J|A|C|S
ARTICLES
Published on Web 03/15/2006

Propeller-like Hydrogen-Bonded Banana−Melamine Complexes Inducing Helical Supramolecular Organizations

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

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

Received December 16, 2005; E-mail: joseluis@unizar.es; tsierra@unizar.es

Abstract: The results of the study presented here show a new example of the use of liquid crystals and the interactions involved in the mesomorphic state to build up complex molecular organizations. We have pursued a design strategy in which hydrogen bonding allows the combination of the π-stacking tendency of melamine and the lateral interaction capability of V-shaped molecules, which has been extensively demonstrated through nematic, smectic, or columnar mesophases. This combination addresses the formation of columnar arrangements with inherent helical organization. In this work, nonmesomorphic as well as mesomorphic V-shaped acids, with a structure similar to banana liquid crystals, have been complexed to a 2,4,6-triamino-1,3,5-triazine derivative in a proportion 3 to 1, respectively. Hydrogen-bonded supramolecules whose formation and stability in solution have been proven by infrared and NMR techniques have been thus obtained. DOSY experiments have allowed us to assess in solution the presence of the complexes and their tetrameric composition. All the complexes display mesogenic ability, and their mesomorphic organization has been studied by X-ray diffraction and CD spectroscopy. Results allow us to propose a helical columnar model for the mesophase originated from a propeller-like conformation of the supramolecular complexes.

Introduction

Building helical organizations with controlled structure, imitating nature, is a major point of interest in supramolecular chemistry and material science. Furthermore, if these organizations are achieved by means of simple but unconventional molecular units, this study can attract interest from researchers on molecular materials. Hydrogen bonding and π-interactions are frequently employed as driving forces to give well-defined supramolecular architectures.[1] In this context, melamine and its derivatives, which can be involved in both types of interaction, have provided a variety of elegant approaches to new types of material through self-assembly.[2] A number of examples of these systems have been reported within the liquid crystals field.[3]

In the work described here, we explored a new strategy to design columnar liquid crystalline organizations that employ both types of noncovalent interaction, which arise from a melamine derivative and from one of the newest types of mesogenic structure: banana-like molecules. The latter compounds promote the appearance of special classes of nematic,[4] smectic, or columnar[5] mesophases with unique molecular packing that comes from their peculiar V-shape.

In an effort to achieve our objective, we chose two supramolecular synthons to design supramolecular complexes capable of stacking within the mesophase. First, 2,4-diamino-6-dodecylamino-1,3,5-triazine can be used as the central part of a disklike structure that can stack within the mesophase and offers the possibility of hydrogen-bond interaction with acids (Figure

---

(1) (a) Lindoy, L. F.; Atkinson, I. M. *Self-Assembly in Supramolecular Systems*; Royal Society of Chemistry: Cambridge, 2000. (b) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071−4097. (c) Bushey, M. L.; Nguyen, T. Q.; Zhang, W.; Horoszewski, D.; Nuckolls, C. *Angew. Chem., Int. Ed.* **2004**, *43*, 5446−5453. (d) van Gestel, J.; Palmans, A. R. A.; Titulaer, B.; Vekemans, J. A. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **2005**, *127*, 5490−5494. (e) For a very recent review on liquid crystal materials based on supramolecular chemistry, see: Kato, T.; Mizoshita, N.; Kishimoto, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 38−68.

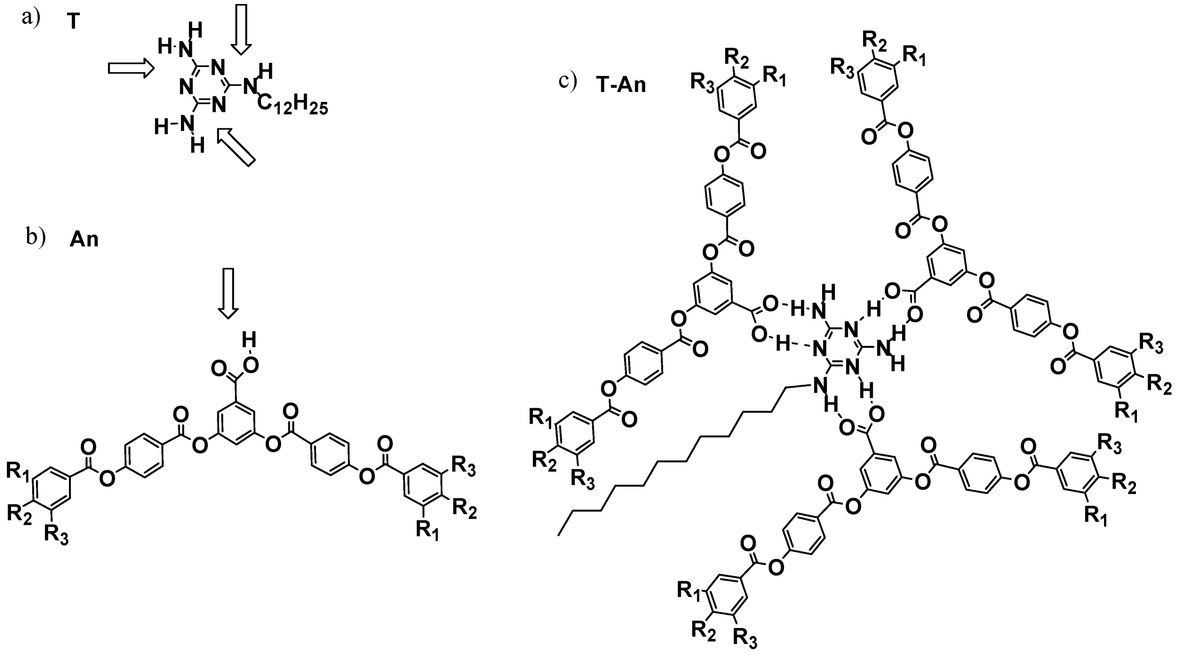
(2) (a) MacDonald, J. C.; Whitesides, G. M. *Chem. Rev.* **1994**, *94*, 2383−2420. (b) Kimizuka, N.; Kawasaki, T.; Hirata, K.; Kunitake, T. *J. Am. Chem. Soc.* **1995**, *117*, 6360−6361. (c) Whitesides, G. M.; Simanek, E. E.; Mathias, J. P.; Seto, C. T.; Chin, D. N.; Mammen, M. *Acc. Chem. Res.* **1995**, *28*, 37−44. (d) Wurthner, F.; Thalacker, C.; Sautter, A.; Schartl, W.; Ibach, W.; Hollricher, O. *Chem.−Eur. J.* **2000**, *6*, 3871−3886. (e) Prins, L. J.; De Jong, F.; Timmerman, P.; Reinhoudt, D. N. *Nature* **2000**, *408*, 181−184. (f) Prins, L. J.; Reinhoudt, D. N.; Timmerman, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2383−2426. (g) Loontjens, T.; Put, J.; Coussens, B.; Lange, R.; Palmen, J.; Sleijpen, T.; Plum, B. *Macromol. Symp.* **2001**, *174*, 357−371. (h) Highfill, M. L.; Chandrasekaran, A.; Lynch, D. E.; Hamilton, D. G. *Cryst. Growth Des.* **2002**, *2*, 15−20. (i) Plater, M. J.; Sinclair, J. P.; Aiken, S.; Gelbrich, T.; Hursthouse, M. B. *Tetrahedron* **2004**, *60*, 6385−6394. (j) Thalacker, C.; Wurthner, F. *Adv. Funct. Mater.* **2002**, *12*, 209−218. (k) Thalacker, C.; Miura, A.; De Feyter, S.; De Schryver, F. C.; Wurthner, F. *Org. Biomol. Chem.* **2005**, *3*, 414−422.

(3) (a) Goldmann, D.; Janietz, D.; Schmidt, C.; Wendorff, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 1851−1854. (b) Wurthner, F.; Thalacker, C.; Diele, S.; Tschierske, C. *Chem.−Eur. J.* **2001**, *7*, 2245−2253. (c) Lee, C. J.; Lee, S. J.; Chang, J. Y. *Tetrahedron Lett.* **2002**, *43*, 3863−3866. (d) Goldmann, D.; Janietz, D.; Schmidt, C.; Wendorff, J. H. *J. Mater. Chem.* **2004**, *14*, 1521−1525.

(4) (a) Madsen, L. A.; Dingemans, T. J.; Nakata, M.; Samulski, E. T. *Phys. Rev. Lett.* **2004**, *92*, 145505(4). (b) Wiant, D.; Gleeson, J. T.; Éber, N.; Fodor-Csorba, K.; Jákli, A.; Tóth-Katona, T. *Phys. Rev. E* **2005**, *72*, 041712-(12).

(5) For reviews on banana liquid crystals, see: (a) Pelzl, G.; Diele, S.; Weissflog, W. *Adv. Mater.* **1999**, *11*, 707−724. (b) Tschierske, C.; Dantlgraber, G. *Pramana* **2003**, *61*, 455−481. (c) Walba, D. M. In *Materials Chirality*; Green, M. M., Nolte, R. J. M., Meijer, E. W., Eds.; Topics in Stereochemistry, 24; Wiley & Sons: New York, 2003; pp 457−518. (d) Reddy, R. A.; Tschierske, C. *J. Mater. Chem.* **2006**, *16*, 907−961. (e) Takezoe, H.; Takanishi, Y. *Jpn. J. Appl. Phys.* **2006**, *45*, 597−625.

10.1021/ja0585477 CCC: $33.50 © 2006 American Chemical Society



An	R_1	R_2	R_3
A1	H	$-OC_{10}H_{21}$	H
A2	H	$-OC_{12}H_{25}$	H
A3	H	$-OC_{14}H_{29}$	H
A4*	H	(S)-$CH_2CH_2CH(CH_3)CH_2CH_2CH_2CH(CH_3)_2$	H
A5	$-OC_{10}H_{21}$	$-OC_{10}H_{21}$	H
A6	$-OC_{10}H_{21}$	$-OC_{10}H_{21}$	$-OC_{10}H_{21}$

Figure 1. General structure of the (a) triazine (T), (b) V-shaped acids (An), and (c) the tetrameric complex (T−An). The arrows indicate the positions in triazine capable of hydrogen bonding interactions.

1a). The introduction of a dodecyl tail increases the solubility in a variety of solvents and is sufficiently small in terms of space demand to allow three coordinating positions. Second, we chose six symmetric banana-like derivatives functionalized with a carboxylic group in the central aromatic ring (Figure 1b). Both structures are capable of associating through hydrogen bonding in a 3-to-1 ratio (acid-to-melamine) to build up a complex (Figure 1c), which should be susceptible of organizing into columns.

A further level of organization should be reached if the columnar organization of these supramolecules shows a tendency to adopt a helical architecture[6] and, moreover, if it is possible to transfer existing molecular chiral information, due to the presence of a chiral V-shaped acid, to the columnar mesophase.[7] It is then possible that chirooptical properties corresponding to chiral helical columns, with a helical arrangement biased toward a given sense, could appear and these should not be present in the nonorganized complexes (i.e., isotropic liquid).

Results and Discussion

The 2,4-diamino-6-dodecylamino-1,3,5-triazine (T) studied was prepared by the reaction of dodecylamine with 2,4-diamino-6-chloro-1,3,5-triazine using sodium hydrogencarbonate as a base. The V-shaped acids (A1, A2, A3, A4*, A5, and A6) were prepared following the synthetic pathway outlined in Scheme 1.

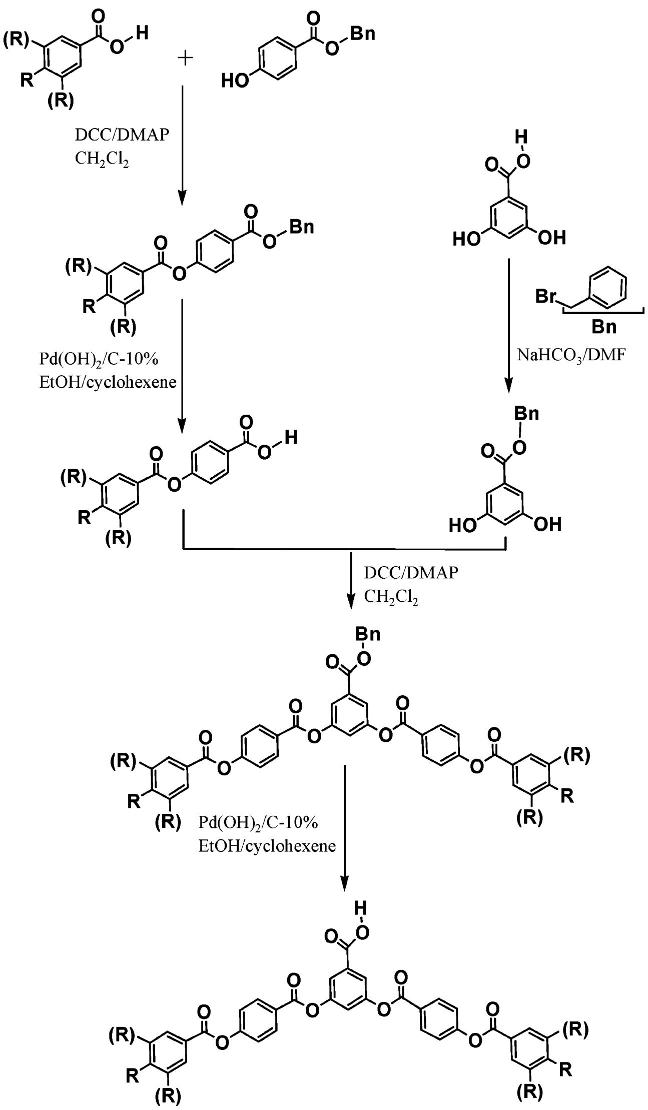
4-Decyloxybenzoic acid and 4-dodecyloxybenzoic acid were used as purchased. The other benzoic acids were synthesized by Williamson etherification of the corresponding methyl

---

(6) (a) Nuckolls, C.; Katz, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 9541−9544. (b) Trzaska, S. T.; Hsu, H. F.; Swager, T. M. *J. Am. Chem. Soc.* **1999**, *121*, 4544−4544. (c) Vyklicky, L.; Eichhorn, S. H.; Katz, T. J. *Chem. Mater.* **2003**, *15*, 3594−3601. (d) Barberá, J.; Cavero, E.; Lehmann, M.; Serrano, J. L.; Sierra, T.; Vazquez, J. T. *J. Am. Chem. Soc.* **2003**, *125*, 4527−4533. (e) Bushey, M. L.; Nguyen, T. Q.; Zhang, W.; Horoszewski, D.; Nuckolls, C. *Angew. Chem., Int. Ed.* **2004**, *43*, 5446−5453. (f) Cardinels, T.; Ramaekers, J.; Guillon, D.; Donnio, B.; Binnemans, K. *J. Am. Chem. Soc.* **2005**, *127*, 17602−17603.

(7) (a) Palmans, A. R. A.; Vekemans, J.; Havinga, E. E.; Meijer, E. W. *Angew. Chem., Int. Ed.* **1997**, *36*, 2648−2651. (b) Brunsveld, L.; Zhang, H.; Glasbeek, M.; Vekemans, J.; Meijer, E. W. *J. Am. Chem. Soc.* **2000**, *122*, 6175−6182. (c) Brunsveld, L.; Schenning, A.; Broeren, M. A. C.; Janssen, H. M.; Vekemans, J.; Meijer, E. W. *Chem. Lett.* **2000**, 292−293. (d) Serrano, J. L.; Sierra, T. *Chem.−Eur. J.* **2000**, *6*, 759−766. (e) Brunsveld, L.; Lohmeijer, B. G. G.; Vekemans, J.; Meijer, E. W. *J. Inclusion Phenom. Macrocyclic Chem.* **2001**, *41*, 61−64. (f) Serrano, J. L.; Sierra, T. *Coord. Chem. Rev.* **2003**, *242*, 73−85. (g) Kato, T.; Matsuoka, T.; Nishii, M.; Kamikawa, Y.; Kanie, K.; Nishimura, T.; Yashima, E.; Ujie, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1969−1972.

Scheme 1



4-hydroxybenzoate, methyl 3,4-dihydroxybenzoate, and methyl 3,4,5-trihydroxybenzoate with the appropriate alkyl bromide, followed by alkaline ester cleavage (see Supporting Information).

Study of the Formation and Stability of the Hydrogen-Bonded Complexes. Once the complexes were prepared,[8] their formation and stability of intermolecular hydrogen-bond associations between the triazine, T, and the V-shaped acids, An ($n = 1$ to 6), were initially studied in neat samples as KBr pellets (infrared spectroscopy) and in deuterated chloroform solution (nuclear magnetic resonance).

Infrared spectroscopy showed a shift of the C=O stretching band to lower wavenumbers upon formation of the complex. Significant changes in the wavenumber region corresponding to the N−H and O−H stretching bands were also detected (see Supporting Information). Further evidence of hydrogen-bond formation between 2,4-diamino-6-dodecylamino-1,3,5-triazine (T) and the An acids was found in the ^{1}H NMR spectra obtained from $CDCl_3$ solutions. In general, proton signals involved in complexation as well as those near the complexating groups experimented field shift in a correlated way. Thus, all five N−H protons of the nonassociated triazine (T) appeared as overlapped peaks at around 4.8 and 5.0 ppm. These signals were significantly resolved in three different types of NH proton and were downfield-shifted upon complexation, especially those corresponding to protons involved in hydrogen-bonding interactions. A representative example is shown in Figure 2 that corresponds to the complex T−A4*. The triplet corresponding to the NH proton of the dodecylamine group appears at 6.95 ppm in the complex, a singlet corresponding to two associated NH protons appears at 6.57 ppm, and a broad signal that most likely corresponds to two nonassociated NH protons appears between 5.9 and 5.2 ppm. In addition, the triplet corresponding to the methylene group of the dodecylamino tail shifts downfield upon complexation. In contrast, protons belonging to the central ring shift upfield upon complexation. The displacement of these signals is strongly indicative of the presence in $CDCl_3$ of the tetrameric supramolecular complex, in which three types of NH proton in the ratio 1:2:2 appear.

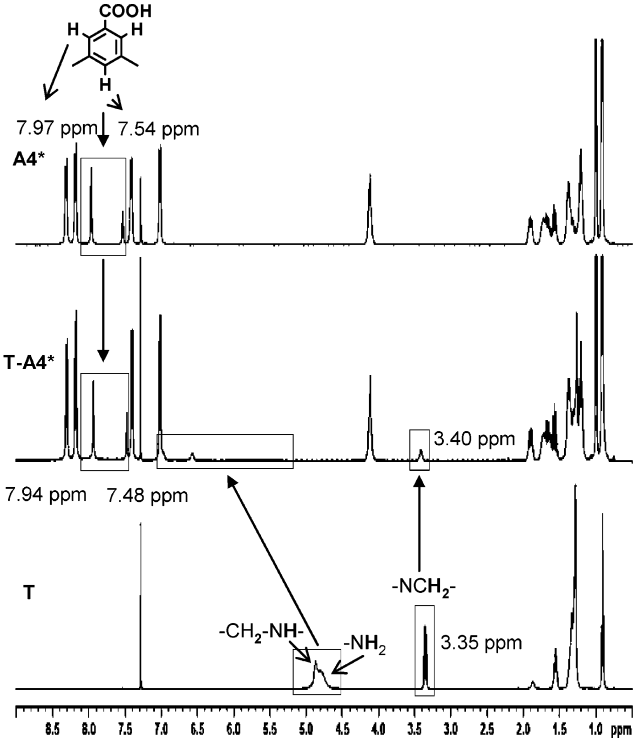


Figure 2. ^{1}H NMR of the acid A4*, the triazine T, and their tetrameric complex T−A4*. Protons belonging to the amino groups of the triazine, as well as the methylene group of the alkyl tail of the triazine and the hydrogens of the central aromatic ring of the acid, are marked to emphasize the shift of their chemical displacements upon formation of the complex.

To achieve further proof of the presence in solution of the proposed tetramer formed through hydrogen-bonding interactions, NMR diffusion-ordered spectroscopy (DOSY) experiments were performed.[9] This technique allows diffusion coefficients to be correlated with molecular composition by observing

---

[8] The complexes were prepared by dissolving the corresponding amounts of the appropriate components separately in THF, mixing the solutions, and slow evaporation of THF solutions containing the two components (see Supporting Information). The mixtures were melted to the isotropic liquid and subsequently cooled to room temperature prior to characterization. The samples thus prepared were mesomorphic at room temperature.

[9] (a) Price, W. S. *Concepts Magn. Reson.* **1997**, *9*, 299−337. (b) Price, W. S. *Concepts Magn. Reson.* **1998**, *10*, 197−237. (c) For a recent review on the use of DOSY experiments in supramolecular chemistry, see: Cohen, Y.; Avram, L.; Frish, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 520−554.

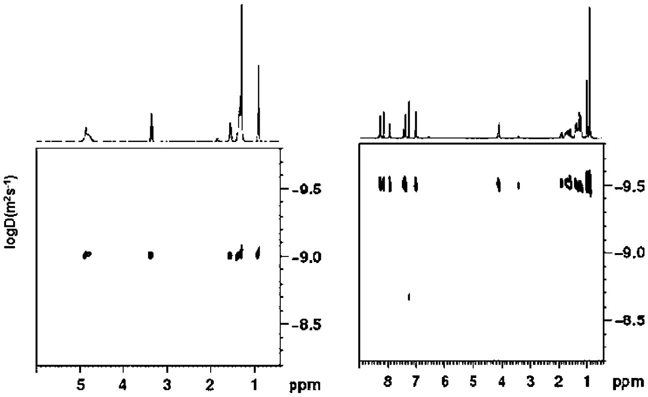


Figure 3. 2D spectrum, in $CDCl_3$, representing chemical shifts versus diffusion coefficients (logarithmic scale) for the triazine T and for the complex T−A4*.

Table 1. Thermal Properties, Transition Temperatures, °C (Enthalpies, kJ mol^{-1}) of the Triazine (T), V-Shaped Acids (An), and Complexes (T−An)[a]

	Triazine
T	Cr 102.7 [15.4] (SmA[b] 38.6 [0.4]) I
	V-Shaped Acids (An)
A1	Cr 163.7 [47.1] I
A2	Cr 148.3 [42.4] I
A3	Cr 146.8 [31.5] I
A4*	Cr 152.5 [31.3] I
A5	Col$_h$ 90.4 [7.9] I
A6	Col$_r$ 73.9 [10.3] I
	Complexes T−An
T−A1	I 98.4 [13.0] **Col$_r$**[c]
T−A2	I 101.0 [13.9] **Col$_r$**[c]
T−A3	I 93.7 [14.7] **Col$_r$**[c]
T−A4*	I 74.5 [8.9] **Col$_r$***[c]
T−A5	I 95.0 [3.6] **Col$_h$**[c]
T−A6	I 63.3 [5.7] **Col$_h$**[c]

[a] Thermal data of complexes are given in the cooling process. [b] Monotropic mesophase. [c] No crystallization was observed on slow cooling until −20 °C.

Table 2. Lattice Parameters Measured by X-ray Diffraction for the Mesophases of Triazine T, Acids A5 and A6, and the Six Complexes[a]

compound	lattice parameters (Å)	phase
T	$d = 32.2$	SmA
A5	$a = 47.2$	Col$_h$
A6	$a = 77$	Col$_r$
	$b = 36$	
T−A1	$a = 77$	Col$_r$
	$b = 66$	
T−A2	$a = 81$	Col$_r$
	$b = 69$	
T−A3	$a = 85$	Col$_r$
	$b = 71.6$	
T−A4*	$a = 77$	Col$_r$*
	$b = 65.6$	
T−A5	$a = 48.8$	Col$_h$
T−A6	$a = 49.0$	Col$_h$

[a] All the experiments were carried out at room temperature.

chemical shifts. Self-diffusion of a chemical species in a solvent depends on its molecular size and its hydrodynamic volume. According to this principle, molecular association can promote changes in self-diffusion coefficients, which can allow detecting the presence of an hydrogen-bonded complex in solution.[10] In the present work, DOSY experiments were performed in $CDCl_3$ for all T−An complexes (see results in Supporting Information). As an example (Figure 3), signals corresponding to all the protons within the complex T−A4* exhibit the same diffusion coefficient ($3.14 \times 10^{-10} \pm 0.04$ m^2/s). Since there is fast exchange between the complex and the components on the NMR time scale, this value corresponds to the apparent diffusion coefficient of the complex. Moreover, this is the only coefficient measured for the complex, which, furthermore, is much lower than that of the triazine itself, $9.74 \times 10^{-10} \pm 0.03$ m^2/s, indicating that the triazine and the acids diffuse in the solvent as a unique supramolecular entity. In the case of negligible association, which would indicate high weakness of the complex in solution, the coefficients of the triazine and the acid would have remained unchanged in the DOSY spectrum of the mixture.

Mesomorphic Behavior. Table 1 gathers the thermal properties of triazine, T, the V-shaped acids, and the corresponding heterocomplexes 1:3 determined by POM and DSC. The triazine showed a monotropic mesophase, which was identified as SmA by texture observation. The V-shaped acids with a total of two tails, A1, A2, A3, and A4*, did not show mesomorphic behavior, whereas the acids with a total of four, A5, or six, A6, tails showed hexagonal and rectangular columnar mesophases, respectively.

All the T−An complexes were found to show mesomorphic behavior as obtained. Moreover, the mesomorphic state achieved upon cooling from the isotropic liquid was stable over time at room temperature (textures observed by POM and DSC thermograms are shown in Supporting Information). It should also be noted that the dynamic nature of hydrogen-bonding interactions is strongly involved in the formation and stability of the mesophases of the complexes. This is revealed by the singular thermal behavior observed for these materials under the polarizing microscope and DSC. Once the isotropic liquid state is reached, rapid cooling unavoidably causes partial crystallization of the material. Under these conditions, the coexistence of both crystalline state and the columnar mesophase can be observed. In contrast, gradual cooling from the isotropic liquid (i.e., 10 °C/min) completely prevents crystallization, and the materials give the mesophase at the corresponding temperatures indicated in Table 1. It seems that the components (i.e., acid and triazine) dissociate in the liquid to a considerable extent and, on cooling, must come together again to assemble into the mesogenic supramolecular complex. Moreover, the actual mesogenic complex, according to the aforementioned NMR experiments, must consist of three molecules of acid hydrogen-bonded to the triazine. This would mean that four units must coordinate to provide mesomorphic character to the supramolecular entity, and that any other combination of the supramolecular synthons gives rise to crystalline, nonmesomorphic complexes.

X-ray Measurements. The mesophases of the mesogenic triazine T and acids A5 and A6 were studied, and their parameters were measured, by X-ray diffraction at room temperature (Table 2). For all the complexes, X-ray experiments were carried out on samples slowly cooled from the isotropic liquid, so that the mesophase could completely develop. Three of the complexes, namely T−A1, T−A2, and T−A4*, yielded X-ray patterns characteristic of rectangular columnar (Col$_r$) mesophases (Figure 4). On the other hand, the X-ray patterns of T−A3 contained reflections from both the crystalline and

---

(10) Kaucher, M. S.; Lam, Y.-F.; Pieraccini, S.; Gotarelli, G.; Davis, J. T. *Chem.−Eur. J.* **2005**, *11*, 164−173.

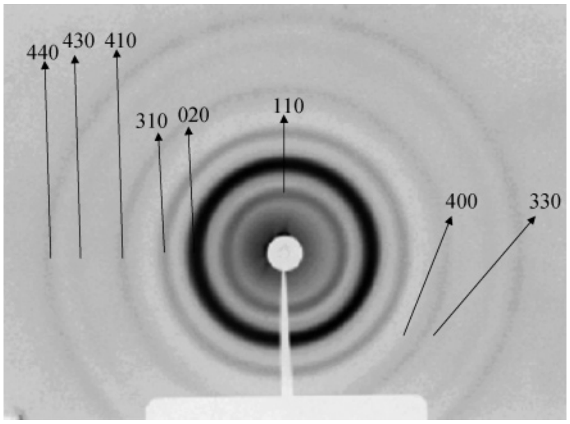


Figure 4. SAXS diagram of the mesophase of complex T−A1 taken at room temperature after cooling from the isotropic liquid.

the mesomorphic phases, because of its higher tendency to crystallize. However, by comparison with the other analogous complexes, it could be deduced which reflections corresponded to the mesomorphic phase. Complexes T−A5 and T−A6 gave diagrams consistent with a hexagonal columnar mesophase.

From the results gathered in Table 2, the number of columns per unit cell in the $\mathrm{Col_r}$ mesophase can be predicted on the basis of packing density (see Supporting Information). Considering a density close to 1 g $\mathrm{cm^{-3}}$, reasonable values for the average stacking distance between complexes are only obtained if there are four columns per cell ($Z = 4$). Under these assumptions, the deduced distances would be about 4.0 Å for T−A1 and T−A4*, 3.9 Å for T−A2, and 3.8 Å for T−A3. These values are reasonable compared to those found in other columnar mesophases. However, since densities have not been experimentally measured, the variation in the calculated stacking distances probably only reflects differences in density. The actual distances could be the same in all cases, and therefore density must probably decrease as the hydrocarbon chain length increases. Although in most rectangular columnar mesophases described in the literature there are usually two columns per lattice, a few examples have been reported with four columns.[11]

The parameters of the rectangular lattices measured for all four complexes depended on the size of the tails in the acid. Thus, T−A3 showed the biggest a and b parameters, and these decreased according to the sequence T−A3, T−A2, T−A1. The mesophase parameters of the complex T−A4* are similar to those of T−A1, as expected for compounds with equal number of carbon atoms in their peripheral tails. On the other hand, the X-ray patterns of complexes T−A5 and T−A6 are consistent with a hexagonal columnar mesophase. Whereas the complex derived from acid A6, with a total of nine tails, showed a number of diffraction maxima at low angles corresponding to a well-organized hexagonal lattice, the complex T−A5 showed only one maximum. This situation makes difficult the unambiguous determination of the mesophase structure. However, texture observation indicated that it was a hexagonal columnar mesophase by comparison with T−A6. The hexagonal lattice parameter of T−A5, $a = 48.8$ Å, is slightly bigger than that of its corresponding acid A5, $a = 47.2$ Å. This gives an idea of the formation of dimers in the acid itself, which accounts for the apparition of columnar arrangements and that is broken upon complexation with the melamine derivative.

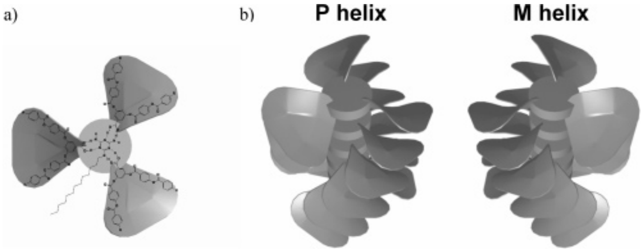


Figure 5. Shape models proposed for the (a) tetrameric complex and (b) the helical columnar organization within the mesophase. Both enantiomeric stacking possibilities, right-handed (P) and left-handed (M), are shown.

It can be deduced from these results that the total number of peripheral tails in the 1:3 heterocomplex influences significantly the mesophase organization. The high number of peripheral tails of complexes T−A5 and T−A6 is mainly responsible for their organization into a columnar arrangement with hexagonal symmetry,[12] which is promoted by a circular section of the columns. However, it is also interesting to note that regardless of the number of peripheral tails, both complexes showed the same value for the parameter a of the hexagonal lattice.

The way in which intermolecular interactions can address columnar ordering in the mesophase is an intriguing question taking into account the shape of these complexes with six long rigid arms around a very small planar nucleus. This structure leads to three cavities that could make efficient space filling difficult upon stacking, especially if these complexes were to adopt a planar conformation (as in Figure 1c). We propose that the origin of the mesomorphic ordering must lie in an advantageous combination of the tendency of triazine rings to stack on top of one another (promoted by π-interactions) and the tendency of the V-shaped molecules, with long rodlike arms, to interact parallel to each other. A disposition that would favor the simultaneous occurrence of both types of interaction can well be a propeller-like conformation of the complex in which the V-shaped acids rotate through a certain angle with respect to the triazine plane. In this way, the acid arms could lie up and down with respect to the triazine core (Figure 5a). Such an arrangement could give rise to a columnar structure consistent with propeller-like supramolecules interpenetrated along the column, in which the tilted V-shaped acids of neighboring complexes can interact in way parallel to each other. Compact columnar packing should then occur by formation of a helical arrangement within the column (Figure 5b). This crucial role of lateral interactions between the V-shaped acids along the column was indirectly supported upon studying two additional complexes in which the acids (nonmesogenic) have shorter arms (i.e., 3,5-bis(4-decyloxybenzoyloxy)benzoic acid[13] and 3,5-bis-(3,4,5-tridecyloxybenzoyloxy)benzoic acid).[14] Results indicated that these complexes do not show mesomorphic behavior despite the possibility of forming a planar aromatic core surrounded by six peripheral tails.

---

(11) (a) Billard, J.; Dubois, J. C.; Vaucher, C.; Levelut, A. M. *Mol. Cryst. Liq. Cryst.* **1981**, *66*, 115. (b) Scherowsky, G.; Chen, X. H.; Levelut, A. M. *Liq. Cryst.* **1998**, *24*, 157.

(12) Donnio, B.; Heinrich, B.; Allouchi, H.; Kain, J.; Diele, S.; Guillon, D.; Bruce, D. W. *J. Am. Chem. Soc.* **2004**, *126*, 15258−15268.

(13) The thermal behavior of both the acid and the complex was studied by POM and DSC: Acid, C 97.4 °C (55.1 kJ $\mathrm{mol^{-1}}$) I, and complex, C 39.1 °C (5.7 kJ $\mathrm{mol^{-1}}$) I.

(14) The thermal behavior of both the acid and the complex was studied by POM and DSC: Acid, C 76.7 °C (93.3 kJ $\mathrm{mol^{-1}}$) I, and complex, $\mathrm{C_1}$ 35.0 °C (50.7 kJ $\mathrm{mol^{-1}}$), $\mathrm{C_2}$ 58.1 °C (91.1 kJ $\mathrm{mol^{-1}}$) I.

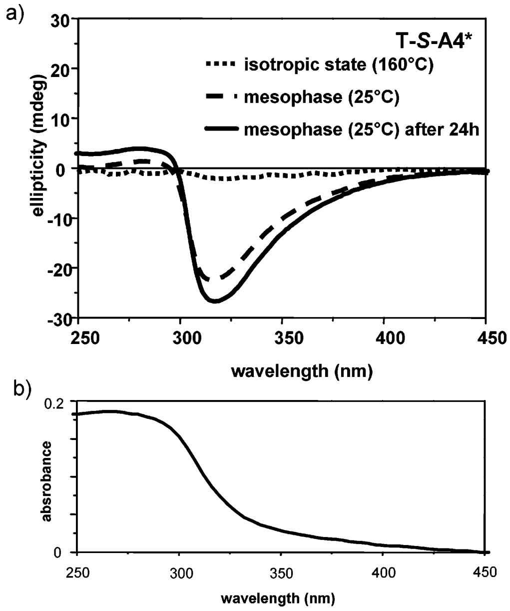


Figure 6. (a) CD spectra recorded on thin films of T−A4*, between quartz plates, under different conditions. (b) UV spectrum of the same sample of T−A4* taken at 25 °C.

Circular Dichroism Studies. On the basis of the helical model proposed above, we planned to achieve a chiral helical organization. If we can transfer the chiral information from a chiral acid partner to the mesophase through hydrogen-bonding, we should be able to influence the formation of the propeller-like complexes toward a given chiral configuration and, hence, to a chiral columnar organization. This idea was explored by investigating the complex derived from the chiral V-shaped acid A4* by circular dichroism spectroscopy. The spectrum of the mesophase[15] shows significant bands, corresponding to absorption bands, which are not present in the isotropic melt and are stable at room temperature over time (Figure 6).

Furthermore, when the acid bears the enantiomeric chiral tail, the CD bands of the mesophase show the opposite sign (Figure 7). Thus, it can be stated that there is formal optical activity arising from a chiral superstructure within the mesophase and that this is biased toward a chiral sense determined by the configuration of the stereogenic center. This chiral columnar superstructure could indeed correspond to a helical arrangement of the complexes within the column. Moreover, the CD signal of T−*S*-A4* (Figure 6) can be interpreted to belong to the negative part of a positive exciton coupling centered at the wavelength of the $\pi - \pi^*$ transition of the chromophores (278 nm, Figure 6b).[16] This might be assigned to a right-handed helical disposition of at least two chromophores, which is in agreement with the helical model along the column proposed in Figure 5. The enantiomeric helical disposition would explain the CD spectrum observed for T−*R*-A4* in the mesophase.

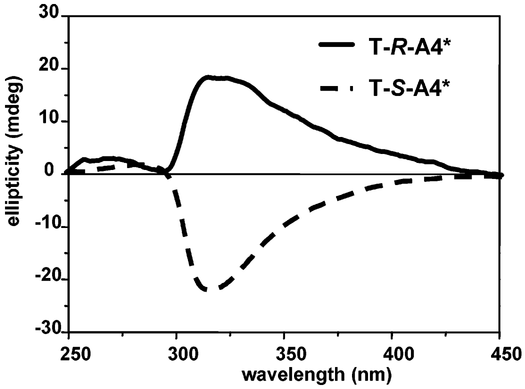


Figure 7. CD spectra recorded on thin films in the mesophase (25 °C) of complexes prepared from the enantiomeric acids (i.e., T−*R*-A4* and T−*S*-A4*).

Conclusions

In summary, V-shaped acids, with a structure similar to that of banana liquid crystals, have been proven to display mesogenic ability when forming tetrameric hydrogen-bonded supramolecules consisting of three acid molecules around a 2,4,6-triamino-1,3,5-triazine derivative. Remarkably, nonmesogenic V-shaped acids containing a total of two terminal alkoxylic chains are able to give rise to rectangular columnar mesophases when forming this type of complex. Hydrogen bonding allows the combination of the π-stacking tendency of melamine and the lateral interaction capability of V-shaped molecules. This combination addresses the formation of columnar arrangements with inherent helical organization. Indeed, the unusual mesogenic core of this supramolecule can be interpreted in terms of a propeller-like structure, which leads to the appearance of stable helical columnar mesophases with a well-defined bidimensional packing. Moreover, this arrangement can be biased toward a chiral conformation by incorporating chiral tails in the acid partner.

Acknowledgment. This work was supported by the CICYT project MAT2003-07806-CO2-01, FEDER funding (EU), and the DGA. We warmly thank Blanca Serrano for her effort in the drawings of the models presented in Figure 5.

Supporting Information Available: Infrared experiments. DOSY spectrum of the acid A4*. Diffusion coefficients measured for all the acids and their corresponding complexes. POM microphotographs in the mesophase. X-ray diffraction data for the mesophases of all the complexes and WAXS diagram of T−A1. DSC thermograms of T−A4* and T−A6. Experimental procedures for the synthesis of the melamine derivative and the V-shaped acids as well as their corresponding analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0585477

---

(15) CD experiments were performed on the corresponding neat sample between untreated quartz plates at both the mesophase temperature and in the isotropic state. Linear dichroism effects were eliminated by averaging several CD spectra, recorded at different film positions rotated around the light beam.

(16) Barbera, J.; Puig, L.; Romero, P.; Serrano, J. L.; Sierra, T. *Chem. Mater.* **2005**, *17*, 3763−3771.