Strict Steric Requirements for the Formation of Helical Mesophases Consisting of H-Bonded Supramolecules

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The possibility of achieving chiral helical superstructures in the columnar mesophase of H-bonded complexes of 2,4,6-triarylamino-1,3,5-triazines and chiral benzoic acids is pursued in this work. A series of heterodimeric complexes have been prepared and their mesomorphic states studied by polarized optical microscopy, differential scanning calorimetry, X-ray diffraction, and circular dichroism. It is concluded that steric requirements strongly influence the mesomorphism of these H-bonded complexes. Hence, well-defined columnar arrangements, characterized by high transition enthalpies and a large number of X-ray diffraction rings, are exhibited by complexes with a given number of peripheral tails and a steric compromise between the sizes of the triazine and the acid partners. Optical activity derived from a chiral columnar organization within the mesophase appears for these well-defined hexagonal columnar mesophases.

Introduction

Chirality in liquid crystals[1] is a topic that attracts a great deal of interest within materials science due to the possibility of achieving highly organized functional supramolecular organizations. Chiral helically organized functional materials provide a way to achieve the performance provided by certain properties that result from the existence of a preferred direction, i.e., the helix axis. Such properties include those that require polar order[2] (NLO[3] or electrooptic effects[4]) or those derived from a special interaction with light (selective reflection).[5] Columnar mesophases have revealed themselves to be particularly advantageous in terms of tailoring helically well structured materials using a twofold organization process. First, a preferred direction is defined within the column. Second, twisting of the columns into helices biased toward a given sense will allow the appearance of properties that originate from a helical organization. Moreover, the sense of the helix can be readily dictated by the molecular chirality.[6]

The formation of columnar mesophases mostly relies on $\pi-\pi$ interactions for this type of molecular self-assembly.[7] In addition, hydrogen bonding is also used as a versatile tool for the construction of new liquid crystalline materials.[8] Indeed, a combination of π stacking and hydrogen bonding interactions has been reported for partners that interact to build up helically organized systems.[9] In most cases, hydrogen bonding has been used as a way of reinforcing $\pi-\pi$ interactions to achieve well-organized dynamic molecular stacks.[10]

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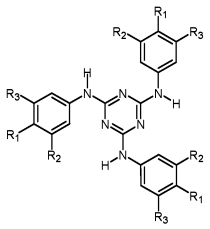
Chart 1



	R_1	R_2	R_3
T1	$OC_{10}H_{21}$	H	H
T2	$OC_{10}H_{21}$	$OC_{10}H_{21}$	H
T3	$OC_{10}H_{21}$	$OC_{10}H_{21}$	$OC_{10}H_{21}$

Likewise, hydrogen bonding interactions have also been used as a means of transferring molecular chirality to a supramolecular columnar organization.[11] In the work described here, we pursued this strategy and have combined both approaches to obtain helical columnar organizations. For this purpose, we considered three types of 2,4,6-triarylamino-1,3,5-triazine (T1−T3 in Chart 1) with different substitution patterns in the aromatic ring. These molecules have already been described as discotic liquid crystals either in their own right or as part of discotic supramolecular systems that are capable of organizing into columnar mesophases due to their H-bonding character with benzoic acids in a 1:1 ratio.[12] In a previous study, we performed an in-depth structural investigation into the steric requirements this type of complex needs to display columnar mesomorphism.[13] On the basis of this study, we have designed and prepared hetereodimeric complexes from the triazines T1−T3 (Chart 1) with chiral polycatenar benzoic acids A1−A5 in Chart 2. Thus, chirality is introduced into the system through alkoxy (A1) and dialkoxy (A2 and A3) benzoic acids with stereogenic centers in the alkoxy tails. We also studied the effect of the number and position of the chiral terminal chains on the appearance of both mesomorphism and a formal optical activity derived from a helical organization within the column. Furthermore, with the same aim in mind, we employed two benzoic acids with an extended aromatic core (A4 and A5), which differ from each other in the position of the stereogenic center in the terminal chains.

Results

Synthesis. The 2,4,6-triarylamino-1,3,5-triazines (T1−T3) were prepared by the reaction of the corresponding alkoxy-substituted anilines with cyanuric chloride using potassium carbonate as a base in 2-butanone as a solvent.[12b] 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.[14]

Chiral benzoic acids A1−A3 were prepared by Mitsunobu etherification[15] of the corresponding alkyl hydroxybenzoate with *S*-(+)-2-octanol, followed by alkaline ester cleavage.

Acids A4 and A5 were synthesized by Williamson etherification of methyl 3,4,5-trihydroxybenzoate with the appropriate benzyl chloride, followed by alkaline ester cleavage according to the method given in detail elsewhere.[16]

When the solvent was removed from a solution of equimolar amounts of both a triazine (T1−T3) and one of the benzoic acids (A1−A5) and the resulting 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 of formation of a complex.

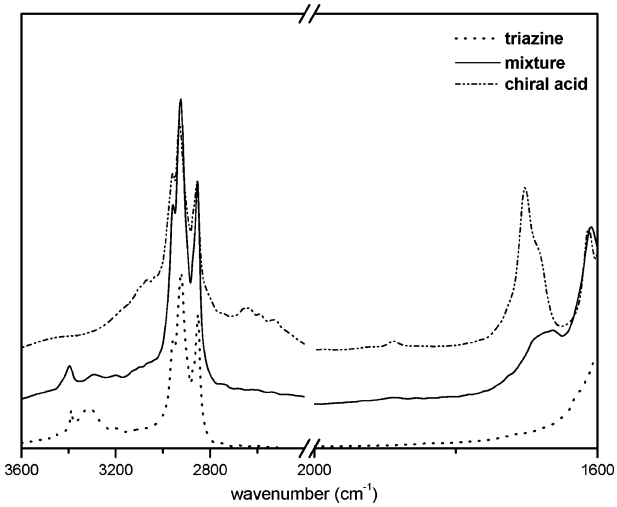


Figure 1. FTIR spectra of the pure triazine (T2), the equimolar mixture (T2−A4), and the acid (A4).

Characterization and Stability of the H-Bonded Complexes. The formation of the 1:1 H-bonded complex (Chart 3) was readily deduced from infrared spectra. The infrared spectra of the separate components (triazine and acid) and that of the corresponding mixture were recorded on KBr pellets. As a representative example, the infrared spectra of T2, A4, and their corresponding T2−A4 complex are shown in Figure 1. An apparent change in the characteristic carbonyl bands is observed when the spectrum of the acid is compared with that of the mixture. In the acid, a C═O stretching band appears at 1702 cm^{-1} with a shoulder at 1683 cm^{-1}, and they correspond to the nonassociated form and to the dimeric form, respectively. After H-bonding association with the triazine, however, a broad signal around 1662 cm^{-1} is observed, which corresponds to the associated triazinecarboxylic acid. Changes in the region corresponding to the N−H stretching band are also significant. Triazine T2 gives a simpler spectrum than the mixture. T2 shows a sharp peak

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Chart 2

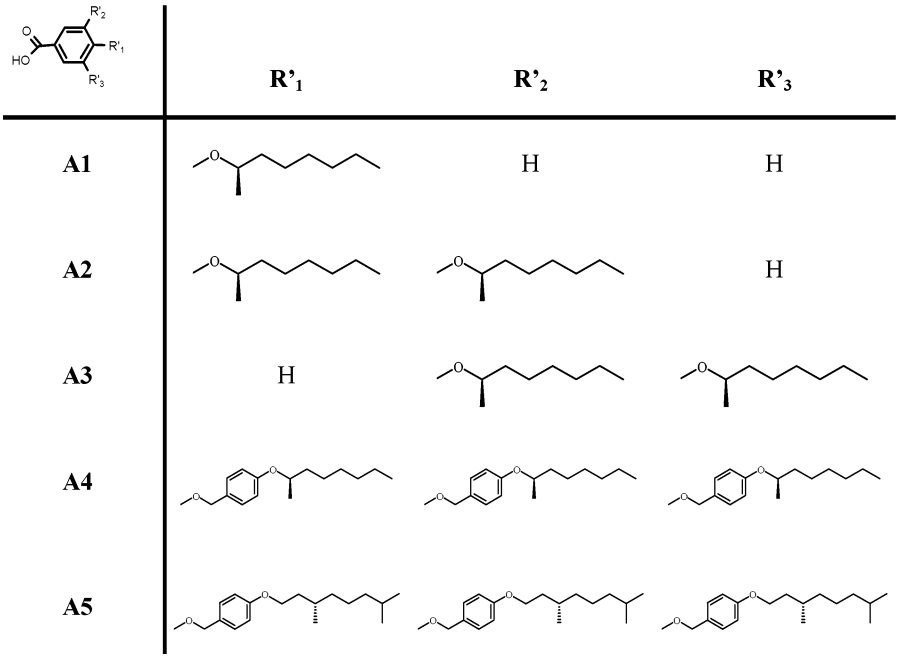
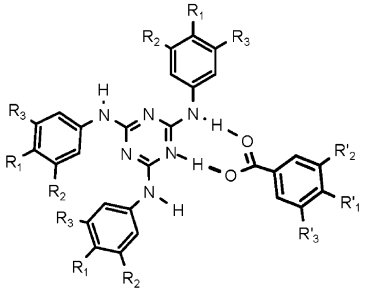


Chart 3



(3388 cm^{-1}) and a broad band (3313 cm^{-1}) that can be assigned to nonassociated and H-bonded N−H bonds, respectively. In contrast, a sharp peak (3396 cm^{-1}) and several broad bands within this region are observed in the mixture.

Evidence for complex formation was also found in ^1H NMR spectra recorded in $CDCl_3$ solutions. The N−H proton appears as a singlet in the pure triazine (e.g., 7.0 ppm for T2), and this becomes broader and shifted to a lower field upon H-bonding association with the acid (7.2−7.4 ppm for the T2−A4 complex).

Further evidence of formation of stable H-bonding interactions in solution was obtained by NMR diffusion-ordered spectroscopy, i.e., DOSY experiments.[17] This technique allows diffusion coefficients to be correlated with molecular composition via observation of chemical shifts. It has been successfully applied to the study of molecular association in different complex systems, including rotaxanated polymers, H-bonded complexes, and liquid crystalline polymers.[18] DOSY experiments were performed in $CDCl_3$ for all the heterodimeric complexes. The experiments were undertaken on the assumption that the heterodimers, triazine/acid, should be distinguishable from the acid and the triazine on their own due to their significantly different diffusion coefficients.

The two-dimensional spectra shown in Figure 2 represent chemical shifts against diffusion coefficients (logarithmic scale) for acid A4 (Figure 2a), pure triazine T2 (Figure 2c), and the corresponding T2−A4 complex (Figure 2b). Signals corresponding to all the protons within the complex exhibit the same diffusion coefficient (3.45×10^{-10} m^2/s). None of the protons in the complex exhibit a diffusion coefficient of 4.20×10^{-10} m^2/s, which corresponds to that of triazine T2 (Figure 2c). The diffusion coefficient of the complex is, however, quite similar to that of acid A4 (3.55×10^{-10} m^2/s). This fact can be explained in terms of the similar hydrodynamic volume of the acid, which should consist of dimeric species, and the heterodimeric complex. In any case, all of these results provide conclusive evidence that acid A4 and triazine T2 are associated within a discrete supramolecule, in a 1:1 ratio, and that this system is stable in $CDCl_3$.

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−cooling cycle at a rate of 10 °C/min. Transition temperatures and enthalpy values are given in Table 1.

Only two of the substituted benzoic acids employed in this study exhibit mesomorphic behavior in their pure state. Acids A4 and A5 show a hexagonal columnar phase over a wide temperature range. In both cases, the formation of dimers is responsible for the observed columnar mesomorphic behavior.

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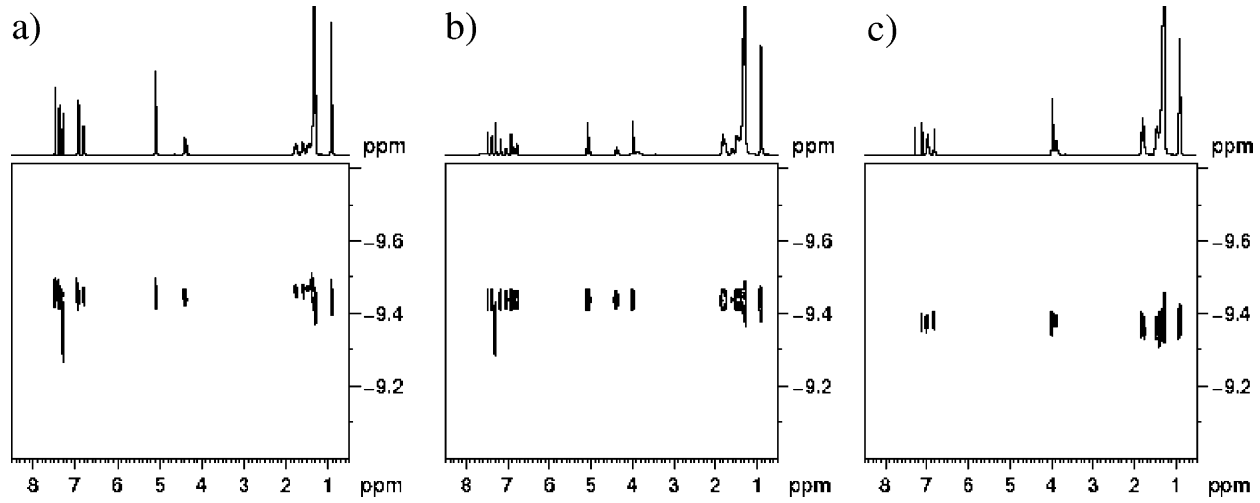

Figure 2. DOSY spectra of (a) the acid (A4), (b) the complex (T2−A4), and (c) the pure triazine (T2).

Table 1. Thermal Properties, Transition Temperatures (°C) and Enthalpies (kJ/mol), of the Pure Chiral Benzoic Acids, 1,3,5-Triaryltriazines, and Their Corresponding Heterodimeric Chiral Complexes (as the intersection cell between the corresponding A1−A5 entry and T1−T3 entry)[a]

	A1 Cr-I 63.1 (14.3)	A2 isotropic liquid	A3 isotropic liquid	A4 Cr-Col_h 65.8 (15.2) Col_h-I 91.6 (8.5)	A5 Cr-Col_h 42.4 (30.3) Col_h-I 122.8 (11.8)
T1					
Cr-I 105.1 (44.7) I-SmA 66.0 (2.0)	Cr-I 37.0 (30.1)	Cr-I 63.5 (8.1)	Cr-I 71.6 (11.4)	Cr-I 110.3 (7.9) [I-Col_h 115.5 (5.4)]	Cr-Col_h 49.6 (7.6) Col_h-I 107.3 (4.8)
T2					
Cr-Col_h 71.1 (83.0) Col_h-I 86.6 (2.8)	Col_h-I 47.6 (4.5)	Col_h-I 37.6 (5.8)	Cr-I 44.6 (23.9)	Col_{h1}-Col_{h2} 60.3 (10.4) Col_{h2}-I 114.9 (11.9)	Col_{h1}-Col_{h2} 84.4 (14.6) Col_{h2}-I 116.0 (10.0)
T3					
Col_h-I 34.0 (2.0)	Col_h-I 46.3 (21.9)	Col_h-I 23.2 (13.9)	isotropic liquid	Col_h-I 44.0 (6.4)	Col_h-I 50.2 (1.5)

[a] Abbreviations: Cr, crystal; SmA, smectic A mesophase; Col_h, hexagonal columnar mesophase; I, isotropic liquid.

All three 1,3,5-triaryltriazines employed in this study show mesomorphic behavior. Triazine T1, which bears 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 T2 and T3. Moreover, T3 is mesomorphic at room temperature.

Mesomorphism of the Complexes. From the data gathered in Table 1, it can be deduced that columnar mesomorphism appears in the complexes with a sufficiently large number of peripheral tails (at least six). The exception is found for complexes that incorporate acid A3, none of which show any liquid crystalline properties. This observation must be related to the 3,5-disubstitution pattern of the acid component. On the other hand, and considering the size of the acid involved in the complex, it seems clear that 3,4,5-tribenzyloxy-substituted acids (A4 and A5), which show a hexagonal columnar mesophase in their own right, give rise to mesomorphic materials regardless of the size of the triazine.

Another remarkable fact is that some complexes, i.e., T2−A4, T2−A5, T3−A1, and T3−A2, have high enthalpy values associated with their phase transitions when compared to the other complexes. Moreover, T2−A4 and T2−A5 complexes show two hexagonal columnar mesophases, as determined by X-ray diffraction, with high enthalpy values for the transition between the two mesophases.[10a,19] Upon considering the molecular composition of these complexes, there is no apparent reason for this phenomenon. The answer must lie in highly organized columnar arrangement within the hexagonal lattice, as deduced from X-ray measurements (see below).[20]

Structural Characterization of the Mesophases. All of the mesogenic 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 lattice constants, the observed and calculated spacings, and the proposed indexing are listed in Tables 2 and 3.

Mesophase Structure of the Pure Triazines and Benzoic Acids. X-ray diffraction data for the mesophases of the pure triazines are listed in Table 2 and have been discussed in more detail elsewhere.[13]

Acids A4 and A5 yielded X-ray patterns that are characteristic of a hexagonal columnar (Col_h) mesophase (see Table 2). These patterns are characterized by the presence of a set of three sharp maxima in the low-angle region with a reciprocal spacing ratio of $1:\sqrt{3}:\sqrt{4}$. These maxima can be assigned to the (1 0 0), (1 1 0), and (2 0 0) reflections from the two-dimensional hexagonal lattice. A diffuse ring corresponding to a mean distance of 4.5−4.9 Å was also

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Table 2. X-ray Diffraction Data for the Mesophases of the Pure Triazines and Benzoic Acid Derivatives

compd	T (°C)	phase	lattice constants (Å)	d_{obs} (Å)	d_{calc} (Å)	*hkl*
T1	room temp	SmA	$d = 34.0$	33.6	34.0	001
				17.2	17.0	002
				4.4 (br)		
T2	room temp	Col_h	$a = 33.4$	28.9	28.9	100
				4.4 (br)		
T3	room temp	Col_h	$a = 29.8$	25.7	25.8	100
				15.0	14.9	110
				4.4 (br)		
A4	80	Col_h	$a = 34.1$	29.5	29.5	100
				17.1	17.0	110
				14.7	14.8	200
				4.5 (br)		
A5	75	Col_h	$a = 38.2$	33.0	33.1	100
				19.3	19.1	110
				16.5	16.5	200
				4.9 (br)		

observed, and this is characteristic of the liquidlike arrangement of the aliphatic chains.

Mesophase Structure of the Complexes. The X-ray patterns of all the complexes considered in Table 3 are qualitatively very similar, and all of them are consistent with hexagonal columnar mesophases. It is worth noting that some of the patterns contain a large number of diffraction rings. This occurs for the low-temperature columnar mesophase of T2−A4 and T2−A5 complexes and the mesophases of T3−A1 and T3−A2 complexes. As an example, the pattern for the T3−A1 complex is characterized by the appearance of a set of seven sharp maxima with a reciprocal spacing ratio of $1:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{9}:\sqrt{16}:\sqrt{19}$. This is unambiguously characteristic of a well-defined hexagonal lattice, and the seven maxima can be assigned to the (1 0 0), (1 1 0), (2 0 0), (2 1 0), (3 0 0), (4 0 0), and (3 2 0) reflections. This finding is important since it concerns the optical activity found in these four materials, a property that will be discussed below.

The relationship between the density, ρ, of the complexes in the mesophase and the number of molecules in the unit cell, Z, is given by the equation $\rho = (M/N)/(V/Z)$, where M is the molar mass (grams) of the pure compound or of the complex, N Avogadro's number, and V the unit cell volume (cubic centimeters) [$V = (\sqrt{3}/2)a^2c \times 10^{-24}$]. The density was quantitatively calculated for T2−A1, T2−A2, T3−A1, and T3−A2 complexes, which all show a hexagonal columnar phase with a regular stacking distance (parameter c), and qualitatively estimated for the rest of the complexes by considering a similar interdisk distance of 3.45 Å (values in italics). On the assumption that the density of the complexes should not differ significantly from 1 g cm^{-3}, it is clear that there is one supramolecular complex per unit cell. In all cases where the stacking distance is regular, the calculated density of the mesophase is 0.82−1.23 g cm^{-3} (see Table 3).

The hexagonal lattice constant (parameter a) depends on the particular complex. A general increase in the intercolumnar distance is observed on increasing the number of chains and the length of the alkoxy groups attached to the central core of the benzoic acid derivatives. Complexes containing small benzoic acids, i.e., A1 or A2, have lattice parameters similar to those of the corresponding triazine.

Table 3. X-ray Diffraction Data for the Mesophases of the 1:1 Complexes of the 2,4,6-Tris(4-decyloxyphenylamino)-1,3,5-triazine (T1), 2,4,6-Tris(3,4-didecyloxyphenylamino)-1,3,5-triazine (T2), and 2,4,6-Tris(3,4,5-tridecyloxyphenylamino)-1,3,5-triazine (T3) with the Substituted Benzoic Acids

compd	T (°C)	phase	lattice constants (Å)	d_{obs} (Å)	d_{calc} (Å)	*hkl*	calcd density[a] (g cm^{-3})
T1−A4	room temp	Col_h	$a = 35.6$	30.8	30.8	100	*0.72*
				4.5 (br)			
T1−A5	80	Col_h	$a = 34.1$	29.5	29.5	100	*0.83*
				4.6 (br)			
T2−A1	room temp	Col_h	$a = 32.3$	28.0	28.0	100	0.82
			$c = 3.45$	4.4 (br)			
				3.45 (br)			
T2−A2	room temp	Col_h	$a = 32.9$	28.5	28.5	100	0.84
			$c = 3.45$	4.4 (br)			
				3.45 (br)			
T2−A4	80	Col_h	$a = 34.1$	29.5	29.5	100	*0.93*
				4.5 (br)			
	room temp	Col_h	$a = 35.5$	30.6	30.7	100	
				15.3	15.4	200	
				11.7	11.6	210	
				4.5 (br)			
T2−A5	100	Col_h	$a = 35.1$	30.4	30.4	100	*0.88*
				4.6 (br)			
	room temp	Col_h	$a = 37.3$	32.2	32.3	100	
				18.5	18.65	110	
				16.5	16.2	200	
				10.6	10.8	300	
				8.1	8.1	400	
				4.6 (br)			
T3−A1	room temp	Col_h	$a = 30.3$	26.4	26.2	100	1.19
			$c = 3.45$	15.4	15.15	110	
				12.8	13.1	200	
				10.1	9.9	210	
				8.3	8.7	300	
				6.6	6.6	400	
				6.1	6.0	320	
				4.4 (br)			
				3.45 (br)			
T3−A2	room temp	Col_h	$a = 30.8$	26.4	26.7	100	1.23
			$c = 3.45$	15.5	15.4	110	
				10.1	10.1	210	
				6.2	6.1	320	
				4.4 (br)			
				3.45 (br)			
T3−A4	room temp	Col_h	$a = 32.0$	27.7	27.7	100	*1.40*
				4.4 (br)			
T3−A5	room temp	Col_h	$a = 33.1$	28.7	28.7	100	*1.35*
				4.6 (br)			

[a] Densities in italics correspond to values estimated on the basis of an interdisk distance of 3.45 Å.

A significant difference is observed for complexes with bulkier 3,4,5-tribenzyloxybenzoic acids (A4 and A5), which have values larger than those of their corresponding triazines.

The X-ray measurements discussed above allowed a detailed study of the packing conditions of the disklike heterodimeric complexes within the corresponding columnar mesophase. On the basis of the data gathered in Tables 1−3, we propose that two types of steric factors determine and influence the mesomorphic properties of these complexes. (i) It has already been pointed out that at least six terminal chains are necessary for the complexes to display columnar mesomorphism. Hence, the T1−A1 complex, which bears a total of four terminal tails (3 + 1), and T1−A2 and T1−A3 complexes , which bear a total of five terminal tails (3 + 2), do not exhibit mesomorphic behavior. (ii) It is not only the number of tails in the triazine but also the size of the acid partner (cf. acids A1 and A2 vs 3,4,5-tribenzyloxybenzoic acids A4 and A5) that influences the mesomorphic arrange-

ment in the complexes. This conclusion is deduced from the well-defined columnar arrangement found in some of the complexes. Examples of this type of complex include triazine T2 with bulky acids A4 and A5 and triazine T3 with small acids A1 and A2. We believe that the well-organized columnar arrangement may correspond to a kind of steric compromise between the number of tails in the triazine and the size of the acid. In this respect, it is worth recalling the high enthalpy values measured for these complexes for the thermal transition in which these well-defined hexagonal mesophases are involved. For example, T3−A1 and T3−A2 complexes show an extraordinarily high Col_h-I enthalpy value (21.9 and 13.9 kJ/mol, respectively), a situation in contrast to the enthalpy values displayed by complexes formed between triazine T2 and the same acids, i.e., T2−A1 (4.5 kJ/mol) and T2−A2 (5.8 kJ/mol).

These observations are important since, as discussed in the next section, only complexes with highly organized columnar arrangements exhibit optical activity in the mesophase. Such activity is a consequence of a possible helical organization within the column.

Circular Dichroism. Circular dichroism (CD) experiments were carried out in an effort to study the effect of the chirality of the tails in the acid partner on the columnar mesophase of the corresponding complex, particularly in terms of the induction of a formal optical activity derived from chiral helical organization. All of the mesogenic complexes were checked to confirm the existence of optical activity in the mesophase. Experiments were performed on the corresponding neat samples both at the temperature of the mesophase and in the isotropic state. The cells were prepared by sandwiching each material in its isotropic liquid state between two clean, nontreated, quartz plates. The cells were allowed to cool with no external influence such as mechanical stress. In four cases, i.e., the low-temperature Col_h mesophase of T2−A4 (Figure 3a) and T2−A5 (Figure 3b) complexes, as well as T3−A1 (Figure 4a) and T3−A2 (Figure 4b) complexes, the spectra of the mesophase exhibited significant bands that corresponded to absorption bands in the UV spectrum. Moreover, these CD bands were not present either in the isotropic melt or in dilute solutions (in either hexanes or chloroform) (Figures 3 and 4). Intermolecular interactions between electronic transition dipoles of stacked supramolecular chromophores arranged in a helical manner can account for these signals in the mesophase. Linear dichroism effects were eliminated 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 that is biased toward a chiral sense, which is determined by the configuration of the stereogenic center.

The CD spectrum of the T2−A4 complex shows a positive exciton splitting, whereas the CD spectrum of the T2−A5 complex shows a negative exciton splitting. Both of these signals are centered at the wavelength of the $\pi-\pi^*$ transition of the chromophores (274 and 282 nm, respectively). An additional Cotton effect is visible in both spectra (clearer in the T2−A4 complex than in the T2−A5 complex), and this corresponds to a shoulder in each of the UV spectra at 325 nm. These results confirm the existence of a helical arrangement within the column, the optical activity of which is maintained for prolonged time periods. Moreover, the opposite sign of the exciton splitting may arise from an inversion of the configuration of the chiral center [from the (*R*)-T2−A4 complex to the (*S*)-T2−A5 complex], while the center remains in an even-numbered position from the aromatic ring. This result is reminiscent of the odd−even rules described for cholesteric materials[21] but also found in helical polymers such as polyisocyanides composed of chiral promesogenic monomers.[22] The CD spectra of T3−A1 and

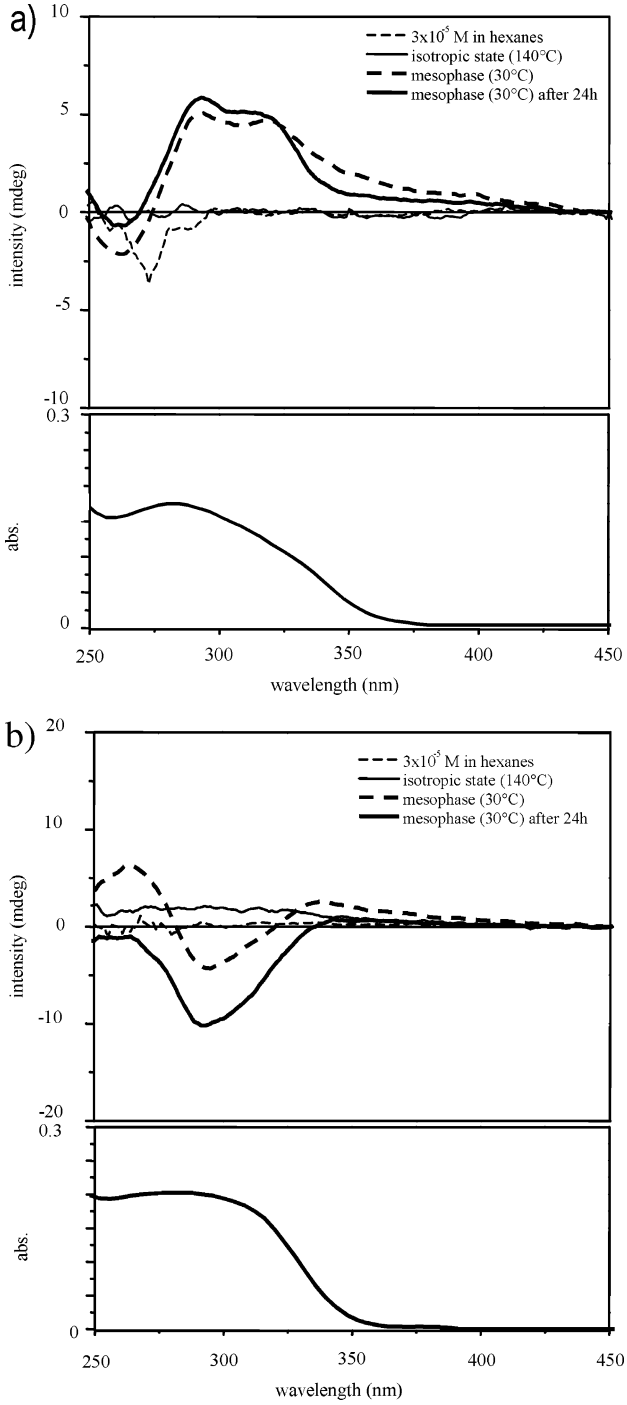

Figure 3. Comparison of CD spectra of (a) T2−A4 and (b) T2−A5 complexes, in the isotropic liquid, in solution (10 mm cell, 3×10^{-5} M in hexanes), and in the mesophase, both in the freshly formed mesophase and after 24 h. The UV spectrum in the region under study for each material in the mesophase is shown below the corresponding CD spectrum.

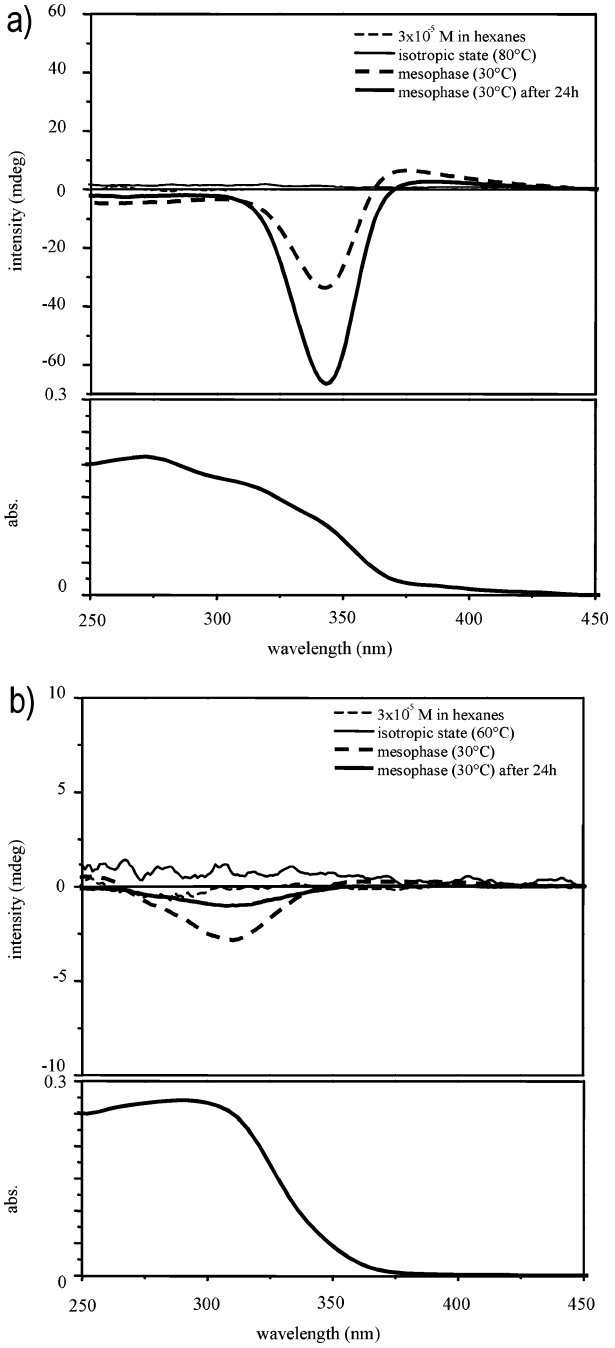

Figure 4. Comparison of CD spectra of (a) T3−A1 and (b) T3−A2 complexes, in the isotropic liquid, in solution (10 mm cell, 3×10^{-5} M in hexanes), and in the mesophase, both in the freshly formed mesophase and after 24 h. The UV spectrum in the region under study for each material in the mesophase is shown below the corresponding CD spectrum.

T3−A2 complexes are difficult to interpret. Both of these spectra show optical activity that is not present in either the isotropic liquid or solution, and this is due to some type of helical organization of the chromophores. In contrast to T2−A4 and T2−A5 complexes, the optical activity of the T3−A2 complex decreases over time, and is quite small compared to those of T2−A4 and T2−A5 complexes. The most distinct and surprising behavior was found for the T3−A1 complex, which shows a strong CD signal with a minimum at 343 nm. This wavelength may correspond to a UV shoulder that does not appear in the other complexes. One possible explanation for this absorption could be the formation of chiral aggregates, which disappear in the isotropic state and are not present in the other complexes due to the increased size of the acid partners. In addition, at the wavelength at which the rest of the complexes exhibit CD bands, this complex does not show any significant intensity. The different appearance of the CD curves with respect to T2−A4 and T2−A5 complexes could be related to the size of triazine T3, with nine peripheral tails, that modifies the steric requirements for the formation of a well-defined chiral organization within the column.

It is important to point out that the four mesophases for which optical activity has been detected were those that display well-organized hexagonal columnar arrangements, as observed from X-ray experiments. If we take into account the composition of the corresponding complexes, it is clear that the appearance of optical activity is not directly related to the number of stereogenic centers in the supramolecule. We can deduce that an optimal combination of the steric requirements of the two partners, i.e., triazine and acid, gives rise to disklike supramolecules that are able to organize themselves into a well-defined hexagonal columnar mesomorphic arrangements with chiral helical organization within the column.

Experimental Section

Preparation of the Materials. The 2,4,6-triarylamino-1,3,5-triazines (T1−T3) were prepared by the reaction of the corresponding alkoxy-substituted anilines with cyanuric chloride using potassium carbonate as a base in 2-butanone as a solvent.[12b] Full characterization of the triazines used in this study appears in ref 13.

The synthesis of A4 and A5 involved the preparation of benzyl alcohols from their corresponding ester precursors.

General Procedure for the Preparation of Alkyl (R-1′-Methylheptyloxy)benzoates. To a solution of methyl 4-hydroxybenzoate (30 mmol) or alkyl dihydroxybenzoate (15 mmol), (*S*)-(+)-2-octanol (30 mmol), and triphenylphosphine (TPP) (30 mmol) was added diisopropyl azodicarboxylate (DIAD) (30 mmol) in dry dichloromethane (150 mL) under argon. The reaction mixture was stirred at room temperature for 24 h. After this time, water (a few drops) was added and the mixture was stirred for an additional 1 h. The solvent was removed under reduced pressure, and the resulting solid was stirred in a mixture of hexane and ethyl acetate (7:3) (200 mL) for 1 h. The white precipitate was filtered off, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel, eluting with a 10:1 hexane/ethyl acetate mixture, with a yield of 50−80%.

Analytical Data. Methyl 4-(*R*-1′-methylheptyloxy)benzoate. R_f = 0.5 (90:10 hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (t, J = 6.9 Hz, 3H), 1.20−1.45 (m, 11H), 1.50−1.65 (m, 1H), 1.65−1.74 (m, 1H), 3.85 (s, 3H), 4.37−4.39 (m, 1H), 6.85 (d, J = 8.1 Hz, 2H), 7.94 (d, J = 8.1 Hz, 2H). IR (Nujol, NaCl): 1719 (C═O), 1253, 1169 (C−O) cm^{-1}.

Ethyl 3,4-bis(*R*-1′-methylheptyloxy)benzoate. R_f = 0.6 (10:1 hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (t, J = 6.3 Hz, 6H), 1.20−1.45 (m, 25H), 1.50−1.65 (m, 2H), 1.68−1.75 (m, 2H), 4.27−4.41 (m, 4H), 6.85 (d, J = 8.4 Hz, 1H), 7.55 (s,

(21) Gray, G. W.; McDonnell, D. G. *Mol. Cryst. Liq. Cryst.* **1977**, *34*, 211.
(22) Ramos, E.; Bosch, J.; Serrano, J. L.; Sierra, T.; Veciana, J. *J. Am. Chem. Soc.* **1996**, *118*, 4703−4704.

1H), 7.60 (d, $J = 8.4$ Hz, 1H). IR (Nujol, NaCl): 1713 (C═O), 1269, 1206, 1131 (C−O) cm^{-1}.

Methyl 3,5-bis(*R*-1′-methylheptyloxy)benzoate. $R_f = 0.6$ (10:1 hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (t, $J =$ 6.6 Hz, 6H), 1.20−1.45 (m, 22H), 1.50−1.65 (m, 2H), 1.68−1.75 (m, 2H), 3.87 (s, 3H), 4.32−4.38 (m, 2H), 6.58 (s, 1H), 7.11 (s, 2H). IR (Nujol, NaCl): 1725 (C═O), 1232, 1158 (C−O) cm^{-1}.

General Procedure for the Preparation of 4-Alkoxybenzyl Alcohols. To a suspension of $LiAlH_4$ (35 mmol) in THF (50 mL) cooled in an ice bath was added a solution of the corresponding methyl 4-alkoxybenzoate (31 mmol) in THF (30 mL). The reaction mixture was stirred under argon at room temperature for 1 h (monitoring by thin-layer chromatography determined the end of the reaction). The reaction mixture was cooled in an ice bath, and H_2O (100 mL) was added cautiously dropwise. The mixture was extracted into dichloromethane (three times), and the combined organic phases were washed with 1 N HCl, saturated $NaHCO_3$, and brine and finally dried over $MgSO_4$. The mixture was filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel, eluting with a 80:20 hexane/ethyl acetate mixture, with a yield of 75−90%.

Analytical Data. 4-(*R*-1′-Methylheptyloxy)benzyl alcohol. $R_f =$ 0.4 (80:20 hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (t, $J = 6.9$ Hz, 3H), 1.10−1.45 (m, 11H), 1.50−1.65 (m, 1H), 1.65−1.80 (m, 1H), 4.28−4.34 (m, 1H), 4.55 (s, 2H), 6.84 (d, $J =$ 8.7 Hz, 2H), 7.23 (d, $J = 8.7$ Hz, 2H). IR (Nujol, NaCl): 3550−3300 (O−H), 1242, 1173, 1120 (C−O) cm^{-1}.

4′-(*S*-3,7-Dimethyloctyloxy)benzyl alcohol. $R_f = 0.4$ (80:20 hexane/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (d, J = 6.4 Hz, 6H), 0.94 (d, $J = 6.8$ Hz, 3H), 1.10−1.45 (m, 6H), 1.50−1.75 (m, 3H), 1.80−1.88 (m, 1H), 3.95−4.05 (m, 2H), 4.60 (s, 2H), 6.90 (d, $J = 8.4$ Hz, 2H), 7.30 (d, $J = 8.4$ Hz, 2H). IR (Nujol, NaCl): 3550−3300 (O−H), 1299, 1243, 1171 (C−O) cm^{-1}.

General Procedure for the Preparation of 4-Alkoxybenzyl Chlorides. Thionyl chloride (3 mL) was added dropwise to a mixture of the corresponding benzyl alcohol (7 mmol) and DMF (5 drops) in dry dichloromethane. The mixture was heated at 60 °C for 1 h under argon. The excess thionyl chloride was removed by distillation under reduced pressure. The resulting slightly yellow oil was used without further purification (quantitative yield).

Analytical Data. 4-(*R*-1′-Methylheptyloxy)benzyl chloride. $R_f =$ 0.7 (10:1 hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (t, $J = 6.9$ Hz, 3H), 1.10−1.45 (m, 11H), 1.50−1.65 (m, 1H), 1.65−1.80 (m, 1H), 4.31−4.36 (m, 1H), 4.52 (s, 2H), 6.82 (d, $J =$ 8.7 Hz, 2H), 7.25 (d, $J = 8.7$ Hz, 2H).

4′-(*S*-3,7-Dimethyloctyloxy)benzyl chloride. $R_f = 0.8$ (10:1 hexane/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (d, J = 6.4 Hz, 6H), 0.96 (d, $J = 6.4$ Hz, 3H), 1.10−1.45 (m, 6H), 1.50−1.75 (m, 3H), 1.81−1.88 (m, 1H), 3.98−4.03 (m, 2H), 4.57 (s, 2H), 6.88 (d, $J = 8.4$ Hz, 2H), 7.30 (d, $J = 8.4$ Hz, 2H).

General Procedure for the Preparation of Methyl 3,4,5-Tris(4-alkoxybenzyloxy)benzoates. To a solution of methyl 3,4,5-trihydroxybenzoate (4 mmol) were added anhydrous K_2CO_3 (24 mmol), KI (4 mmol), and the corresponding 4-alkoxybenzyl chloride (12 mmol) in dry acetone (75 mL). The mixture was heated at 60 °C for 8 h under argon. The reaction mixture was poured into water and extracted into dichloromethane (three times). The combined organic phases were washed with brine and finally dried over $MgSO_4$. The mixture was filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel, eluting with a 90:10 hexane/ethyl acetate mixture, with a yield of 70−80%.

Analytical Data. Methyl 3,4,5-tris[4-(*R*-1′-methylheptyloxy)-benzyloxy]benzoate. $R_f = 0.6$ (85:15 hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (t, $J = 6.7$ Hz, 9H), 1.0−1.45 (m, 33H), 1.50−1.65 (m, 3H), 1.65−1.80 (m, 3H), 3.87 (s, 3H), 4.29−4.38 (m, 3H), 4.97 (s, 2H), 5.02 (s, 4H), 6.73 (d, $J = 8.4$ Hz, 2H), 6.86 (d, $J = 8.1$ Hz, 4H), 7.24 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.1$ Hz, 4H), 7.36 (s, 2H). IR (Nujol, NaCl): 1720 (C═O), 1244, 1175, 1105 (C−O) cm^{-1}.

Methyl 3,4,5-tris[4′-(*S*-3,7-dimethyloctyloxy)benzyloxy]benzoate. $R_f = 0.6$ (85:15 hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (d, $J = 6.6$ Hz, 18H), 0.93 (d, $J = 6.6$ Hz, 9H), 1.10−1.40 (m, 18H), 1.50−1.70 (m, 9H), 1.80−1.85 (m, 3H), 3.87 (s, 3H), 3.99−4.01 (m, 6H), 4.99 (s, 2H), 5.03 (s, 4H), 6.75 (d, J = 8.4 Hz, 2H), 6.88 (d, $J = 8.4$ Hz, 4H), 7.24 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 4H), 7.35 (s, 2H). IR (Nujol, NaCl): 1717 (C═O), 1244, 1222, 1170 (C−O) cm^{-1}.

General Procedure for the Preparation of Benzoic Acids (A1−A5). To a solution of alkyl benzoates (11 mmol) in 1,4-dioxane (75 mL) was added a solution of potassium hydroxide (50%, 5 mL), and the reaction mixture was refluxed for 6 h and then allowed to cool to room temperature. Concentrated HCl was added until an acidic pH was attained. The solvent was removed under reduced pressure. The mixture was extracted into dichloromethane (three times), and the combined organic phases were washed successively with 10% NaOH and brine and dried over $MgSO_4$. The mixture was filtered, and the solvent was removed under reduced pressure. The product was purified by column chromatography on silica gel, eluting with hexane/ethyl acetate mixtures, with a yield of 85−90%.

Analytical Data. 4-(*R*-1′-Methylheptyloxy)benzoic acid (A1). R_f = 0.3 (80:20 hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (t, $J = 6.9$ Hz, 3H, C*H*$_3$), 1.20−1.45 (m, 11H, C*H*$_2$), 1.50−1.65 (m, 1H, C*H*$_2$), 1.68−1.7 5 (m, 1H, C*H*$_2$), 4.44 (q, $J = 6.3$ Hz, 1H, CH$_3$-C*H*O-Ar), 6.89 (d, $J = 8.4$ Hz, 2H, Ar*H*), 8.03 (d, $J =$ 8.4 Hz, 2H, Ar*H*). ^{13}C NMR (400 MHz, $CDCl_3$): δ 14.1, 19.6, 22.6, 25.4, 29.2, 31.7, 36.3, 74.1, 115.1, 121.1, 132.4, 162.9, 172.1. IR (Nujol, NaCl): 3300−2500 (O−H), 1684 (C═O), 1252, 1170 (C−O) cm^{-1}. Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.85; H, 8.78.

3,4-Bis(*R*-1′-methylheptyloxy)benzoic acid (A2). $R_f = 0.5$ (80:20 hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (t, $J = 6.3$ Hz, 6H, C*H*$_3$), 1.20−1.45 (m, 22H, C*H*$_2$), 1.50−1.65 (m, 2H, C*H*$_2$), 1.70−1.82 (m, 2H, C*H*$_2$), 4.32 (q, $J = 6.0$ Hz, 1H, CH$_3$-C*H*O-Ar), 4.41 (q, $J = 6.0$ Hz, 1H, CH$_3$-C*H*O-Ar), 6.89 (d, $J =$ 8.4 Hz, 1H, Ar*H*), 7.61 (s, 1H, Ar*H*), 7.70 (d, $J = 8.4$ Hz, 1H, Ar*H*). ^{13}C NMR (400 MHz, $CDCl_3$): δ 14.1, 19.7, 22.6, 25.4, 29.3, 31.8, 36.5, 75.5, 114.8, 119.3, 121.5, 124.9, 148.3, 154.5, 172.0. IR (Nujol, NaCl): 3300−2500 (O−H), 1682 (C═O), 1267, 1216, 1136 (C−O) cm^{-1}. Anal. Calcd for $C_{23}H_{38}O_4$: C, 72.98; H, 10.12. Found: C, 72.91; H, 9.98.

3,5-Bis(*R*-1′-methylheptyloxy)benzoic acid (A3). $R_f = 0.5$ (80:20 hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (t, $J = 6.6$ Hz, 6H, C*H*$_3$), 1.20−1.45 (m, 22H, C*H*$_2$), 1.50−1.65 (m, 2H, C*H*$_2$), 1.66−1.75 (m, 2H, C*H*$_2$), 4.37 (q, $J = 6.0$ Hz, 2H, CH$_3$-C*H*O-Ar), 6.63 (s, 1H, Ar*H*), 7.18 (s, 2H, Ar*H*). ^{13}C NMR (400 MHz, $CDCl_3$): δ 14.1, 19.6, 22.6, 25.4, 29.2, 31.8, 36.4, 74.2, 109.2, 109.9, 130.9, 159.4, 172.2. IR (Nujol, NaCl): 3300−2500 (O−H), 1691 (C═O), 1265, 1162 (C−O) cm^{-1}. Anal. Calcd for $C_{23}H_{38}O_4$: C, 72.98; H, 10.12. Found: C, 72.79; H, 10.01.

3,4,5-Tris[4-(*R*-1′-methylheptyloxy)benzyloxy]benzoic acid (A4). $R_f = 0.3$ (80:20 hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (t, $J = 6.6$ Hz, 9H, C*H*$_3$), 1.10−1.45 (m, 33H, C*H*$_3$, C*H*$_2$), 1.50−1.65 (m, 3H, C*H*$_2$), 1.65−1.80 (m, 3H, C*H*$_2$), 4.29−4.38 (m, 3H, CH$_3$-C*H*O-Ar), 5.00 (s, 2H, Ar′-C*H*$_2$O-Ar), 5.04

(s, 4H, Ar′-C*H*$_2$O-Ar), 6.74 (d, $J = 8.1$ Hz, 2H, Ar*H*), 6.87 (d, $J = 8.4$ Hz, 4H, Ar*H*), 7.24 (d, $J = 8.1$ Hz, 2H, Ar*H*), 7.32 (d, $J = 8.4$ Hz, 4H, Ar*H*), 7.42 (s, 2H, Ar′*H*). ^{13}C NMR (300 MHz, $CDCl_3$): δ 14.1, 19.7, 22.6, 25.5, 29.3, 31.8, 36.5, 71.1, 73.8, 73.9, 74.7, 109.8, 115.5, 115.8, 123.9, 128.4, 129.3, 130.3, 152.7, 158.1, 158.2. IR (Nujol, NaCl): 3300−2500 (O−H), 1701 (C═O), 1242, 1175, 1130 (C−O) cm^{-1} Anal. Calcd for $C_{52}H_{72}O_8$: C, 75.69; H, 8.80. Found: C, 75.54; H, 8.65.

3,4,5-Tris[4′-(*S*-3,7-dimethyloctyloxy)benzyloxy]benzoic acid (A5). $R_f = 0.2$ (80:20 hexane/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (d, $J = 6.8$ Hz, 18H, C*H*$_3$), 0.95 (d, $J = 6$ Hz, 9H, C*H*$_3$), 1.10−1.40 (m, 18H, C*H*$_2$), 1.50−1.70 (m, 9H, C*H*, C*H*$_2$), 1.80−1.86 (m, 3H, C*H*), 3.94−4.02 (m, 6H, CH$_2$-C*H*$_2$O-Ar), 5.03 (s, 2H, Ar′-C*H*$_2$O-Ar), 5.06 (s, 4H, Ar′-C*H*$_2$O-Ar), 6.77 (d, $J = 8$ Hz, 2H, Ar*H*), 6.90 (d, $J = 8.4$ Hz, 4H, Ar*H*), 7.26 (s, 2H, Ar*H*), 7.34 (d, $J = 8$ Hz, 4H, Ar*H*), 7.42 (s, 2H, Ar′*H*). ^{13}C NMR (300 MHz, $CDCl_3$): δ 19.7, 22.5, 22.6, 22.7, 22.9, 24.7, 28.0, 29.9, 36.2, 37.3, 37.5, 39.2, 39.4, 66.3, 66.4, 71.1, 74.7, 109.7, 114.1, 114.5, 125.0, 128.5, 129.3, 129.4, 130.3, 152.7, 159.1. IR (Nujol, NaCl): 3300−2500 (O−H), 1690 (C═O), 1247, 1172, 1109 (C−O) cm^{-1}. Anal. Calcd for $C_{58}H_{84}O_8$: C, 76.61; H, 9.31. Found: C, 76.45; H, 9.25.

Preparation of Hydrogen-Bonded Complexes. Equimolar mixtures of the triazines and the chiral benzoic acid derivatives were obtained by mixing a THF solution of the appropriate amount of each component and evaporating the solvent by stirring at room temperature. The mixtures, once heated to their isotropic states, were used for further experiments.

Characterization. Thermal properties were examined by polarizing optical microscopy (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 calorimeters 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 ($\Phi = 1$ mm) and heated when necessary with a variable-temperature attachment. The diffraction patterns were collected on photographic films. NMR experiments were performed on a Varian Unity-300 MHz and a Bruker Avance spectrometer at 400 MHz. IR spectra were obtained with a Nicolet Avatar 380 spectrophotometer. Optical absorption measurements were taken using an ATI Unicam UV4 spectrophotometer. CD spectra were recorded in a Jasco J-710 instrument at room temperature and a speed scan of 200 nm/min. In some cases, high-temperature CD spectra were recorded.

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 have highlighted the importance of effective space filling by a sufficient number of peripheral tails for the appearance of columnar mesophases. In addition, a strict steric compromise between the number of tails in the triazine and the size of the acid partner promotes a well-defined hexagonal columnar arrangement of the complexes. This high degree of organization accounts for the large enthalpy values associated with the transitions involving these mesophases. Moreover, chirality transfer from the benzoic acid to the liquid crystalline organization occurs for the H-bonded complexes that show this well-defined columnar mesophase, as demonstrated by circular dichroism in the mesophase. This means that the stacking of the supramolecules should be wound in a helical manner, the sense of which is dictated by the nature of the stereogenic center. However, the observed chirooptical properties evolve differently depending on the nature of the particular complex. In particular, the complexes with the 3,4,5-tribenzyloxybenzoic acids A4 and A5, i.e., T2−A4 and T2−A5, exhibit a chiral supramolecular organization that is present over an extended time period.

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