers of the molecule. We also found evidence for complex formation in the ^1H NMR spectra recorded in $CDCl_3$ solutions. The N−H proton appears as a singlet in the pure triazine (6.9 ppm for T3, as an example), which is broadened and shifted to lower fields upon H-bonding association with the acid (7.1−7.3 ppm for T3:A3).

Thermal Behavior. The thermal properties of the separate components and the mixtures were determined by polarizing optical microscopy and differential scanning calorimetry on the second heating cycle at a rate of 10 °C min^{-1}. Transition temperatures and enthalpy values are given in Table 1.

Only two of the benzoic acid derivatives employed in this study show mesomorphic behavior. A1 displays smectic C and nematic mesophases[8] whereas A5 shows a hexagonal columnar phase over a wide temperature range.[6] In both cases the formation of dimers is responsible for the observed calamitic and columnar behavior, respectively, and this aspect will be discussed in more detail below.

Three of the five 2,4,6-triaryl-1,3,5-triazines employed in this study show mesomorphic behavior (T3, T4, and T5). All three mesomorphic compounds bear *n*-alkoxy terminal chains. Triazine T3, which bears only one terminal chain in each aromatic ring, shows a monotropic SmA phase. In contrast, the presence of two or three alkoxy tails in each aromatic ring promotes the appearance of columnar mesomorphic behavior. Indeed, an enantiotropic hexagonal columnar mesophase is observed for triazines T4[9] and T5. Moreover, T5 is mesomorphic at room temperature.

On considering the data in Table 1, it can be deduced that at least six terminal chains are necessary for the complexes to display columnar mesomorphism. For example, complexes T1:A1, T2:A1, and T3:A1 bear a total of four terminal tails (3 + 1) each and complexes T1:A2, T2:A2, and T3:A2 bear a total of five terminal tails (3 + 2) each; these do not exhibit mesomorphic behavior. The case of T3:A1 is in agreement with the results reported for a similar triazine and *p*-octyloxybenzoic acid, which gave rise to mesomorphic behavior in the H-bonded complex.[3b] On the other hand, complexes formed between T1 (or T2) with acid A6, which

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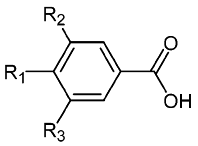
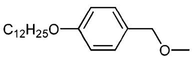
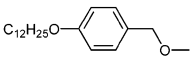
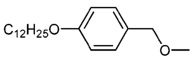
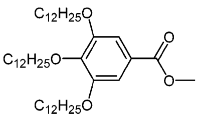
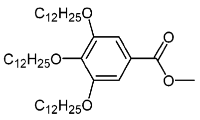
Chart 2



Acid	R_1	R_2	R_3
A1	$OC_{10}H_{21}$	H	H
A2	$OC_{10}H_{21}$	$OC_{10}H_{21}$	H
A3	$OC_{10}H_{21}$	$OC_{10}H_{21}$	$OC_{10}H_{21}$
A4	$OC_{12}H_{25}$	$OC_{12}H_{25}$	$OC_{12}H_{25}$
A5			
A6	H		

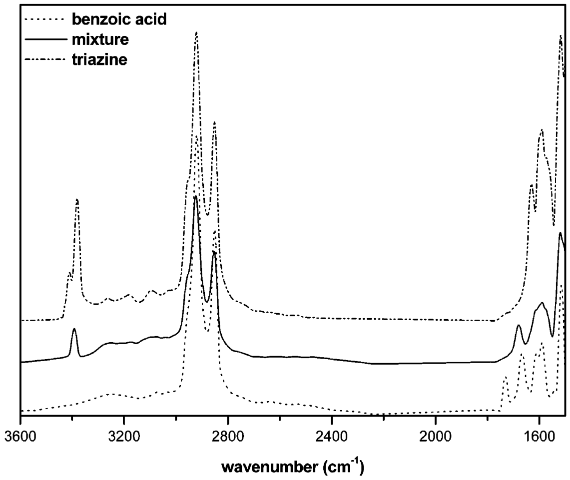


Figure 1. FTIR spectra of the pure triazine (T3), equimolar mixture (T3:A5), and acid A5.

have a total of nine tails, are not mesomorphic. In this case, the reason for the absence of a mesophase can be related to the alkyl character of the tails in the triazines since triazine T3, which also has three terminal tails (but alkoxy rather than alkyl), does show columnar mesomorphism when associated with a molecule of acid A6. It must be borne in mind that T3 is mesomorphic in the pure state, whereas T1 and T2 are not. The increases in both the polarizability and the dipolar moment of the system due to the presence of the oxygen atom favor the intermolecular interactions and, consequently, mesomorphic behavior.

Structural Characterization of the Mesophases. All the compounds were studied by X-ray diffraction with the aim of elucidating the type of mesophase and determining the lattice parameters. Most of the experiments were performed at room temperature; however, in some cases high-temperature experiments were also carried out. The proposed indexing, the lattice constants, and the observed and calculated spacings are gathered in Tables 2−5.

Mesophase Structure of the Pure Triazines. Triazine T3 yielded X-ray patterns characteristic of a smectic mesophase (Sm). The X-ray patterns showed two sharp maxima in the low-angle region with a reciprocal spacing ratio of 1:2. These maxima can be assigned to the (0 0 1) and (0 0 2) reflections from the layered arrangement. Furthermore, a diffuse halo was visible, caused by the liquidlike arrangement of the aliphatic chains. All these features are characteristic of a smectic mesophase. The type-A smectic mesophase (SmA) was confirmed by textural studies.

Triazine T5 yielded X-ray patterns characteristic of a hexagonal columnar (Col_h) mesophase (see Table 2). The pattern for this phase is characterized by the presence of a set of two sharp maxima in the low-angle region with a reciprocal spacing ratio of $1{:}\sqrt{3}$. These maxima can be assigned to the (1 0 0) and (1 1 0) reflections from the two-dimensional hexagonal lattice. A diffuse ring corresponding to a mean distance of 4.3 Å was also observed and this is characteristic of the liquidlike order between the aliphatic chains. In contrast, the presence of a single reflection in the X-ray

Table 1. Thermal Properties—Transition Temperatures, °C, and Enthalpies, kJ/mol—of the Pure Benzoic Acid Derivatives, 1,3,5-Triaryltriazine Derivatives, and Their Corresponding Hetero-dimeric Complexes (as the Intersection Cell between the Corresponding A1−6 Entry and T1−5 Entry)

	A$_1$	**A$_2$**	**A$_3$**	**A$_4$**	**A$_5$**	**A$_6$**
	Cr−SmC 83.3 [32.9] SmC−N 112.2 [1.0] N−I 135.1 [3.4]	Cr$_1$−Cr$_2$ 100.2 [7.4] Cr$_2$ −I 119.1 [49.0]	Cr−I 49.7 [57.9]	Cr$_1$−Cr$_2$ 29.8 [2.4] Cr$_2$−I 50.9 [63.7]	Cr−Col$_h$ 64.6 [74.2] Col$_h$ −I 143.8 [11.1]	Cr−I 76.7 [93.29]
T1 Cr−I 114.6 [44.1]	Cr−I 77.3 [76.7]	Cr−I 80.9 [66.0]	Col$_h$−I 50.3 [1.5]	Col$_h$−I 51.8 [2.5]	Cr−Col$_h$ 79.5 [5.2] Col$_h$−I 95.3 [4.5]	Cr−I 77.7 [77.3]
T2 Cr−I 106.7 [45.4]	Cr−I 77.0 [70.1]	Cr−I 80.4 [70.1]	Col$_h$−I 50.9 [1.9]	Col$_h$−I 70.3 [10.3]	Cr−Col$_h$ 86.3 [11.7] Col$_h$−I* 89.6 [1.0]	Cr−I 56.8 [103.0]
T3 Cr−I 105.1 [44.7] I−SmA 66.0 [2.0]	Cr$_1$−Cr$_2$ 52.6 [17.0] Cr$_2$−I 60.2 [27.8]	Cr$_1$−Cr$_2$ 48.0 [8.1] Cr$_2$−I 78.1 [62.6]	Col$_h$−I 64.3 [1.6]	Col$_h$−I 77.0 [2.9]	Cr−Col$_h$ 84.8 [12.1] Col$_h$−I 118.2 [1.7]	Cr−Col$_h$ 55.2 [69.9] Col$_h$−I 67.7 [5.8]
T4 Cr −Col$_h$ 71.1 [83.0] Col$_h$ −I 86.6 [2.8]	Col$_h$−I 57.3 [4.9]	Cr$_1$−Col$_h$ 46.1[3.2] Col$_h$−I 75.6 [6.3]	Col$_h$−I 71.7 [4.1]	Col$_h$−I 82.2 [9.2]	Cr$_1$−Cr$_2$ 91.6 [4.0] Cr$_2$−Col$_h$ 111.5 [1.9] Col$_h$−I 132.8 [14.1]	Cr$_1$−Cr$_2$ 39.9 [1.3] Cr$_2$−Col$_h$ 62.5 [48.5] Col$_h$−I 66.6 [6.6]
T5 Col $_h$−I 34.0 [2.0]	Cr−Col$_r$ 29.8 [18.0] Col$_r$−I 70.2 [37.7]	Cr$_1$−Cr$_2$ 51.6 [5.3] Cr$_2$−I 81.6 [35.2]	Col$_r$−I 33.9 [9.6]	Col$_r$−I 32.4 [5.5]	no complex	no complex

Table 2. X-ray Diffraction Data for the Mesophases of the Pure Triazines

compound	*T* (°C)	phase	lattice constants (Å)	d_{obs} (Å)	d_{calc} (Å)	*hkl*
T3	rt	SmA	$d = 34.0$	33.6 17.2 4.4 (br)	34.0 17.0	001 002
T4	rt	Col$_{hd}$	$a = 33.4$	28.9 4.4 (br)	28.9	100
T5	rt	Col$_{hd}$	$a = 29.8$	25.7 15.0 4.3 (br)	25.8 14.9	100 110

Table 3. X-ray Diffraction Data for the Mesophases of the 1:1 Complexes of the 1,3,5-Tris(4-alkylarylamino)-triazines, T1 and T2, with the Benzoic Acid Derivatives

compound	*T* (°C)	phase	lattice constants (Å)	d_{obs} (Å)	d_{calc} (Å)	*hkl*	calcd. density (g/cm^3)
T1:A3	rt	Col$_{ho}$	$a = 29.5$ $c = 3.4$	25.5 14.8 12.8 4.45 (br) 3.4 (br)	25.55 14.75 12.77	100 110 200	0.88
T1:A4	rt	Col$_{ho}$	$a = 31.7$ $c = 3.4$	27.4 15.8 13.8 4.4 (br) 3.4 (br)	27.45 15.85 13.73	100 110 200	0.81
T1:A5	rt	Col$_{ho}$	$a = 34.7$ $c = 3.3$	29.6 17.7 4.4 (br) 3.3 (br)	30.05 17.35	100 110	0.86
T2:A3	rt	Col$_{ho}$	$a = 31.8$ $c = 3.4$	27.4 16.0 4.45 (br) 3.45 (br)	27.54 15.90	100 110	0.80
T2:A4	rt	Col$_{ho}$	$a = 32.3$ $c = 3.4$	28.0 16.1 4.4 (br) 3.4 (br)	27.97 16.15	100 110	0.83
T2:A5	rt	Col$_{ho}$	$a = 37.1$ $c = 3.3$	32.2 18.5 4.4 (br) 3.3 (br)	32.13 18.55	100 110	0.80

patterns of triazine T4 made it difficult to unambiguously assign the hexagonal columnar nature of the mesophase. However, the hexagonal mesophase was confirmed by textural studies.

It is interesting to note that the hexagonal lattice constant decreases on increasing the number of alkoxy chains attached to the central molecular core of the triazines. This behavior, although surprising at first sight, can be accounted for by the formation of dimeric disks in T4, as will be discussed below.

Table 4. X-ray Diffraction Data for the Mesophases of the 1:1 Complexes of the 1,3,5-Tris(4-alkoxyarylamino)triazine, T3, and 1,3,5-Tris(3,4-dialkoxyarylamino)triazine, T4, with the Benzoic Acid Derivatives

compound	*T* (°C)	phase	lattice constants (Å)	d_{obs} (Å)	d_{calc} (Å)	*hkl*	calcd. density (g/cm^3)
T3:A3	rt	Col$_{hd}$	$a = 31.8$	27.4 15.6 4.4 (br)	27.54 15.90	100 110	
T3:A4	rt	Col$_{ho}$	$a = 32.9$ $c = 3.4$	28.5 16.5 4.3 (br) 3.4 (br)	28.49 16.45	100 110	0.77
T3:A5	92	Col$_{hd}$	$a = 36.3$	31.4 4.5 (br)	31.4	100	
T3:A6	60	Col$_{hd}$	$a = 37.5$	32.5 4.4 (br)	32.5	100	
T4:A1	rt	Col$_{ho}$	$a = 34.2$ $c = 3.4$	29.6 4.3 (br) 3.4 (br)	29.6	100	0.75
T4:A2	rt	Col$_{hd}$	$a = 35.6$	30.8 4.4 (br)	30.8	100	
T4:A3	rt	Col$_{hd}$	$a = 33.5$	29.0 4.35 (br)	29.0	100	
T4:A4	rt	Col$_{ho}$	$a = 34.3$ $c = 3.4$	29.6 17.2 4.3 (br) 3.45 (br)	29.73 17.16	100 110	0.93
T4:A5	100	Col$_{hd}$	$a = 35.8$	31.4 17.7 4.5 (br)	31.04 17.92	100 110	
T4:A6	59	Col$_{hd}$	$a = 36.3$	31.4 4.4 (br)	31.4	100	

Mesophase Structure of the Complexes. The X-ray patterns of all the complexes considered in Tables 3 and 4 are qualitatively very similar, although the number of diffraction rings observed depends on the particular compound. For instance, the patterns of complexes T1:A3 and T1:A4 have in common the existence of a set of three sharp maxima with a reciprocal spacing ratio of $1{:}\sqrt{3}{:}\sqrt{4}$. This is unambiguously characteristic of a hexagonal lattice, and the three maxima can be assigned to the (1 0 0), (1 1 0), and (2 0 0) reflections. In addition, two diffuse haloes at high angles were detected: one at 4.4−4.5 Å, which is characteristic of the conformationally disordered aliphatic chains, and the other at 3.4 Å, which is indicative of the periodic stacking of the molecular cores within a column (*c* constant of the hexagonal network).[10]

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Table 5. X-ray Diffraction Data for the Mesophases of the 1:1 Complexes of the 1,3,5-Tris(3,4,5-trialkoxyarylamino)-triazine, T5, with the Benzoic Acid Derivatives

compound	*T* (°C)	phase	lattice constants (Å)	d_{obs} (Å)	d_{calc} (Å)	*hkl*
T5:A1	40	Col$_r$	$a = 51.3$	25.7	25.65	200, 110
			$b = 29.6$	19.5	19.39	210
				14.8	14.81	020, 310
				7.8	7.82	430
				6.4	6.41	800, 440
				5.7	5.60	640
				4.3 (br)		
T5:A3	rt	Col$_r$	$a = 52.8$	26.4	26.40	200, 110
			$b = 30.5$	20.0	19.95	210
				15.1	15.24	020, 310
				4.3 (br)		
T5:A4	rt	Col$_r$	$a = 53.0$	27.1	27.30	200, 110
			$b = 30.3$	20.6	20.63	210
				15.8	15.76	020, 310
				4.3 (br)		

Some of the complexes give X-ray patterns that are difficult to interpret as they contain a small number of maxima, some of which are weak or diffuse. Such a situation indicates a high degree of disorder. Despite the presence of only one or two reflections at low angles, the patterns are consistent with a hexagonal columnar mesophase (see Tables 3 and 4). In those cases the hexagonal columnar mesophases were confirmed by polarizing optical microscopy.

The relationship between the density (ρ) of the complexes in the mesophase and the number of the molecules in the unit cell (Z) is given by the following equation: $\rho = (M/N)/(V/Z)$, where M is the molar mass (g) of the pure compound or of the complex, N the Avogadro number, and V the unit cell volume (cm^3): $V = (\sqrt{3}/2)a^2c \times 10^{-24}$. Assuming that the density of the complexes should not be far from 1 g/cm^3, it is clear that there is one complex supermolecule per unit cell and the calculated density of the mesophase is 0.75−0.93 g/cm^3 (see Tables 3 and 4). Although we have no experimental support, these values are reasonable for molecules with a high contribution of hydrocarbon chains.

The hexagonal lattice constant (parameter a) depends on the particular complex. An increase in the intercolumnar distance is observed on increasing the number of chains and the lengths of alkoxy groups attached to the central core of the benzoic acid derivatives. A major change takes place in the complexes with acids A5 and A6 compared to the other acids studied. In complexes T4:A1 to A6, the hexagonal lattice constants are larger than those for the pure triazine T4, which yields a hexagonal columnar mesophase itself.

The complexes in Table 5 yield X-ray patterns that are characteristic of a rectangular columnar mesophase (Col$_r$). This mesophase is identified by the presence of a set of low-angle maxima related to a two-dimensional (2D) array of columns. The spacings can be indexed in a 2D rectangular lattice and the lattice constants are shown in Table 5. Furthermore, a diffuse ring corresponding to a mean distance of 4.3 Å is also observed and is characteristic of the liquidlike order between the aliphatic chains.

It is interesting to note that for these three complexes the rectangular lattice constants a and b (Table 5) are in the ratio $\sqrt{3}$, which in principle should correspond to a hexagonal structure. However, the (2 1 0) reflection observed in all the patterns is not consistent with a hexagonal symmetry. A hexagonal cell is equivalent to a C-centered orthorhombic cell with lattice constants a and b, where b is the lattice constant of the hexagonal cell and a is equal to $b\sqrt{3}$. A C-centered orthorhombic symmetry implies that the molecule located at ($^1/_2$, $^1/_2$, 0) has the same orientation as the molecule located at (0, 0, 0) and thus all the (h k 0) reflections with an odd value for $h + k$ should be systematically absent. This is not the case in the compounds in question, as revealed by the presence of an extra reflection. Hence, it can be concluded that although the column axes are located at the nodes of a hexagonal lattice, the molecules must be tilted and there is an alternation in the tilt direction. The resulting space group is $P2_1$ and the rectangular symmetry arises from a herringbone-like arrangement of the elliptical sections of the columns when viewed along the column axes.[11] The same kind of pseudohexagonal arrangement has been found in a number of nonchiral[12] and chiral[13] columnar mesophases.

Discussion

Pure Compounds. X-ray measurements have shown that, in a similar way to the acids, triazines are susceptible to forming H-bonded dimers. This situation has been clearly confirmed from studies on triazine T4, which bears two decyloxy tails in each aromatic ring. This triazine displays a hexagonal columnar mesophase with a lattice parameter of 33.4 Å, which can only be explained if a column consists of stacked disks formed from two triazine molecules, as shown in Figure 2b. Triazine T5 also shows a hexagonal columnar mesophase, but its lattice parameter (a = 29.8 Å) is significantly smaller than that measured for T4. In this case monomeric species must stack within the columnar mesophase (Figure 2c). Indeed, a hypothetical dimer would need to accommodate 18 chains in a disk within the column, and this is sterically unfavorable.

These results lead us to deduce that due to the size of the rigid core of the dimer, six chains are not sufficient to efficiently fill the space around the disk. Consequently, the three triazines—each bearing a total of three terminal chains (T1, T2, and T3)—cannot show columnar mesophases. In fact, T1 and T2 do not show mesomorphic behavior at all. However, the derivative bearing one decyloxy terminal chain in every aromatic ring (T3) shows a monotropic SmA phase in which the measured smectic layer distance is similar to the parameter of the hexagonal columnar phase measured for T4 (see Figure 2a). Dimeric species must also be present within the smectic layers of this triazine. An extended H-bonded ribbon is improbable due to steric factors since conformations are clearly restricted once a dimer has formed (see Figure 2a).

The above reasoning, especially concerning columnar triazines (i.e., T3 and T4), is supported by a qualitative evaluation of the density of these materials. One can assume an interdisk distance of 4.4 Å, which is typical

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[11] (a) Levelut, A. M. *J. Phys. Lett.* **1979**, *40*, 81. (b) Levelut, A. M.; Oswald, P.; Ghanem, A.; Malthête, J. *J. Phys.* **1984**, 745−754. (c) Levelut, A. M.; Malthête, J.; Collet, A. *J. Phys.* **1986**, *47*, 351−357.

[12] Weber, P.; Guillon, D.; Skoulios, A. *Liq. Cryst.* **1991**, *9*, 369−382.

[13] Barberá, J.; Iglesias, R.; Serrano, J. L.; Sierra, T.; de la Fuente, M. R.; Palacios, B.; Pérez-Jubindo, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 2908−2918.

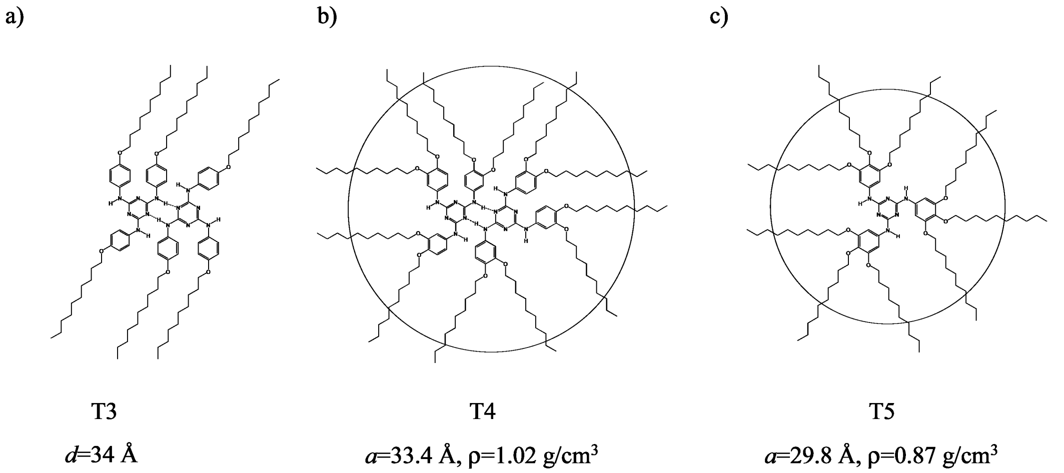


Figure 2. Schematic representation of the proposed dimeric forms of T3 and T4 and the monomeric form of T5.

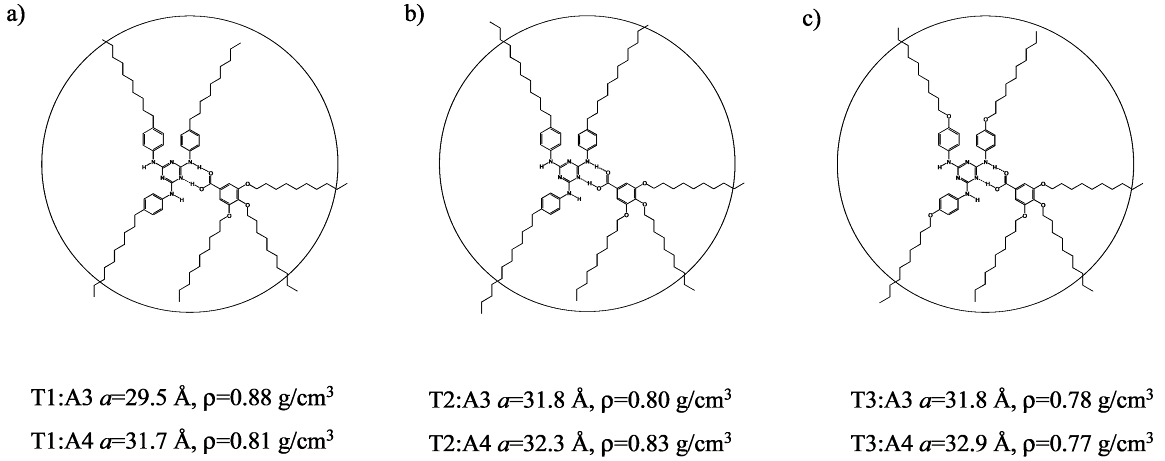


Figure 3. Schematic representation of the disklike hetero-dimers consisting of triazines T1, T2, and T3 and the trialkoxybenzoic acids A3 and A4.

of discotic compounds and corresponds well to the diffuse halo detected in our compounds T4 and T5. On this basis, a density of 1.02 g/cm^3 can be estimated for triazine T4, bearing in mind that each disk within the column is a dimer (the density of the hexagonal organization with a lattice constant a = 33.4 Å consisting of monomeric species would have a density of only 0.51 g/cm^3, which is too low). However, a value of 0.87 g/cm^3 for T5 is calculated if we consider stacking of monomeric triazines within the mesophase. If the structure consisted of columns of dimeric species, then the resulting density should be 1.74 g/cm^3, which is too high for an organic compound. These values are reasonable and close to those found and reported below for the complexes.

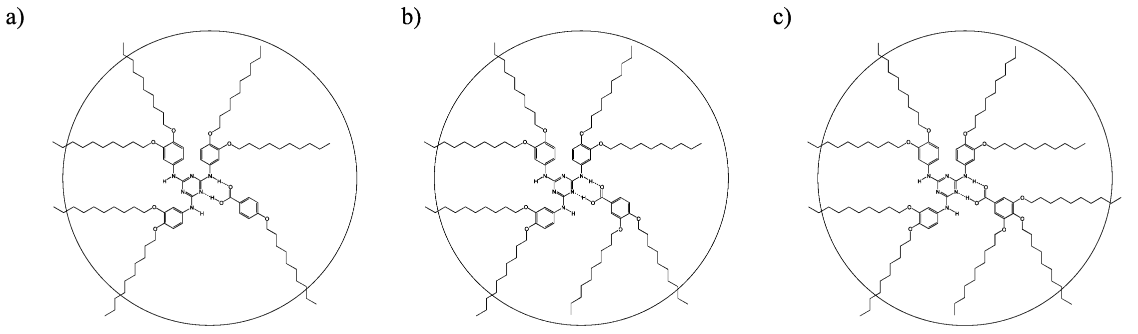
H-Bonded Complexes Triazine:Acid, 1:1. The X-ray measurements reported in the Results section allowed a detailed study of the packing conditions of the disklike complexes within the corresponding columnar mesophase.

H-Bonded Complexes with Mono-, Di-, and Trialkoxybenzoic Acids: A1, A2, A3, and A4. Apart from the complexes described above, which have a total number of peripheral tails of either 3 + 1 or 3 + 2, the rest of the complexes formed from triazines T1, T2, and T3 show a hexagonal columnar mesophase. In the case of acids A3 and A4 this mesophase is stable at room temperature.

The evaluation of the density of these materials was made quantitatively for complexes T1:A3, T1:A4, T2:A3, T2:A4, and T3:A4, which all show a hexagonal columnar phase with a regular stacking distance, as determined by X-ray diffraction. The density of T3:A3 (Figure 3c), which does not show a regular stacking distance, was qualitatively estimated considering a similar interdisk distance, that is, 3.4 Å, to the complexes discussed above. The density values obtained are, respectively, as follows: T1:A3, 0.88 g/cm^3; T1:A4, 0.81 g/cm^3; T2:A3, 0.80 g/cm^3; T2:A4, 0.83 g/cm^3; T3:A3, 0.78 g/cm^3; T3:A4 = 0.77 g/cm^3. These data confirm the composition of every complex as consisting of one triazine molecule per acid molecule, as well as a similar columnar arrangement in all cases.

Triazines T4 and T5, with a total of six and nine peripheral tails, respectively, exhibit columnar hexagonal mesophases in the pure state. As discussed previously, the disk is actually a dimeric species in the former compound and a single molecule in the latter. It is reasonable to expect that the complexes formed by these triazines are much more likely to display columnar mesomorphism. Thus, complexes of T4 with the acids A1, A2, A3, and A4 (Figure 4) all exhibit a columnar hexagonal mesophase, which is even stable at room temperature for derivatives of A1, A3, and A4.

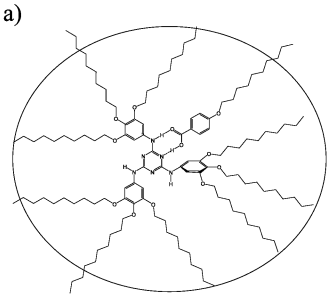
All of these complexes exhibit hexagonal columnar phases with similar lattice constants. Complexes T4:



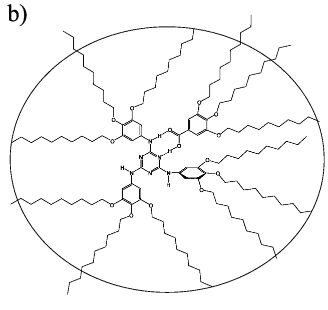
T4:A1 a=34.2 Å, ρ=0.75 g/cm^3 T4:A2 a=35.6 Å, ρ=0.77 g/cm^3 T4:A3 a=33.5 Å, ρ=0.94 g/cm^3

T4:A4 a=34.3 Å, ρ=0.93 g/cm^3

Figure 4. Schematic representation of the disklike hetero-dimers consisting of triazine T4 and the mono-, di-, and trialkoxybenzoic acids A1, A2, A3, and A4.



T5:A1 a=51.3 Å, b=29.6 Å



T5:A3 a=52.8 Å, b=30.5 Å

T5:A4 a=53.0 Å, b=30.3 Å

Figure 5. Schematic representation of the disklike hetero-dimers consisting of triazine T5 and the mono- and trialkoxybenzoic acids A1, A3, and A4.

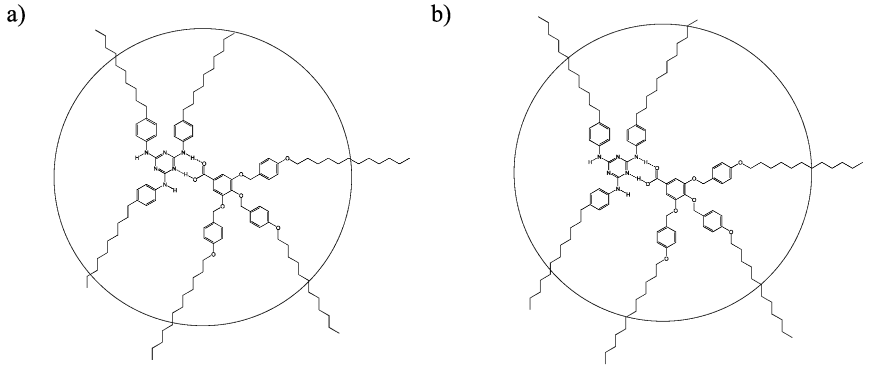
A1 and T4:A4 show ordered phases, a situation that allows us to obtain density values of 0.75 and 0.93 g/cm^3, respectively. On applying a similar approach as before, it is possible to estimate qualitative values for complexes T4:A2 (0.77 g/cm^3) and T4:A3 (0.94 g/cm^3).

Complexation of T5 with acids A1, A3, and A4 gives rise to materials (Figure 5) that exhibit a rectangular columnar mesophase at low temperatures. This indicates a different organization of the complex. The considerable size of triazine T5, which bears a total of nine terminal chains surrounding the triaryl-triazine core, makes it more difficult for the acids to be accommodated within a columnar packing arrangement with hexagonal symmetry. This difficulty is supported by the negative results observed on attempting to achieve H-bonding association between T5 and bulky acids, such as A5 and A6. The three complexes actually formed display a different type of two-dimensional columnar arrangement, that is, Col$_r$.

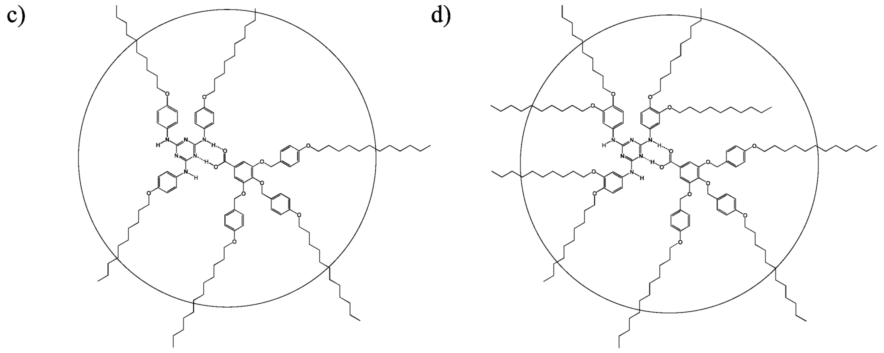
It can also be seen that the different behavior observed for these complexes depends on the size of the acid. Thus, a wide mesophase range is displayed by complex T5:A1, with an extraordinarily high enthalpy value measured for the transition Col$_r$−I (37.7 kJ/mol). In contrast, less stable Col$_r$ mesophases, with clearing temperatures near to room temperature and lower enthalpy values, are shown by complexes T5:A3 (9.6 kJ/mol) and T5:A4 (5.5 kJ/mol). This trend is probably related to steric overcrowding around the rigid core of the disklike supermolecule. The intermediate situation, that is, complex T5:A2, behaves quite unexpectedly. Mesomorphic behavior was not observed for this complex. Similar results were found for the series formed by triazine T4, where the complex with the same acid, A2, does give rise to mesomorphic behavior, but at higher temperatures and over a shorter temperature range than the rest of the complexes with acids A1, A3, and A4.

H-Bonded Complexes with Bulky Benzoic Acids: A5 and A6. Acids with an extended aromatic core were also employed as possible partners for H-bonded complexes with the proposed 1,3,5-triaryltriazines. Acid A5, 3,4,5-tris(4-decyloxybenzyloxy)benzoic acid, displays a columnar mesophase as the pure material. In contrast, 3,5-bis(tridecyloxybenzoyloxy)benzoic acid, A6, does not show mesomorphic behavior. This property determines whether columnar mesomorphism appears upon complexation. For example, complexes with A5 all show a hexagonal columnar mesophase (Figure 6). It is significant that all four of them have close melting temperatures and similar density values within the mesophase. This situation indicates a strong influence of the bulky acid rather than of the structure of the triazine itself.

Finally, the mesomorphic properties of complexes with acid A6 are rather poor (Figure 7). Only the complexes with triazines T3 and T4 show a columnar hexagonal phase and these have only short temperature ranges and similar transition temperatures. As observed for complexes involving acid A5, the influence of the voluminous acid is also important in this case.

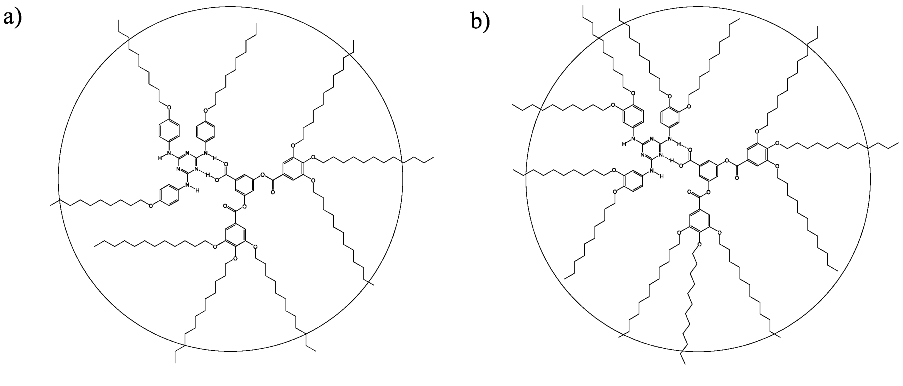


T1:A5 a=34.7 Å, ρ=0.86 g/cm^3 T2:A5 a=37.1 Å, ρ=0.80 g/cm^3



T3:A5 a=36.3 Å, ρ=0.95 g/cm^3 T4:A5 a=35.8 Å, ρ=0.99 g/cm^3

Figure 6. Schematic representation of the disklike hetero-dimers consisting of triazines T1, T2, T3, and T4 and the 3,4,5-tris-(4-docecyloxybenzyloxy)benzoic acid A5.



T3:A6 a=37.5 Å, ρ=0.91 g/cm^3 T4:A6 a=36.3 Å, ρ=1.18 g/cm^3

Figure 7. Schematic representation of the disklike hetero-dimers consisting of triazines T3 and T4 and the 3,5-bis(3,4,5-tridodecyloxybenzoyloxy)benzoic acid A6.

Experimental Section

Preparation of the Materials. The synthesis involved the preparation of alkoxy-substituted anilines from their corresponding nitro precursors. The alkyl-substituted anilines are commercially available.

General Procedure for the Preparation of Alkoxy-Substituted Anilines. An argon-flushed flask containing a suspension of the corresponding alkoxy-substituted nitro compound (14 mmol), ethanol (75 mL), cyclohexene (25 mL), and Pd(OH)$_2$/C-10% (1.4 mmol) was heated under reflux with continuous stirring for 4 h (monitoring by thin-layer chromatography determined the end of the reaction). The mixture was allowed to cool and then filtered through a pad of Celite. The solvent was removed and the product recrystallized from ethanol. Yield: 90−100%.

Analytical Data. (1) p-Decyloxyaniline. R_f 0.5 (2:1, hexane/ethyl acetate). ^{1}H NMR (300 MHz, CDCl$_3$): ∂ 0.86 (t, J = 6.3 Hz, 3H), 1.25−1.75 (m, 18H), 3.88 (t, J = 6.6 Hz, 2H), 6.83 (d, J = 9 Hz, 2H), 7.03 (d, J = 9 Hz, 2H). IR (Nujol, NaCl): 3409, 3328, 3125, 3062−2500, 1618, 1257, 820 cm^{-1}.

(2) 3,4-Didecyloxyaniline. R_f 0.3 (80:20, hexane/ethyl acetate). ^{1}H NMR (300 MHz, CDCl$_3$): ∂ 0.86 (t, J = 6.3 Hz, 6H), 1.25−1.80 (m, 32H), 3.3 (s, broad, 2H), 3.85−3.93 (m, 4H), 6.18 (dd, J = 2.7; 8.4 Hz, 1H), 6.28 (d, J = 2.7 Hz, 1H), 6.71 (d, J = 8.4 Hz, 1H). IR (Nujol, NaCl): 3389, 3299, 3202, 3000−2850, 1614, 1230, 791 cm^{-1}.

(3) 3,4,5-Tridecyloxyaniline. R_f 0.4 (80:20, hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): ∂ 0.86 (t, J = 6.3 Hz, 9H), 1.10−1.77 (m, 51H), 3.44 (s, broad, 2H), 3.80−3.90 (m, 6H), 5.89 (s, 2H). IR (Nujol, NaCl): 3411, 3331, 3206, 3000−2855, 1599, 1237, 815 cm^{-1}.

General Procedure for the Preparation of Alkyl(alkoxy)-Substituted Triarylamino-1,3,5-triazines. A mixture of the corresponding aniline (12 mmol), cyanuric chloride (4 mmol), and anhydrous potassium carbonate (12 mmol) in 2-butanone (75 mL) was refluxed under an argon atmosphere overnight. The reaction mixture was then cooled and the solvent was evaporated under reduced pressure. The residue was dissolved in dichloromethane (100 mL) and poured into water (100 mL). The organic phase was separated and the aqueous phase was extracted with dichloromethane. The combined organic extracts were washed successively with 1 N HCl (100 mL) and brine and then dried over anhydrous magnesium sulfate. The mixture was filtered and the solvent was removed. The product was purified by flash chromatography on silica gel, eluting with hexane/ethyl acetate mixtures. The products were recrystallized from absolute ethanol. Yield: 50−60%.

Analytical Data. (1) 2,4,6-Tris(4-decylphenylamino)-1,3,5-triazine. R_f 0.6 (80:20, hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): ∂ 0.86 (t, J = 6.3 Hz, 9H, CH_3), 1.25−1.68 (m, 48H, CH_2), 2.55 (t, J = 7.2 Hz, 6H, CH_2-phenyl), 7.00 (s, broad, 3H, NH), 7.09 (d, J = 7.5 Hz, 6H, phenyl), 7.41 (d, J = 7.5 Hz, 6H, phenyl). ^{13}C NMR (300 MHz, $CDCl_3$): ∂ 15.2, 23.8, 30.4, 30.7, 32.7, 33.0, 36.5, 122.0, 129.7, 137.2, 139.2, 165.6. IR (Nujol, NaCl): 3403, 3319, 2951−2850, 1614, 1221, 805 cm^{-1}. MS (FAB+) m/z: 386, 501, 648, 744 (100%), 776 ($M^+ + 2H^+$), 1548 ($2M^+$). Elemental analysis: calculated for $C_{51}H_{78}N_6$ (%): C, 79.07; H, 10.08; N, 10.85. Found: C, 79.20; H, 10.10; N, 11.33.

(2) 2,4,6-Tris(4-dodecylphenylamino)-1,3,5-triazine. R_f 0.6 (80:20, hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): ∂ 0.86 (t, J = 6.6 Hz, 9H, CH_3), 1.10−1.68 (m, 60H, CH_2), 2.56 (t, J = 7.8 Hz, 6H, CH_2−Ar), 7.01 (s, broad, 3H, NH), 7.10 (d, J = 8.1 Hz, 6H, HAr), 7.43 (d, J = 8.1 Hz, 6H, HAr). ^{13}C NMR (300 MHz, $CDCl_3$): ∂ 14.1, 22.0, 29.3, 29.4, 29.6, 29.7, 29.7, 31.6, 31.9, 35.4, 121.0, 128.7, 136.0, 138.2, 164.2. IR (Nujol, NaCl): 3402, 3318, 2953−2852, 1615, 1267, 805 cm^{-1}. MS (FAB+) m/z: 131(100%), 156, 287, 557, 717, 860 ($M^+ + 2H^+$). Elemental analysis: calculated for $C_{57}H_{90}N_6$ (%): C, 79.72; H, 10.49; N, 9.79. Found: C, 79.99; H, 11.44; N, 10.33.

(3) 2,4,6-Tris(4-decyloxyphenylamino)-1,3,5-triazine. R_f 0.6 (85:15, hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): ∂ 0.86 (t, J = 6.3 Hz, 9H, CH_3), 1.10−1.77 (m, 48H, CH_2), 3.91 (t, J = 6.6 Hz, 6H, CH_2−O−Ar), 6.82 (d, J = 8.4 Hz, 6H, HAr), 6.86 (s, broad, 3H, NH), 7.38 (d, J = 8.7 Hz, 6H, HAr). ^{13}C NMR (300 MHz, $CDCl_3$): ∂ 14.1, 22.7, 26.1, 29.3, 29.4, 29.6, 31.9, 68.3, 114.6, 122.7, 131.4, 155.5, 164.6. IR (Nujol, NaCl): 3405, 3381, 2951−2852, 1629, 1230, 828 cm^{-1}. MS (FAB+) m/z: 402, 533, 556, 682, 822 (M^+), 824 (100%). Elemental analysis: calculated for $C_{51}H_{78}N_6\ O_3$ (%): C, 74.45; H, 9.49; N, 10.22. Found: C, 74.60; H, 10.10; N, 10.43.

(4) 2,4,6-Tris(3,4-didecyloxyphenylamino)-1,3,5-triazine. R_f 0.3 (10:1, hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): ∂ 0.86 (t, J = 6.3 Hz, 18H, CH_3), 1.1−1.41 (m, 84H, CH_2), 1.72−1.79 (m, 12H, CH_2), 3.87 (s, broad, 6H, CH_2−O−Ar), 3.92 (t, J = 6.3 Hz, 6H, CH_2−O−Ar), 6.77 (d, J = 8.7 Hz, 3H, HAr), 6.95 (d, J = 8.4 Hz, 3H, HAr), 7.01 (s, broad, 3H, NH), 7.06 (s, 3H, HAr). ^{13}C NMR (300 MHz, $CDCl_3$): ∂ 14.1, 22.7, 26.1, 29.3, 29.4, 29.6, 29.7, 30.9, 31.90, 69.1, 69.9, 108.2, 113.4, 114.6, 132.1, 145.5, 149.4, 164.6. IR (Nujol, NaCl): 3405, 3381, 2952−2503, 1625, 1224, 835 cm^{-1}. MS (FAB+) m/z: 449, 845, 1024, 1151, 1290 (M^+), 1292 (100%). Elemental analysis: calculated for $C_{81}H_{138}N_6O_6$ (%): C, 75.34; H, 10.69; N, 6.51. Found: C, 75.39; H, 10.60; N, 6.36.

(5) 2,4,6-Tris(3,4,5-tridecyloxyphenylamino)-1,3,5-triazine. R_f 0.5 (85:15, hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): ∂ 0.86 (t, J = 6.3 Hz, 27H, CH_3), 1.10−1.71 (m, 144H, CH_2), 3.85 (s, broad, 6H, CH_2−O−Ar), 3.89 (t, J = 6.3 Hz, 12H, CH_2−O−Ar), 6.70 (s, 6H, HAr), 6.94 (s, broad, 3H, NH). ^{13}C NMR (300 MHz, $CDCl_3$): ∂ 14.1, 22.7, 26.2, 29.4, 29.5, 29.7, 29.7, 29.8, 30.4, 31.9, 69.1, 73.5, 100.3, 133.7, 134.6, 153.1, 164.3. IR (Nujol, NaCl): 3393−3120, 2919−2853, 1582, 1227, 808 cm^{-1}. MS (FAB+) m/z: 391, 452, 709 (100%), 1758 (M^+), 1761. Elemental analysis: calculated for $C_{111}H_{198}N_6O_9$ (%): C, 75.77; H, 11.26; N, 4.78. Found: C, 76.04; H, 11.78; N, 4.77.

Preparation of Hydrogen-Bonded Complexes. Equimolar mixtures of the triazines and the benzoic acid derivatives were obtained upon evaporating a THF solution of both components by stirring at room temperature. The mixtures, once heated to their isotropic states, were used for further experiments.

Characterization. Thermal properties were examined using an Olympus BH-2 polarizing microscope equipped with a Linkam THMS600 hot stage and a Linkam TMS91 controller, and differential scanning calorimetry (TA Instruments 2910 and Perkin-Elmer DSC-7). Both instruments were calibrated with indium (156.6 °C, 28.44 J/g). Powder X-ray diffraction patterns were obtained using a Pinhole (Anton-Paar) diffractometer and Ni-filtered Cu Kα radiation. The samples were held in Lindemann glass capillaries (Φ = 1 mm) and heated with a variable temperature attachment. The diffraction patterns were collected on photographic films.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity-300 and Bruker ARX-300 spectrometers at 300 MHz. IR spectra were obtained with a Nicolet Avatar 380 spectrometer. Elemental analyses were performed with a Perkin-Elmer 2400 analyzer and the MS studies were carried out on a VG AutoSpec EBE spectrometer.

Conclusion

A number of different H-bonded complexes with a disklike structure have been prepared and give rise to columnar mesomorphism. X-ray diffraction studies, along with density calculations, have highlighted the importance of effective space filling by a sufficient number of peripheral tails on the appearance of columnar mesophases. A complementary effect between the number of tails in the triazine and the number of tails in the acid dictates a minimum of six peripheral chains in order to obtain mesomorphic behavior. In this respect, trialkoxybenzoic acids (A3 and A4) are particularly effective in promoting columnar mesomorphism, which is either hexagonal (complexes with T1, T2, T3, and T4) or rectangular (complexes with T5) depending on the size of the triazine.

The use of acids A5 and A6, with an extended aromatic core, showed that steric requirements are extremely important for the formation of supramolecular complexes between complementary units such as 2,4,6-triamino-1,3,5-triazines and carboxylic acids. Thus, when the triazine component experiences tail overcrowding around its aromatic core, bulky acids cannot be accommodated to form a stable H-bonded complex. Examples of this phenomenon include the combination of triazine T5 (derived from trialkoxyaniline) and acids A5 and A6. However, when a stable complex is finally obtained, the influence of the acid is predominant in defining the polymorphism of the material. For example, in the case of acid A5 the mesomorphic properties of the acid prevail and the influence of the triazine component is less marked in the behavior of the final complex. All the complexes show hexagonal columnar mesomorphism. The same conclusion, but with negative consequences, is deduced from the thermal behavior of complexes involving the acid A6. The substitution pattern of this polycatenar acid seems to be responsible for less stable mesophases (complexes T3:A6 and T4:A6), as well as for the nonuniform distribution of peripheral tails in complexes T1:A6 and T2:A6, which do not show mesomorphic behavior even though the final molecule contains nine tails in its periphery.

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