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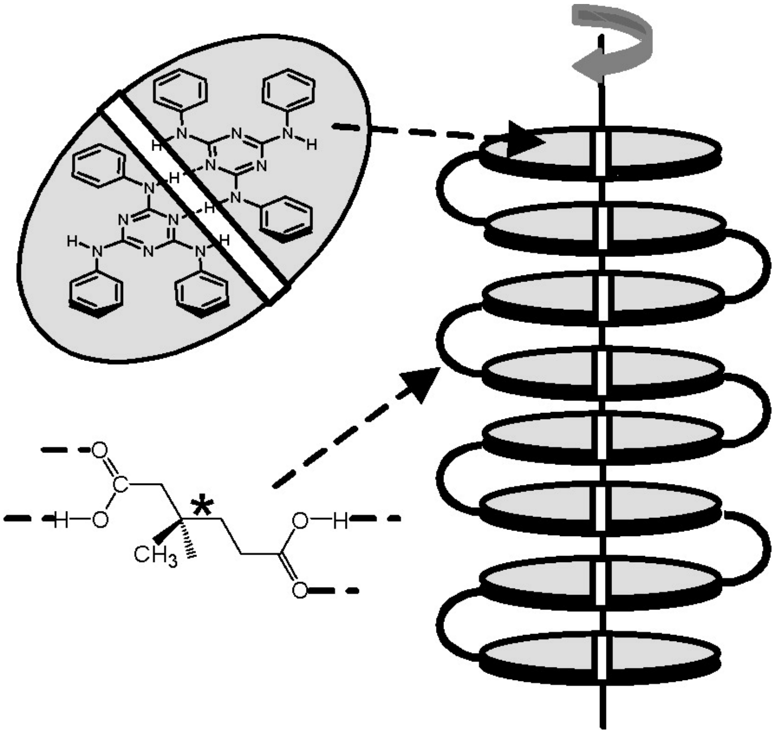

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Supramolecular Helical Mesomorphic Polymers. Chiral Induction through H-Bonding

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

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Abstract: The work described here concerns a challenge of general interest in supramolecular chemistry: the achievement of chiral helical organizations with controlled structures. This work provides a strategy to obtain supramolecular polymers in which a chiral helical conformation has been induced by a noncovalent association, that is, through hydrogen bonding. Polycatenar 2,4,6-triarylamino-1,3,5-triazines, which organize into columnar mesophases and are susceptible to H-bonding interactions, were chosen as a starting point to build up the chiral supramolecular structure. The stacking of these mesogens has been forced to wind in a helical way by means of H-bond association with (*R*)-3-methyladipic acid, within the mesophase. The optically active columnar organization has been studied in depth by optical microscopy, differential scanning calorimetry (DSC), X-ray diffraction, and circular dichroism. Formation of stable complexes between the triazine units and (*R*)-3-methyladipic acid has also been investigated by means of NMR diffusion-ordered spectroscopy (DOSY) experiments in chloroform.

Introduction

The significant role of helical organizations in nature [e.g., α-helical proteins, nucleic acids, tobacco mosaic virus (TMV)] has stimulated the curiosity of researchers in materials chemistry. As an example, the structure of TMV (in which the self-assembly of 2130 polypeptide units gives rise to a columnar organization that is driven to form a helical conformation by interaction with an RNA chain through specific and directional H-bonding interactions)[1] has already been used as a model for synthetic supramolecular columnar organizations prepared from simple molecular units.[2] Furthermore, many appealing research works aimed at building and controlling supramolecular chiral architectures based on helical superstructures have been reported.[3,4] Indeed, interesting linear optical[5] and nonlinear optical properties,[6] electrooptical behavior,[7,8] energy transfer,[9] etc., have been found in synthetic helical superstructures, which are often prepared according to the principles of supramolecular chemistry.[10] In this respect, our research program has been devoted to liquid crystalline organizations and the possibility of achieving helical columnar organizations by $\pi-\pi$ stacking of chiral mesogenic molecules synthesized by means of metal coordination.[8,11]

In the work described here, we developed a simple strategy based on two types of noncovalent intermolecular interaction, that is, $\pi-\pi$ interactions and H-bonding, which enabled the construction of a number of supramolecular liquid crystalline assemblies.[12] Furthermore, since the first chiral helical supramolecular polymer was reported by Lehn and co-workers,[13] these types of interaction have been successfully employed as a tool to synthesize supramolecular structures that are capable of adopting chiral helical organizations.[14−17]

Our approach consists of merging mesomorphic arrangements based on molecular stacking, which is promoted by $\pi-\pi$

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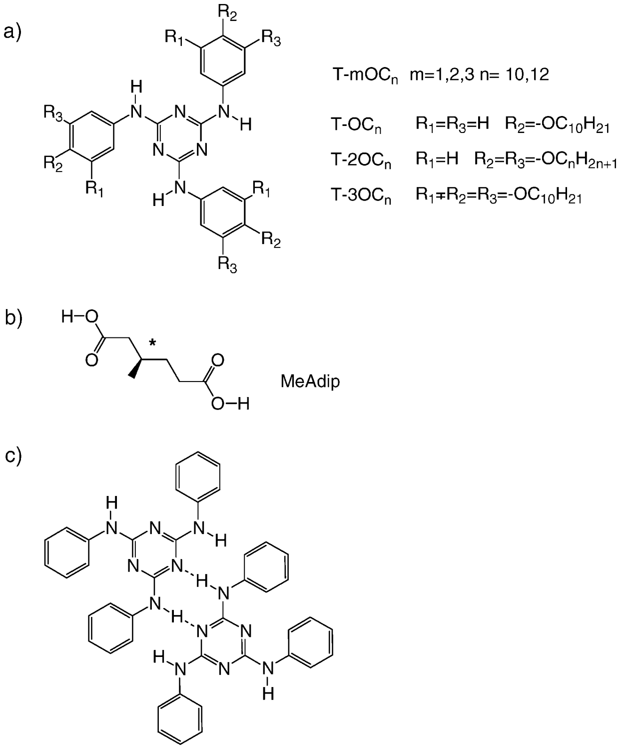

Figure 1. (a) Structure of the triarylaminotriazines. (b) (*R*)-3-Methyladipic acid molecule. (c) General structure of the dimeric form found for T-OC_{10} and T-2OC_{10}.[20]

interactions of simple molecules, and the possibility of anchoring the structure of the mesophase using H-bonding interactions with a second type of molecule. In this way we should be able to build up stable helical polymeric assemblies in which chirality can be induced by a stereogenic center and transferred to the mesophase through hydrogen bonding. For this purpose, it was necessary to choose molecular units that are capable of organizing into columnar mesophases—by virtue of a disklike promesogenic structure—and can also participate in intermolecular hydrogen-bonding interactions. We therefore decided to employ 2,4,6-triarylamino-1,3,5-triazines (Figure 1a).[18] It was also necessary to introduce chirality into the system and for this purpose we selected (*R*)-3-methyladipic acid as a chiral clip (Figure 1b). It was envisaged that this diacid would not only fix the supramolecular organization by building a polymerlike structure but also be able to imprint its chiral character onto the resulting self-assembled structure. This diacid was selected on the basis of its appropriate length: it is long enough to promote intracolumnar interactions between triazine disks but is too short for undesired intercolumnar associations, given the length of the peripheral tails in the triazine. Moreover, the methyl group in this diacid induces a bent conformation that favors the possibility of interdisk association within the column. This conclusion was reached after unsuccessful attempts to prepare homogeneous liquid crystalline materials of this type by use of adipic acid. The most probable extended conformation of the adipic acid ruled out any possibility of association with triazine disks along the column, thus maintaining a columnar arrangement. This design uses highly directional $\pi-\pi$ and H-bonding interactions and it was expected that a supramolecular organization would be produced with a one-dimensional helical arrangement along the column.[19]

It was planned to prepare supramolecular materials with different proportions of 2,4,6-triarylamino-1,3,5-triazine (T-mOC_n) and (*R*)-3-methyladipic acid (MeAdip) in order to establish the structural requirements to ensure the stability of any resulting columnar supramolecular liquid crystal organization.

Results and Discussion

The synthesis of all the triazines was carried out according to methods described in the literature.[18]

Structural studies carried out on different substituted triarylaminotriazines by X-ray diffraction and density calculations[20] led us to conclude that liquid crystalline organizations of 2,4,6-triarylamino-1,3,5-triazines actually consist of H-bonded triazine dimers (Figure 1c) depending upon the number of alkoxy tails in the aniline group. Thus, 2,4,6-tris(4-decyloxyphenylamino)-1,3,5-triazines and 2,4,6-tris(3,4-didecyloxyphenylamino)-1,3,5-triazines formed mesomorphic arrangements (S_A and Col_h, respectively) consisting of dimeric mesogenic units. In contrast, 2,4,6-tris(3,4,5-tridecyloxyphenylamino)-1,3,5-triazine, which has a higher degree of peripheral-tail crowding, shows a columnar mesophase with a lattice parameter and a density value that agree with the stacking of monomeric species. On the basis of these results we selected three different proportions of T-mOC_n and (*R*)-3-methyladipic acid. Mixtures containing one triazine unit per diacid molecule (T-mOC_n/MeAdip[1:1]), two triazine units per diacid molecule (T-mOC_n/MeAdip[2:1]), and four triazine units per diacid molecule (T-mOC_n/MeAdip[4:1]) were prepared.[21]

Only mixtures consisting of MeAdip and 2,4,6-tris(3,4-dialkoxyphenylamino)-1,3,5-triazine, T-2OC_n, resulted in homogeneous materials. All these mixtures were first studied by optical microscopy, and all of them showed mesomorphic behavior that was different than that shown by the separate triazine component. Surprisingly, mixtures containing mono- and trialkoxy-substituted aniline groups within the triazine (T-OC_{10} and T-3OC_{10}) show phase separation with independent thermal transitions corresponding to those of the individual components, as determined by optical microscopy.

Study of the Formation and Stability of the Complexes. The formation and stability of intermolecular H-bond associations between triazines and (*R*)-3-methyladipic acid was initially assessed in deuterated chloroform solution (nuclear magnetic resonance) and in neat samples as KBr pellets (infrared spectroscopy).

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(20) Structural studies carried out on different substituted triphenylaminotriazines have shown that columnar organizations of 2,4,6-tri(dialkoxyphenylamino)-1,3,5-triazines consist of H-bonded triazine dimers stacking within the mesophase. See Barberá, J.; Puig, L.; Serrano, J. L.; Sierra, T. *Chem. Mater.* **2004**, *16*, 3308−3317.

(21) Mixtures of different proportions were prepared by dissolving the corresponding amounts of the components separately in THF, mixing the solutions, and slow evaporation of THF solutions containing the two components. Subsequent heating above the clearing point was then carried out.

The first evidence of H-bond formation between 2,4,6-tris-(3,4-dialkoxyphenylamino)-1,3,5-triazine (T-2OC$_{10}$ and T-2OC$_{12}$) and (*R*)-3-methyladipic acid (MeAdip) was found in the ^{1}H NMR spectra obtained from CDCl$_3$ solutions. The N−H proton gives rise to a singlet in the triazine itself (7.01 ppm for T-2OC$_{10}$), and this becomes broader and is shifted to lower field upon H-bonding association with the diacid (7.25 ppm for T-2OC$_{10}$/MeAdip[2:1]). However, definitive proof of the formation of stable H-bonding interactions in solution was obtained by NMR diffusion-ordered spectroscopy (DOSY) experiments.[22] This technique allows diffusion coefficients to be correlated with molecular composition by observing 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 be significant enough to be detected in DOSY experiments and be considered as corroboration of complex formation. Thus, DOSY has been successfully applied to the study of molecular association in different complex systems including rotaxanated polymers,[23] H-bonded complexes,[24] and liquid crystalline polymers.[25]

In the present work, DOSY experiments were performed in CDCl$_3$ for all three mixtures containing the triazine T-2OC$_{10}$ that gave rise to homogeneous materials. These experiments were undertaken on the assumption that the 3-methyladipic acid associated with triazine units should be distinguishable from the acid that is not associated due to significantly different diffusion coefficients. The results, from a qualitative point of view, are extremely helpful and support the structural model proposed for the supramolecular organization after further study by different techniques, as discussed below.

Figure 2a shows a 2D spectrum that represents chemical shifts against diffusion coefficients (logarithmic scale) for the complex T-2OC$_{10}$/MeAdip[2:1]. Signals corresponding to all the protons within the complex exhibit the same diffusion coefficient (ca. 3.2×10^{-10} m^2/s), which means that both (*R*)-3-methyladipic acid and T-2OC$_{10}$ combine to form a single entity in CDCl$_3$. In contrast, the diffusion coefficient of (*R*)-3-methyladipic acid itself was measured to be around 4.6×10^{-10} m^2/s, indicating a smaller molecular volume than the complex. As a preliminary conclusion we can state that the diacid and the triazine are indeed forming discrete supramolecules in solution. This conclusion will be used as a foundation for the hypothesis that the mesophase exhibited by this mixture consists, at least, of stacks of these supramolecules. When DOSY experiments were carried out on the mixtures with [1:1] and [4:1] proportions, the formation of stable heterocomplexes in solution was not as evident. In the case of T-2OC$_{10}$/MeAdip[1:1], even though this material forms a homogeneous liquid crystalline material, the stability of the complexes in solution was not as great. Indeed, the proton signals of (*R*)-3-methyladipic acid give a different diffusion coefficient (Figure 2b), which is probably due to the coexistence in solution of nonassociated triazine and acid molecules. Further evidence of this lack of stability will be discussed later (see below: circular dichroism experiments). A similar situation was also found in the case of T-2OC$_{10}$/MeAdip-[4:1], which forms a homogeneous mesomorphic material. DOSY experiments in CDCl$_3$ were not as conclusive for the formation of a heterocomplex as they were in the case of T-2OC$_{10}$/MeAdip[2:1] (see Supporting Information). DOSY experiments were also performed on mixtures of mono- and tridecyloxyaniline-derived triazines that did not give rise to homogeneous materials when mixed with (*R*)-3-methyladipic acid (see Supporting Information). Peaks corresponding to protons in the acid and those corresponding to the 2,4,6-tris-(3,4,5-tridecyloxyphenylamino)-1,3,5-triazine clearly have different diffusion coefficients, which means that they are present in independent molecules. Steric hindrance due to the peripheral tails could account for the fact that a stable complex with (*R*)-3-methyladipic acid is not formed. However, it is unclear as to why 2,4,6-tris(4-decyloxyphenylamino)-1,3,5-triazine does not give rise to a homogeneous liquid crystalline material, since diffusion experiments show the formation of a stable complex in chloroform solution. We tentatively propose that even though this triazine and the diacid can form stable heterocomplexes in solution, the SmA mesophase of the triazine itself is not the best arrangement for incorporation of the methyladipic acid molecules. In contrast, both components separate in the neat samples.

The formation of hydrogen-bonding interactions in the neat material was also investigated by infrared spectroscopy for all the mixtures. Figure 3 shows infrared spectra corresponding to thin films of the separate components (triazine and diacid) and one of the homogeneous mixtures, T-2OC$_{10}$/MeAdip[2:1].

Significant changes include the shift of the C═O stretching band to lower wavenumbers (from 1704 to 1675 cm^{-1}) upon formation of the supramolecular association, together with the disappearance of sharp bands that are present in the triazine spectrum and correspond to the N−H stretching vibration. Several peaks appear for this vibration in the mixture, indicating the coexistence of different types of associated N−H bonds, that is, those involved in homo- and heterocomplexes.

Mesomorphic Behavior: Study of the Supramolecular Organization. All of the materials containing 2,4,6-tris(3,4-dialkoxyphenylamino)-1,3,5-triazines were initially studied by optical microscopy and DSC. All of these materials were found to show mesomorphic behavior that is stable at room temperature. The type of mesophase was identified on the basis of optical textures (see Supporting Information) and was classified as hexagonal columnar, the same as that shown by the pure triazines T-2OC$_n$. The thermal data are gathered in Table 1. Despite the marked decrease in the clearing points of the mixtures, their liquid crystalline arrangement is stable at room temperature. The enthalpy difference between the Col$_h$−I transitions of T-2OC$_{10}$ and T-2OC$_{10}$/MeAdip[4:1] and the Col$_h$−I transitions of T-2OC$_{10}$/MeAdip[1:1] and T-2OC$_{10}$/MeAdip[2:1] might well be due to the polymeric nature of the latter,[26] as will be discussed below.

The dynamic nature of hydrogen-bonding interactions, and hence their role in the formation of the mesophase, was studied by infrared spectroscopy on KBr pellets. When the spectra were recorded at different temperatures (Figure 4), it became clear that the characteristic bands are modified according to the

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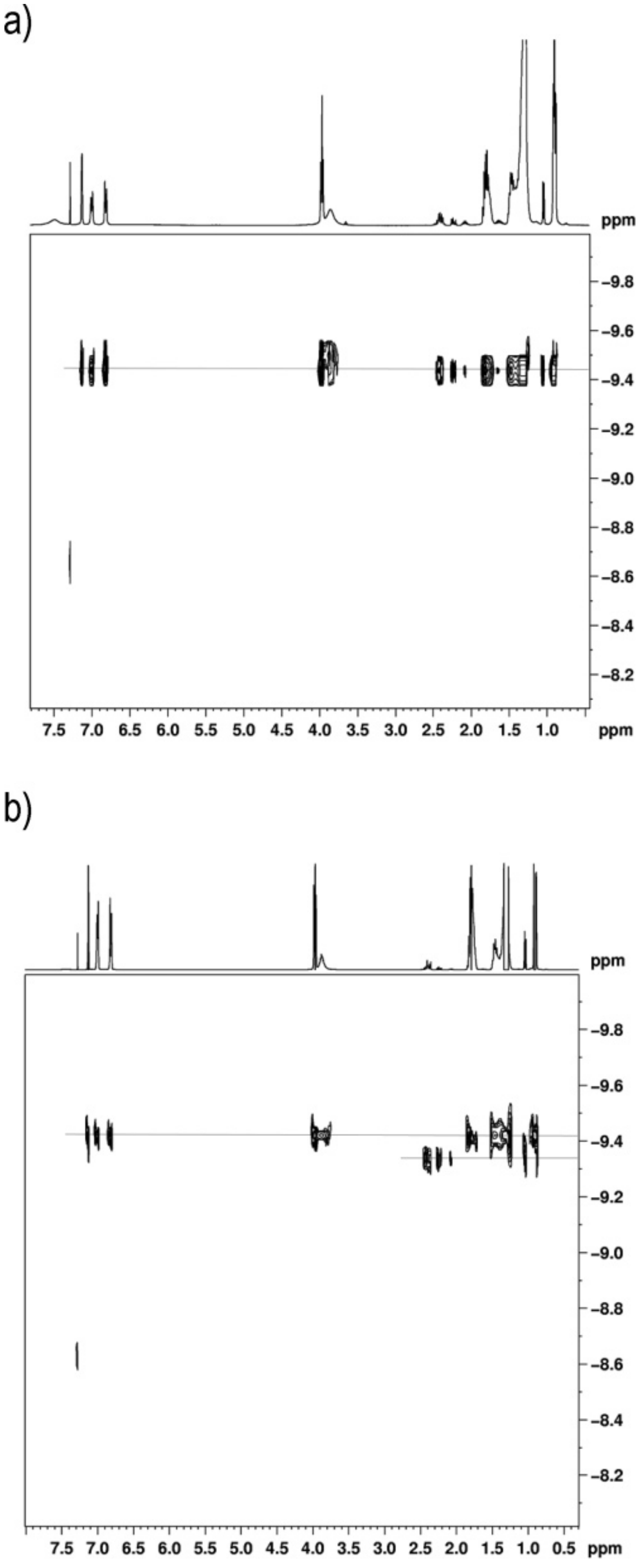

Figure 2. DOSY spectra of (a) T-2OC$_{10}$/MeAdip[2:1] and (b) T-2OC$_{10}$/MeAdip[1:1].

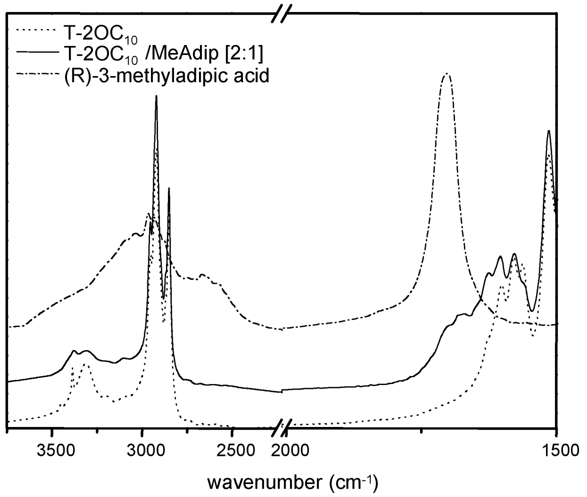

Figure 3. Comparative plot of the infrared spectra of separate (*R*)-3-methyladipic acid and triazine T-2OC$_{10}$ and a mixture, T-2OC$_{10}$/MeAdip-[2:1]. The spectra were recorded at room temperature on KBr pellets.

Table 1. Thermal Properties of the Pure Triazines and Their Corresponding Three Mixtures with (*R*)-3-Methyladipic Acid

compound	thermal transitions
T-2OC$_{10}$	Cr-Col$_h$ 71.1°C (83 kJ/mol) Col$_h$-I 86.6 °C (2.8 kJ/mol)
T-2OC$_{12}$	Cr-Col$_h$ 52.7°C (12 kJ/mol) Col$_h$-I 88.4 °C (4.1 kJ/mol)
T-2OC$_{10}$/MeAdip[1:1]	Col$_h$-I 51.2 °C (43.9 kJ/mol)
T-2OC$_{10}$/MeAdip[2:1]	Col$_h$-I 53.3 °C (29.6 kJ/mol)
T-2OC$_{10}$/MeAdip[4:1]	Cr-I 53.1°C (9.8 kJ/mol) I-Col$_h$ 38.9 °C (1.2 kJ/mol)monotropic transition
T-2OC$_{12}$/MeAdip[1:1]	Col$_h$-I 60.5 °C (66.9 kJ/mol)
T-2OC$_{12}$/MeAdip[2:1]	Col$_h$-I 64.3 °C (64.1 kJ/mol)
T-2OC$_{12}$/MeAdip[4:1]	Cr-I 61.6 °C (24.6 kJ/mol) I-Col$_h$ 58.8 °C (2.5 kJ/mol)monotropic transition

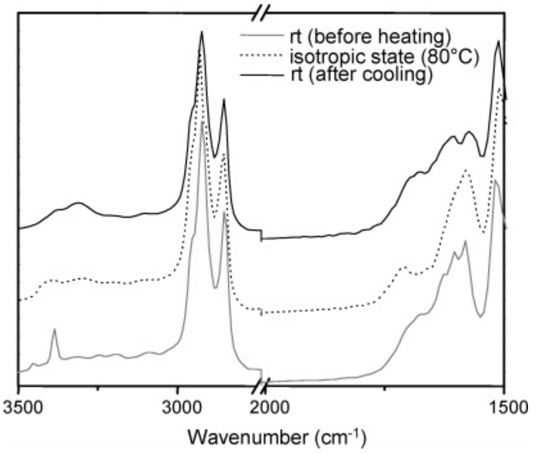

Figure 4. Spectra corresponding to T-2OC$_{10}$/MeAdip[2:1] recorded at different temperatures: (thin solid line) room temperature, (dotted line) 80 °C, and (bold solid line) room temperature after cooling from the isotropic liquid (80 °C) and annealing for 1 day.

heating and cooling process and change in a reproducible manner that is consistent with the dynamic nature of the supramolecular material prepared. The intensity of the N−H stretching bands that appear at 3387 and 3312 cm^{-1} decreases and the bands broaden on heating, whereas the C═O stretching band shifts to higher wavenumbers (from 1675 to 1706 cm^{-1}). However, it is worth noting that some H-bonds are still present in the liquid. Hence, the transition to the isotropic liquid mostly takes place when the columnar organization collapses through weakening of $\pi-\pi$ interactions and partial breaking of H-bonds rather than being a consequence of complete H-bond cleavage within the supramolecular species.

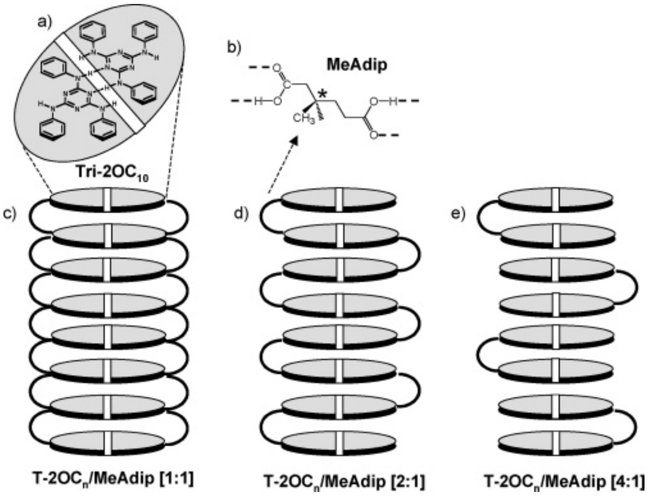

Figure 5. Idealized representation of the structure for the three supramolecular materials prepared with different proportions of (*R*)-3-methyladipic acid.

Table 2. Lattice Parameters for the Columnar Mesophases Found for All the Materials, As Measured by X-ray Diffraction[a]

compound	hexagonal lattice constants	calcd density
T-2OC$_{10}$	$a = 31.3$ Å	
T-2OC$_{10}$/MeAdip[1:1]	$a = 38.7$ Å, $c = 3.6$ Å	1.03
T-2OC$_{10}$/MeAdip[2:1]	$a = 38.7$ Å, $c = 3.6$ Å	0.98
T-2OC$_{10}$/MeAdip[4:1]	$a = 35.6$ Å, $c \approx 3.7$ Å	1.09
T-2OC$_{12}$	$a = 33.3$ Å	
T-2OC$_{12}$/MeAdip[1:1]	$a = 44.3$ Å, $c = 3.6$ Å	0.88
T-2OC$_{12}$/MeAdip[2:1]	$a = 44.3$ Å, $c = 3.6$ Å	0.83
T-2OC$_{12}$/MeAdip[4:1]	$a = 38.4$ Å	1.05[a]

[a] The density value was calculated with 3.7 Å as an intracolumnar distance.

At this stage, we envisaged an ideal model for each of the supramolecular species according to the percentage of (*R*)-3-methyladipic acid present. These models will be used as starting points to discuss the supramolecular organization of these materials at room temperature on the basis of the results found from different techniques. According to these models (Figure 5), T-2OC$_n$/MeAdip[1:1] should be comparable to a ladderlike polymeric structure that is cross-linked within the column. T-2OC$_n$/MeAdip[2:1] would behave as a typical main-chain supramolecular polymer, and T-2OC$_n$/MeAdip[4:1] would be expected to exist as oligomeric species of different sizes stacked within the mesophase.

X-ray Diffraction. X-ray studies were carried out at room temperature on all three mixtures along with the triazine mesogen itself. At this temperature, all four materials show mesomorphic behavior (gradual crystallization was observed in subsequent X-ray diffraction experiments carried out on all three materials containing the triazine T-2OC$_{10}$ after several weeks; in contrast, crystallization was observed within a few days for T-OC$_{12}$ derivatives). Lattice parameters are listed in Table 2. Diffraction patterns from these experiments are shown in Figure 6.

The most significant result is the appearance of a second diffuse halo at angles higher than that observed for the molten chains. The spacing corresponding to this halo was accurately measured for T-2OC$_{10}$/MeAdip[1:1] and T-2OC$_{10}$/MeAdip[2:1] and was found to be 3.6 Å. This halo was less visible for T-2OC$_{10}$/MeAdip[4:1] and so the measurement was not as precise; however, an approximate value of 3.7 Å was estimated. This halo, which was not visible at all in the pattern of T-2OC$_{10}$, can be explained in terms of a regular stacking within the columns induced by the presence of (*R*)-3-methyladipic acid molecules fixing distances between disks by means of hydrogen bonding. Further support for the role of the (*R*)-3-methyladipic acid as a clip within a regular columnar arrangement, which enables the formation of a stable mesophase, was obtained from experiments carried out with T-2OC$_{10}$ and two types of carboxylic acid, (i) adipic acid and (ii) caproic acid, respectively. The first one keeps the 2-fold functionality of (*R*)-3-methyladipic acid, and hence the possibility of forming interdisk associations. It lacks the methyl branch that can affect the conformation of the diacid. The second one has only one carboxylic group, and hence it will give rise to single supramolecules upon association.

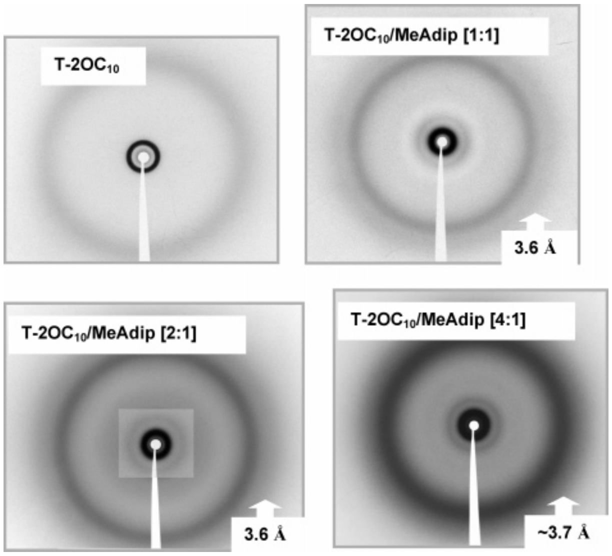

Figure 6. Diffraction patterns corresponding to the triazine T-2OC$_{10}$ and the three supramolecular mixtures T-2OC$_{10}$/MeAdip[1:1], T-2OC$_{10}$/MeAdip[2:1], and T-2OC$_{10}$/MeAdip[4:1]. Arrows indicate the diffuse halo due to the regular stacking that appears because of the presence of H-bonding clips [(*R*)-3-methyladipic acid].

(i) Experiments with Adipic Acid. Three mixtures were prepared in which the same ratio of T-2OC$_{10}$ to adipic acid was maintained, [1:1], [2:1], and [4:1]. DOSY experiments indicated that the adipic acid clearly belongs to a supramolecular entity that includes triazine units and the diacid itself when the proportion is [2:1]. This arrangement is stable in $CDCl_3$ solution (see Supporting Information). However, none of these mixtures appeared as a homogeneous material that displayed mesomorphic behavior. This experimental result led us to believe that the most probable extended conformation of the adipic acid ruled out any possibility of association between supramolecular triazine-acid disks within a column—a situation that prevents mesophase formation. Consequently, the methyl group in the (*R*)-3-methyladipic acid must encourage a bent conformation that favors the possibility of interdisk association along the column, and this would help to maintain the columnar arrangement.

(ii) Experiments with Caproic Acid. Two mixtures were prepared with molar ratios of T-2OC$_{10}$ to caproic acid, [1:2] and [1:1]. As far as the number of carboxylic groups associated with each triazine dimer is concerned, these proportions are equivalent to those of T-2OC$_{10}$ and 3-methyladipic acid with ratios [1:1] and [2:1], respectively. Both mixtures showed a

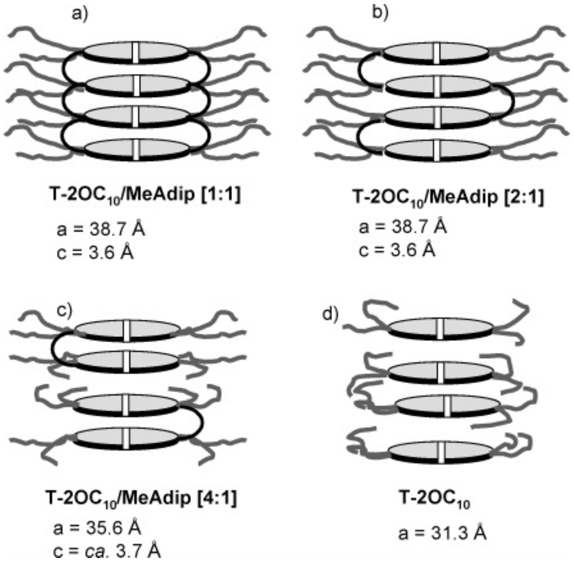

Figure 7. Schematic drawings of a column corresponding to each of the supramolecular species prepared (a, T-2OC$_{10}$/MeAdip[1:1]; b, T-2OC$_{10}$/MeAdip[2:1]; c, T-2OC$_{10}$/MeAdip[4:1]) as well as the triazine itself (d), showing the possible disposition of the peripheral tails within the column on the basis of the measured interdisk and intercolumnar distances. The aim of these drawings is to represent the effect of the different proportions of diacid on the hexagonal lattice constant (*a* parameter).

hexagonal columnar mesophase with similar clearing temperatures and lower enthalpy values than the corresponding MeAdip-containing complexes: for T-2OC$_{10}$/caproic acid [1:1], Col$_h$−I 64.1 °C (3.4 kJ/mol); for T-2OC$_{10}$/ caproic acid [1:2], Col$_h$−I, 55.7 °C (2.6 kJ/mol). It is clear that incorporation of additional alkylic tails within te supramolecular disk decrease clearing temperatures as occurs with the chiral diacid (MeAdip). However, and more important, X-ray diffraction experiments have not shown the high-angle halo characteristic of periodicity along the column (see Supporting Information). This means that incorporation of these acids does not promote interdisk additional order and allows us to confirm the model in which the chiral diacid gives rise to a regular stacking of supramolecular disks.

In addition, the hexagonal lattice constants can be deduced from the sharp maximum at low angles (100 reflection). At first sight (Table 2), a marked increase in the lattice parameter occurs on changing from the triazine T-2OC$_{10}$ (31.3 Å) to the supramolecular mixtures. The lattice parameter reaches the highest values (38.7 Å) when an ideal polymeric structure is formed, that is, T-2OC$_{10}$/MeAdip[1:1] and T-2OC$_{10}$/MeAdip[2:1] (see Figure 5c,d). This situation can only occur provided that there is sufficient diacid present.

These measurements are in full agreement with an ordered columnar arrangement induced by the addition of (*R*)-3-methyladipic acid to the triazine-based liquid crystal. The results also support the accuracy of the ideal model we initially considered for the supramolecular structures (Figure 5). The model allows a correlation to be made between the percentage of diacid present and the intracolumnar distances and lattice parameters. (*R*)-3-Methyladipic acid units must act as clips that bring together triazine dimers along the column by means of hydrogen bonding. One would expect that moderate or high methyladipic acid concentrations will force peripheral chains to stretch out to overcome the steric hindrance caused by the shorter stacking distance (Figure 7a,b). In this situation the column diameter will increase (a distance between columns of 38.7 Å was measured for T-2OC$_{10}$/MeAdip[1:1] and T-2OC$_{10}$/MeAdip[2:1]) with respect to the mesophase formed by pure triazine dimers (T-2OC$_{10}$). On the other hand, the irregular stacking of the pure triazine dimers means that there is sufficient space between disks for peripheral chains to fold inward toward the column (Figure 7d), thus explaining the shorter lattice parameter (31.3 Å) measured for this material. An intermediate situation could explain the lattice parameter found for T-2OC$_{10}$/MeAdip[4:1] (35.6 Å). In this case it is proposed that oligomeric species, rather than a continuous polymeric structure, stack within the mesophase and give rise to a less-defined order within the column (Figure 7c).

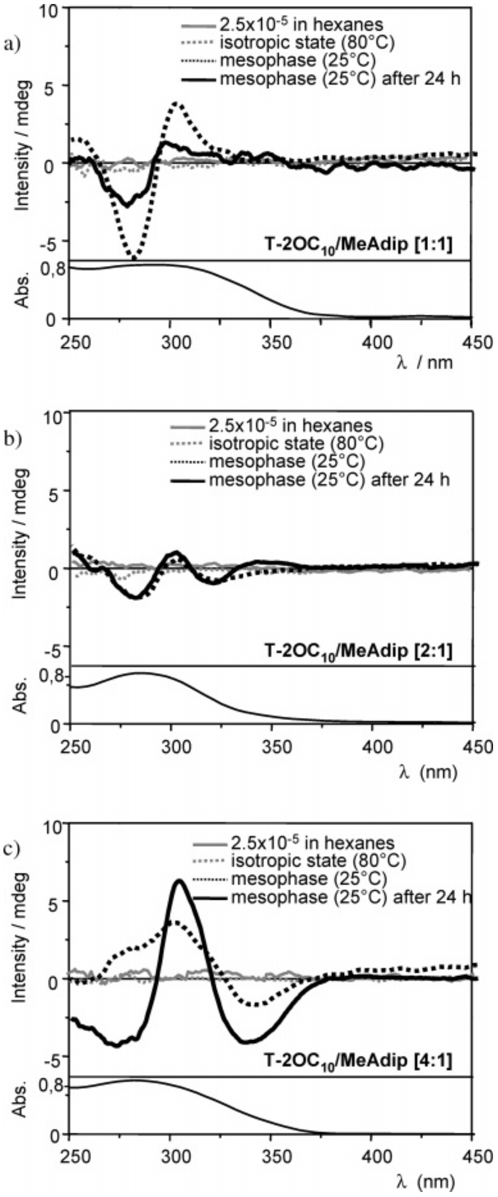

Figure 8. CD spectral comparison of (a) T-2OC$_{10}$/MeAdip[1:1], (b) T-2OC$_{10}$/MeAdip[2:1], and (c) T-2OC$_{10}$/MeAdip[4:1], in the isotropic liquid (80 °C), in solution (10 mm cell, 2.5×10^{-5} M in hexanes), and in the mesophase, both in the freshly formed mesophase and after 24 h. The UV spectrum in the region under study for each material in the mesophase is shown below the corresponding CD spectrum.

Circular Dichroism. Having confirmed the role of the diacid units as inducers of the supramolecular polymerlike columnar architecture within the mesophase, the next step was to investigate whether its chiral character was transferred to the overall system by means of H-bonding interactions. The study of the chirooptical properties of all the materials was carried out by circular dichroism. Experiments were performed on the corresponding neat samples between quartz plates both at the temperature of the mesophase and in the isotropic state. The thickness of the sandwich cells was not rigorously controlled, and hence qualitative study of the different materials, rather than quantitative, was undertaken. In all cases, the spectrum of the mesophase (as it appears upon rapid cooling) shows significant bands (Figure 8), corresponding to absorption bands, which are not present either in the isotropic melt or in dilute solutions (in hexanes or in chloroform). These signals in the mesophase can be accounted for by intermolecular interactions between electronic transition dipoles of stacked triazine chromophores arranged in a helical manner, having eliminated linear dichroism effects by averaging several CD spectra (recorded at different film positions rotated around the light beam). Thus, it can be stated that there is formal optical activity due to a helical superstructure biased toward a chiral sense that is determined by the configuration of the stereogenic center.

Moreover, optical activity is apparent in all three samples after several hours, which means that the chiral supramolecular organization is present over an extended time period. However, the chirooptical properties observed evolve differently for the three materials, which again reveals the dynamic nature of H-bonds in allowing the supramolecular material to progress toward a thermodynamically stable organization that depends on the proportion of “clipping” chiral moieties. The chiral superstructure formed by T-2OC$_{10}$/MeAdip[1:1] below the clearing temperature does not seem to be as thermodynamically stable as those formed when lower percentages of the diacid are present, that is, [2:1] and [4:1], given the low intensity of the spectrum after annealing (Figure 8a). This situation can be interpreted in terms of overcrowding of (*R*)-3-methyladipic acid units within the structure. If we consider the triazine units we can envisage that, once the triazine dimer is formed, one of the positions that is susceptible to H-bond formation is no longer as accessible (Figure 1c). This situation could well give rise to weak H-bonds (these could be a single H-bond between the −OH group of the acid and the triazine nitrogen) that can cleave during annealing. Such a situation would give rise to (*R*)-3-methyladipic acid molecules within the mesophase that are either nonassociated or associated with one another. Evidence for this instability had been observed in previously discussed DOSY experiments in deuterated chloroform solutions (see above). The supramolecular polymer system of T-2OC$_{10}$/MeAdip[2:1] maintains the same optical activity for prolonged periods. This fact suggests that the backbone of the supramolecular polymer has a thermodynamically stable helical conformation that appears just below the transition from the isotropic liquid and is stable over time (Figure 8b). T-2OC$_{10}$/MeAdip[4:1] shows more intense optical activity than T-2OC$_{10}$/MeAdip[2:1]. However, in this case we do not deal with a polymeric supramolecular since there is not enough diacid to allow a long-distance interdisk association within the columns. This leads to a more flexible structure, which is able to further reorganize during annealing as deduced from the increased intensity of the CD signals with time (Figure 8c).

Experimental Section

NMR experiments were performed on a 400 MHz Bruker Avance spectrometer. ^{1}H NMR diffusion measurements were performed by use of a stimulated echo sequence with bipolar gradient pulses. Diffusion time (Δ) was set to 100 ms. The pulsed gradients were incremented from 2% to 95% of the maximum strength in 16 spaced steps with a duration ($\delta/2$) of 1.4−2 ms. Data were acquired in CDCl$_3$ with sample rotation, and the temperature was controlled at 298 K to minimize convection effects.

Infrared spectra for all the complexes were obtained by use of a Mattson Genesis II FTIR spectrophotometer in the 400−4000 cm^{-1} spectral range.

The textures of the mesophases were studied with an optical microscope (Nikon) with crossed polarizers and connected to a Mettler FP82 hot stage and a Mettler FP90 central processor. Measurements of the transition temperatures were made on a TA Instruments 2000 differential scanning calorimeter with a heating or cooling rate of 10 °C/min. The apparatus were calibrated with indium (156.6 °C, 28.44 J/g) and tin (232.1 °C, 60.5 J/g).

X-ray diffraction studies were carried out at room temperature with a Pinhole camera (Anton-Paar) operating with a point-focused Ni-filtered Cu Kα beam. The sample was held in Limdemann glass capillaries (1 mm diameter) and heated, when necessary, with a variable-temperature attachment. The diffraction patterns were collected on a flat photographic film.

CD spectra were recorded in a Jasco J-710. UV spectra were recorded in a UV/vis Unicam spectrometer. Neat samples were prepared by sandwiching the material between two quartz plates. As heating stage, a Mettler FP82 with a central processor Mettler FP80 was used, conveniently modified to fix within the sample holder of the CD and UV spectrometers. Solution experiments were carried out in hexanes at room temperature.

Conclusion

In this paper we describe a simple strategy for the induction of chiral mesomorphic superstructures through noncovalent association between functionalized monomers. We propose the use of H-bonds to induce the chiral supramolecular organization of a columnar mesophase promoted by $\pi-\pi$ interactions between disklike systems. The investigation was aimed at using these two types of complementary interactions. In this way, $\pi-\pi$ interactions between disklike triazine dimers lead to the formation of a liquid crystalline columnar organization. The introduction of a suitable chiral diacid, (*R*)-3-methyladipic acid, is responsible for the formation of H-bonds that preserve the structural integrity of this organization through the formation of a supramolecular polymeric structure. The chiral diacid also imprints a chiral helical organization onto the mesophase. The results reported here show that it is possible to control the structure of a chiral supramolecular aggregate by manipulating the type and number of interactions between subunits.

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Supporting Information Available: Synthesis of all materials, density calculations based on X-ray diffraction, additional DOSY spectra of T-2OC$_{10}$/MeAdip[4:1], T-3OC$_{10}$/MeAdip[1:1], T-OC$_{10}$/MeAdip[2:1], and T-2OC$_{10}$/Adip[2:1], texture photomicropraphs, X-ray diffration results of capropic acid complexes, and CD spectra of the complexes based on T-2OC$_{12}$/MeAdip. This information is available free of charge via the Internet at http://pubs.acs.org.

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