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Supramolecular Liquid Crystals. Self-Assembly of a Trimeric Supramolecular Disk and Its Self-Organization into a Columnar Discotic Mesophase

Mauricio Suárez,[†,‡] Jean-Marie Lehn,*[,†] Steven C. Zimmerman,*[,‡] Antoine Skoulios,[§] and Benoit Heinrich[§]

Contribution from the Laboratoire de Chimie Supramoléculaire, ISIS, Université Louis Pasteur, 4 rue Blaise Pascal, 67000 Strasbourg, France, Department of Chemistry, University of Illinois, Urbana, Illinois 61801, and Groupe des Matériaux Organiques, Institut de Physique et Chimie des Matériaux de Strasbourg, 23 rue du Loess, 67037 Strasbourg, France

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Abstract: 6,7-Bis(alkyloxy)-2,3-dihydrophthalazine-1,4-diones self-assemble into lactim−lactam trimeric disks in solution as demonstrated by SEC and NMR. With suitable substituents, as in Phthal**8**, Phthal**12**, and Phthal**16**, these disks self-organize into a thermotropic, columnar, discotic phase. The disubstituted phthalhydrazide unit thus represents a general motif for the recognition-induced generation of supramolecular, discotic liquid crystals by self-assembly.

Introduction

Self-assembly and self-organization[1,2] represent powerful means for the spontaneous and programmed generation of nanoscale architectures, on the basis of the instructions stored in the building components and of the interactive algorithms that bind these components together.[2] They may thus provide direct access to supramolecular materials of well-defined structure via processes bypassing nanofabrication techniques. Self-assembly and self-organization involve the formation of organized, discrete assemblies as well as the collective behavior of ensembles such as molecular crystals, liquid crystals, micelles, phase-separated polymers, and colloids.[3]

Discrete aggregates of varied and intriguing structures have been generated, such as boxes,[4] squares,[5] figure eights,[6] helicates,[7] circular helicates,[8] catenanes,[9] capsules,[10] grids,[11] dendritic species,[12] and many others. Their increasing complexity can be characterized inter alia by the number of components per aggregate (six ligands plus nine metals in a 3 × 3 grid[13] and 10 molecules in a triple-decker aggregate[14]) and high molecular weights (e.g., 34 000 for a dendritic hexamer[15] comparable in weight to small proteins).

One strategy to obtain ordered ensembles of even higher dimensions is by self-organizing these discrete aggregates into an extended lattice. Depending on the fluidity of the self-organized system one may distinguish two cases: hard self-organization and soft self-organization.[16] An example of hard self-organized matter is a crystal in which there is little or no diffusion, while soft self-organized matter is represented by a liquid crystal in which there is mobility in at least one direction. These definitions, although arbitrary since they depend on kinetic properties, are nonetheless useful because hard and soft self-organization have different features which make them better suited for different purposes. In hard self-organization a given structure does not necessarily represent the energy minimum of the system. Thus, crystal engineering has to include the kinetics of nucleation as an important consideration. This

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[†] Université Louis Pasteur.

[‡] University of Illinois.

[§] Institut de Physique et Chimie des Matériaux de Strasbourg.

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feature can also be used to an advantage when one is able to obtain a thermodynamically unfavorable polymorph by seeding. In soft self-organized matter the structure is more or less fluid and is able to sample the energy surface and find its minimum. For example, liquid crystals are sensitive to foreign stimuli (magnetic, electric, or chemical)[3b] to which they respond by finding a new configuration of minimum energy.

We have been interested in the generation of supramolecular liquid crystalline polymers from complementary components, which amounts to the amplification of molecular recognition processes and their expression on the macroscopic scale.[17,18] The control of molecular recognition events through an external stimulus can be used for developing switches and sensors.[19] An interesting approach for the design of such smart materials would be to make use of a system capable of changing its molecular recognition pattern and amplify this change via self-assembly and self-organization. A change in molecular recognition pattern with subsequent amplification is exemplified by DNA mutation. Watson and Crick postulated that tautomerization could be a major cause for misincorporation of a nucleotide into DNA,[20] since it causes a drastic modification in the hydrogen-bonding pattern presented for base pairing. A change in the molecular recognition event is expressed (amplified) as a change in the protein translated in the next generation. An Aufbau approach (molecule-discrete aggregate-ordered phase) to nanoscale structures is illustrated by the self-organization of deoxyguanosine derivatives and their related folic acid salts which associate in water to form tetramers that stack creating a lyotropic, hexagonal phase.[21] Another example[22] is provided by the use of pyridone association (a tested motive in self-assembly)[23] to form a dimeric disk that self-organizes into a thermotropic, columnar liquid crystal. It thus appears that the design of molecules capable of tautomerization, self-assembly, and subsequent self-organization might prove useful for the design of smart materials.

With the idea of combining in a system the capabilities to tautomerize, self-assemble, and self-organize, we studied the properties of 6,7-bis(alkyloxy)-2,3-dihydrophthalazine-1,4-diones (subsequently referred to as phthalhydrazides). Phthalhydrazides can, in principle, exist as an equilibrium of three tautomeric forms: the lactam−lactam (A), the lactim−lactam (B), and the lactim−lactim (C) forms (Figure 1). Spectroscopic studies of the parent phthalhydrazide and its methyl tropic isomers indicate that the lactim−lactam form is the most stable species in ethanol solution.[24] This observation agrees with experimental and theoretical data on the simpler maleic hydrazide. Basicity measurements of maleic hydrazide in water are consistent with the lactim−lactam being the preferred form. The lactam−lactam form has an important contribution, while the lactim−lactim fraction is negligible.[25] Gas-phase calculations predict the three structures to be planar and the energy of the tautomers to follow the order lactim−lactam > lactam−lactam > lactim−lactim.[26] The fact that the lactim−lactam form is more stable can be attributed to the repulsion in the other two tautomers involving adjacent nitrogen atoms of the same hybridization type.[27] Calculations also show solvation to be very important in determining the tautomeric ratio.[25]

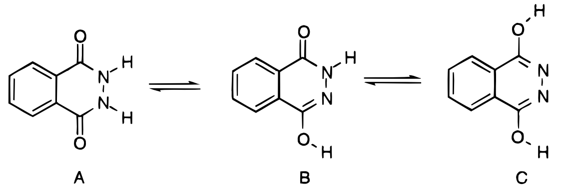
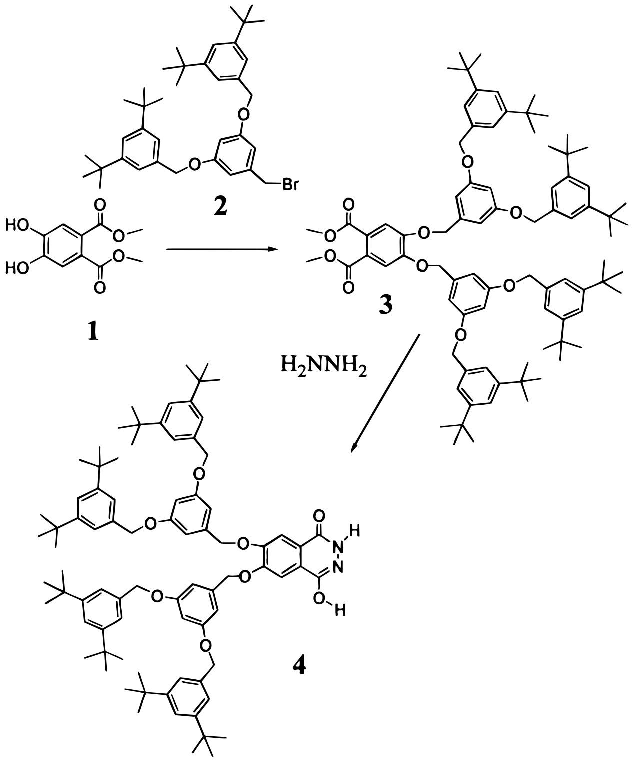


Figure 1. Phthalhydrazide tautomerization: (A) lactam−lactam; (B) lactim−lactam; (C) lactim−lactim tautomer.

Scheme 1. Synthesis of Compound **4** (The Lactim−Lactam Is Represented)



Herein we provide an example of a tautomeric system that can self-assemble into disks and self-organize into a thermo-

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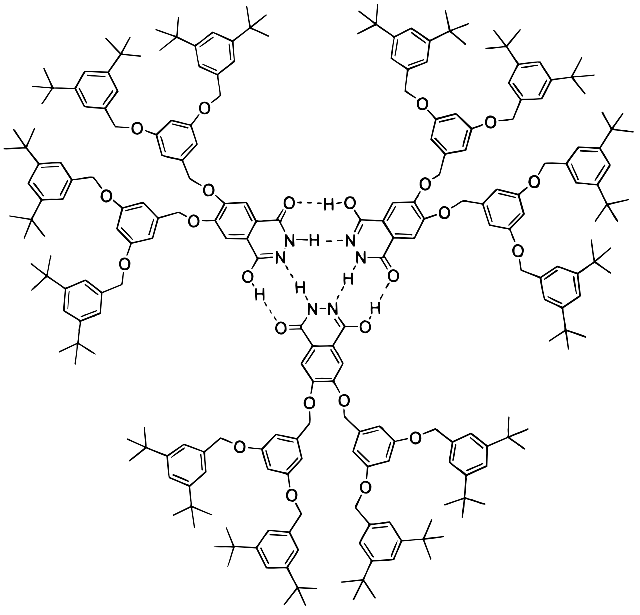
tropic, columnar, discotic liquid crystal. In this way the lactim−lactam hydrogen-bonded trimer joins established systems[28] in the effort to control supramolecular architecture.

Results and Discussion

(i) Self-Assembly in Solution. To study the self-assembly of phthalhydrazides in nonpolar media, compound **4** was synthesized (Scheme 1). The branched substituents[29] were incorporated to ensure high solubility in solvents such as chloroform and toluene. The self-assembly in solution was studied by NMR and size exclusion chromatography (SEC).

Characterization of the Lactim−Lactam Trimeric Disk by NMR Spectroscopy. The ^{1}H NMR signals at low fields (12−15 ppm) are good reporters of the environment around hydrogen-bonded protons. They have been used successfully in determining association constants,[30] aggregation state,[31] and symmetry of hydrogen-bonded aggregates.[32] The ^{1}H NMR spectrum of **4** in chloroform-*d* shows two peaks in this region (14.2 and 13.5 ppm). Two signals for hydrogen-bonded protons and only one signal for the aromatic protons in the phthalhydrazide core are consistent with a lactim−lactam trimeric disk **4T** in which the N−H−N protons are different from the O−H−O protons and the exchange is slow on the NMR time scale (Figure 2). A similar type of hydrogen-bonded motif as the one postulated is found in the crystal structure of Luminol (Figure 3).[33]



4T

Figure 2. Self-assembly of the phthalhydrazide lactim−lactam cyclic trimer of compound **4**.

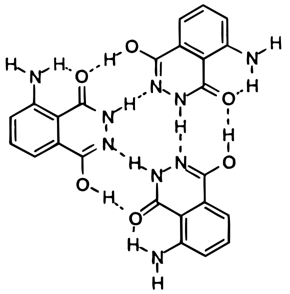


Figure 3. Lactim−lactam trimer found in the X-ray structure of luminol.[32]

Dilution Studies. Dilution over 3 orders of magnitude (100 to 0.1 mM) of a solution of **4** in chloroform-*d* does not change the chemical shift of the low-field signals. Dilution studies of the lactam−lactam dimer **5** and trimer **6**[34] showed that these shifts are dependent on dilution for the dimer **5**, whereas this is not the case for the trimer **6**. The downfield chemical shifts observed for the N−H and O−H protons of **4** and their concentration independence is consistent with the formation of a highly stable cyclic trimer similar to that found with **6**. The high stability of this species may involve positive cooperativity.

Competitive Solvents. Adding a polar solvent (i.e., DMSO) decreased the stability of the aggregate. At a concentration of 122 mM in 9:1 chloroform-*d*/DMSO-d_6 one observes a broad peak at 12.0 ppm. Upon dilution the peak moves upfield approaching 10.5 ppm at infinite dilution. As expected, adding a solvent that competes for the hydrogen-bonding sites decreases

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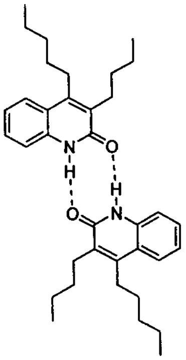

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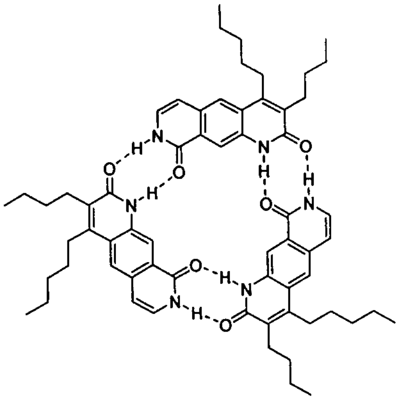

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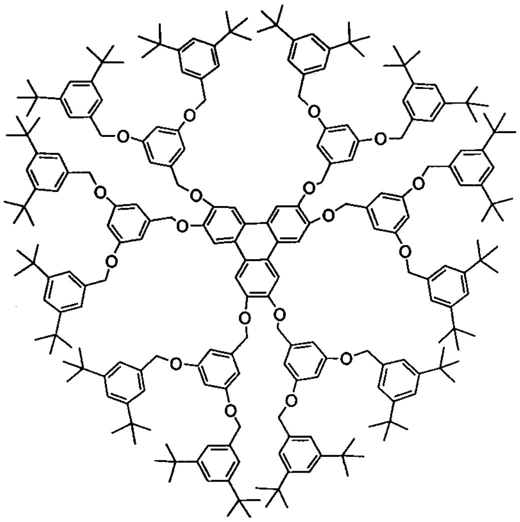

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the thermodynamic and kinetic stability of the aggregate. The peak observed is a weighted average of the species present due to aggregation and tautomerization. This equilibrium is fast relative to the NMR time scale.

Variable-Temperature NMR. Chemical exchange in the phthalhydrazide trimer leads to the coalescence of the high-field signals in a particular solvent. In toluene-d_8 (0.02 M) the signals coalesce at 85 °C (Figure 4). A rate constant (k_n) of 6 $\times$ 10^2 s^{-1} and an activation energy ($\Delta G^{\ddagger}$) of 16.5 kcal/mol can be estimated for the process (at the temperature of coalescence) using standard procedures.[35]

In contrast to the tris(melamine−isocyanuric acid) aggregates, where there are two possible mechanisms for exchange, rotation or dissociation of an isocyanuric acid unit,[36] in the present system, rotation creates a mismatch in hydrogen bonding and is not expected to contribute to exchange. On the other hand, the dissociated species is expected to tautomerize readily (Figure 5). Tautomerization is probably responsible for the signal not coalescing to the average observed under slow exchange. Assuming tautomerization to be fast compared to dissociation,[37] one can assign the values calculated to the limiting step of dissociation of a monomer from the trimer.

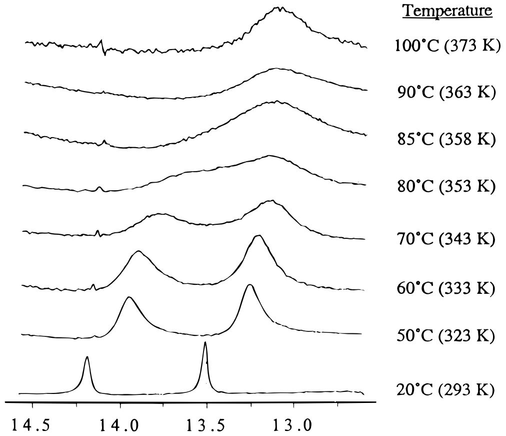

Figure 4. Variable-temperature ^{1}H NMR spectra of a nominally 0.020 M solution of phthalhydrazide **4** in toluene at 400 MHz.

Table 1. Gel Permeation Chromatography (GPC) Data for Phthalhydrazide **4** and Two Unimolecular Controls (Toluene, 0.5 mL/min)

compd	MW	retention time (min)
4 (phthalhydrazide)	1248 (as a trimer, 3743)	16.06
7 (unimolecular size standard for trimer)	3485	16.17
3 (unimolecular size standard for monomer)	1278	17.71

Characterization of the Lactim−Lactam Trimeric Disk by Size Exclusion Chromatography (SEC). SEC is a size separation technique that is frequently used in polymer science to determine the molecular weight distribution of a polymer.[38] It has also been used successfully in the study of supramolecular assemblies.[39]

The SEC trace of compound **4** in toluene showed a sharp peak with an estimated molecular weight (polystyrene standards) of 3029. This corresponds to 2.4 molecules per aggregate. Due to the fact that SEC is not sensitive to molecular weight but to the hydrodynamic volume of a molecule, it was desirable to have a monomolecular analogue of the trimer as a more appropriate size standard. Modeling indicated that molecule **7** would have a hydrodynamic volume similar to that of the cyclic trimer of the lactim−lactam **4**. This molecule was synthesized and showed a SEC retention time nearly identical to that of the trimer of **4** (Table 1).

In conclusion, all available data point to the self-assembly of the phthalhydrazide **4** in solution to a supramolecular cyclic trimer of general structure **T**.

(ii) Self-Organization in the Mesophase. The mesomorphic properties of three 4,5-bis(alkyloxy)phthalhydrazides Phthal**8**, Phthal**12**, and Phthal**16** (Scheme 2) were studied by differential scanning calorimetry (DSC), polarizing optical microscopy, dilatometry, and X-ray diffraction.

The DSC thermograms registered upon heating and subsequent cooling between 25 and 280 °C displayed crystal to mesophase transitions at around 100 °C and mesophase to isotropic liquid transitions above 200 °C (Table 2). The mesophase to crystal transitions showed considerable supercooling.

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[35] (a) Günther, H. *NMR Spectroscopy*, 2nd ed.; John Wiley and Sons: New York, 1992. (b) The rate constant can be calculated by the following equation: $k_n = \pi(\delta\nu)/2^{1/2}$, where $(\delta\nu)$ corresponds to the chemical shift difference (in hertz) of the signals exchanging. A fast evaluation of the energy barrier at the temperaure of coalescence can be obtained with equation: $(\Delta G^{\ddagger}) = RT_c[22.96 + \ln(T_c/(\delta\nu))]$ (J mol^{-1}), where T_c is the temperature of coalescence (K).

[36] Simanek, E. E.; Waazer, M. I. M.; Mathias, J. P.; Whitesides, G. M. *J. Org. Chem.* **1994**, *59*, 4904.

[37] 2-Pyridone−2-hydroxypyridine tautomerization is too rapid to be measured by NMR (THF-d_8; 0.1 M) even at −120 °C.[23b]

[38] Barth, H. G.; Boyes, B. E.; Jackson, C. *Anal. Chem.* **1996**, *68*, 445R.

[39] Mathias, J. P.; Seto, C. T.; Simanek, E. E. Whitesides, G. M. *J. Am. Chem. Soc.* **1994**, *116*, 1725. See also reference 14.

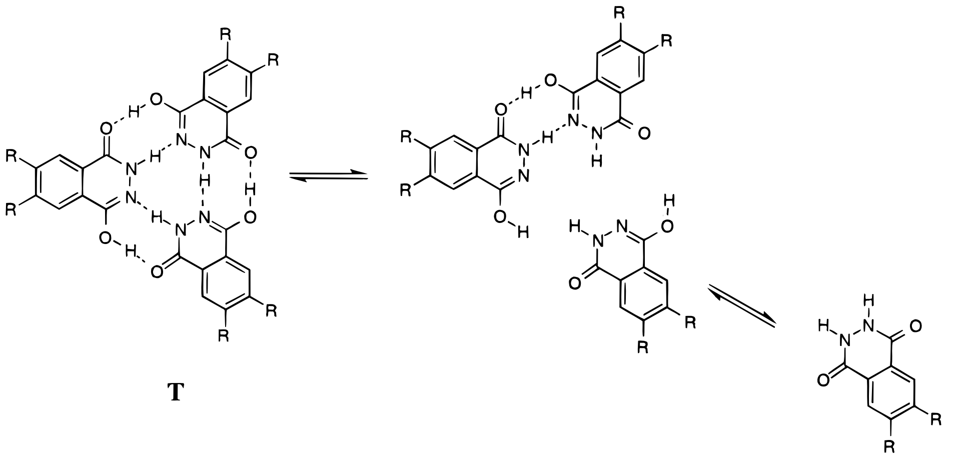


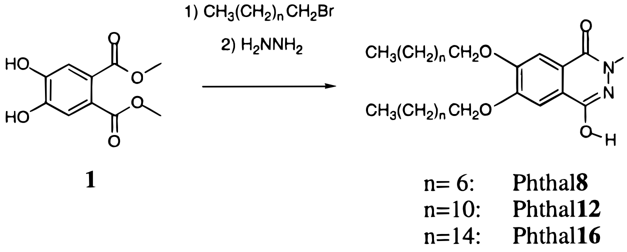
Figure 5. Dissociation of the cyclic trimer **T** and tautomerization of the dissociated species.

Table 2. Phase Behavior of 4,5-Dialkyloxyphthalhydrazides[a]

compd	behavior
Phthal**8**	$K^b \underset{<40\ °\mathrm{C}}{\overset{100\ °\mathrm{C}}{\rightleftharpoons}} \mathrm{Col}_\mathrm{H} \underset{267\ °\mathrm{C}\ (7.6\ \mathrm{J/g})}{\overset{271\ °\mathrm{C}\ (7.8\ \mathrm{J/g})}{\rightleftharpoons}} \mathrm{I}$
Phthal**12**	$K^b \underset{<40\ °\mathrm{C}}{\overset{105\ °\mathrm{C}}{\rightleftharpoons}} \mathrm{Col}_\mathrm{H} \underset{246.5\ °\mathrm{C}\ (5.3\ \mathrm{J/g})}{\overset{250\ °\mathrm{C}\ (5.1\ \mathrm{J/g})}{\rightleftharpoons}} \mathrm{I}$
Phthal**16**	$K^b \underset{<40\ °\mathrm{C}}{\overset{104\ °\mathrm{C}}{\rightleftharpoons}} \mathrm{Col}_\mathrm{R} \overset{c}{\rightleftharpoons} \mathrm{Col}_\mathrm{H} \underset{227.7\ °\mathrm{C}\ (3.3\ \mathrm{J/g})}{\overset{227.9\ °\mathrm{C}\ (4.3\ \mathrm{J/g})}{\rightleftharpoons}} \mathrm{I}$

[a] Transition temperatures (°C) and enthalpies (in parentheses, in J/g) were determined by DSC (10 °C/min). K: crystal. $\mathrm{Col_H}$: columnar hexagonal. $\mathrm{Col_R}$: columnar rectangular. I: isotropic. [b] Crystalline polymorphism. [c] The $\mathrm{Col_H}$ to $\mathrm{Col_R}$ transition was not observed by DSC.

Scheme 2. Synthesis of 4,5-Bis(alkyloxy)phthalhydrazides



The optical textures observed upon cooling from the isotropic melt showing birefringent areas in the form of "petals" coalescing to produce broken-fan-shaped units (Figure 6, left), dark areas of uniform extinction indicating optical uniaxiality, and a tendency of the material to orient its optical axis normal to the surface of the glass slide were interpreted as an indication of columnar mesophases of hexagonal symmetry ($\mathrm{Col_H}$).[40] In the case of Phthal**16**, a fingerprint texture that developed up to 200 °C was taken as an indication of an additional, nonhexagonal columnar ($\mathrm{Col_R}$) mesophase (Figure 6; right).[40]

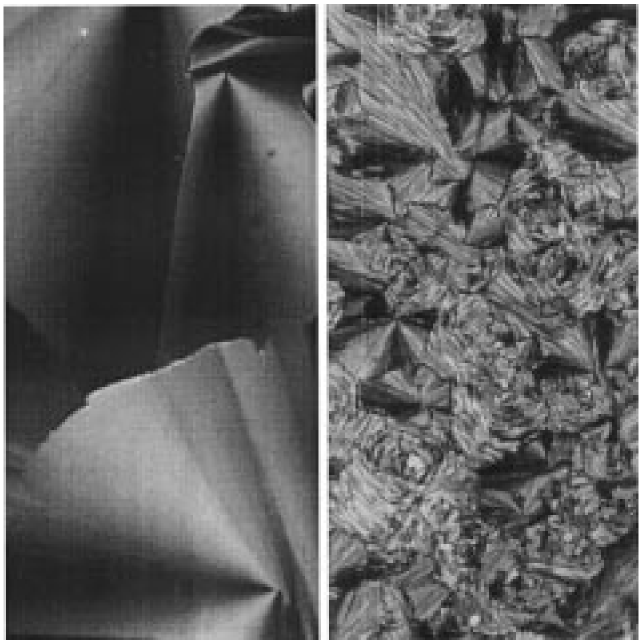


Figure 6. (left) Optical texture of the mesophase of Phthal**8** at 260 °C. (right) Optical texture of the mesophase of Phthal**16** at 200 °C.

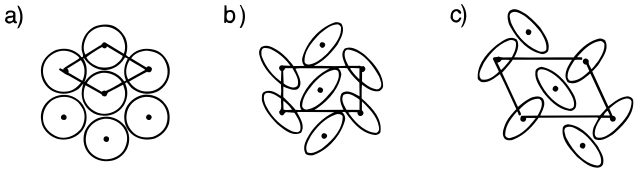


Figure 7. Examples of two-dimensional lattice symmetries of columnar phases: (a) hexagonal; (b) rectangular (*p*2*gg*); (c) oblique.[39]

The structures of the $\mathrm{Col_H}$ and $\mathrm{Col_R}$ columnar mesophases were established by X-ray diffraction (Figure 7). The hexagonal symmetry of $\mathrm{Col_H}$ was unambiguously demonstrated for Phthal**12** and Phthal**16** by the presence in the diffraction patterns of a diffuse ring at ~4.5 Å, related to a disordered conformation of the aliphatic chains; of a narrower and weaker diffuse ring at ~3.45 Å, related to stacking correlations between the aromatic cores; and of three sharp small-angle reflections with reciprocal Bragg spacings in the ratio $1{:}\sqrt{3}{:}\sqrt{4}$, characteristic of a two-dimensional hexagonal crystal lattice.[41] The $\mathrm{Col_H}$ structure consists of the stacking of the aromatic cores of the molecules in columns surrounded by the disordered aliphatic chains and packed laterally in a hexagonal fashion. For Phthal**8** the $\sqrt{3}$ and $\sqrt{4}$ reflections were hardly visible, simply because the diameter of the aromatic cores happens in this particular case to be close to the thickness of the aliphatic crowns. Declining slowly with increasing temperature ($\delta D/\delta T = -8.1 \times 10^{-3}$ Å deg^{-1}), the lattice parameters measured at 200 °C were $D =$

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(40) (a) Destrade, C.; Gasparoux, H.; Foucher, P.; Nguyen, H. T.; Malthête, J.; Jacques, J. *J. Chim. Phys.* **1983**, *80*, 137. (b) Destrade, C.; Foucher, P.; Gasparoux, H.; Nguyen H. T.; Levelut, A. M.; Malthête, J. *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 121.

(41) (a) Abied, H.; Guillon, D.; Skoulios, A.; Weber, P.; Giroud-Godquin, A. M.; Marchon, J. C. *Liq. Cryst.* **1987**, *2*, 269. (b) Chandrasekhar, S.; Ranganath, G. S. *Rep. Prog. Phys.* **1990**, *53*, 57. (c) Weber, P.; Guillon, D.; Skoulios, A. *Liq. Cryst.* **1991**, *9*, 369. (d) Zheng, H.; Lai, C. K.; Swager, T. M. *Chem. Mater.* **1994**, *6*, 101.

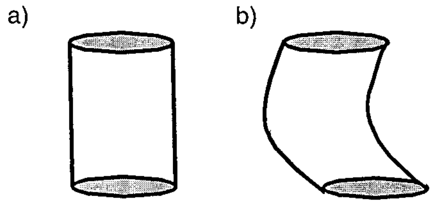

Figure 8. (a) Rectilinear column. (b) Undulating column.

30.8, 34.7, and 38.9 Å for Phthal**8**, Phthal**12**, and Phthal**16**, respectively.

The rectangular symmetry of Col$_R$ was proved by the presence in the diffraction patterns of the same diffuse rings at ~4.5 and ~3.45 Å and of a series of five sharp reflections in the small-angle region, indexed as (11), (20), (12), (22), and (40) reflections from a two-dimensional rectangular lattice. The lattice parameters were varying slowly with temperature from $a = 69.9$ and $b = 48.8$ Å at 110 °C to $a = 68.3$ and $b = 51.0$ Å at 180 °C. The Miller indices of the reflections observed and the size of the unit cell compared to the molecular dimensions suggest that the columns are arranged with the *p*2*gg* space-group symmetry.[42]

To describe the Col$_H$ phase more thoroughly, it is useful to calculate the stacking period h of the discotic supermolecules inside the columns. With the reasonable assumption that the phthalhydrazide trimeric disk is responsible for the mesophase behavior, we can calculate the parameter h with the following formula: $\sqrt{3}D^2h/2 = NV$, where N is the number of molecules per supermolecule, D is the unit cell parameter obtained by X-ray diffraction, and V is the molecular volume obtained from dilatometry.[43] The stacking period (h) at 200 °C is calculated to be 2.66, 2.77, and 2.78 Å for Phthal**8**, Phthal**12**, and Phthal**16**, respectively. The fact that these values are significantly smaller than the mean stacking spacing h_0 of the aromatic cores determined from the wide-angle X-ray ring (respectively 3.43, 3.46, and 3.47 Å) suggests that, instead of being rectilinear, the columns are strongly undulating to cover a wider area in the lattice plane, the flat trimers being shifted outward and tilted away from the columnar axis (Figure 8). The presence of such undulations is supported by the temperature growth of h ($\Delta h = 0.35$ Å for $\Delta T = 100$ °C), which goes well beyond the temperature growth of h_0 ($\Delta h_o = 0.07$ Å), indicating that the amplitude of the columnar undulations decreases upon heating due to a stretching of the columns as a result of a thermal conformational expansion of the aliphatic chains.

(iii) Columnar Mesophase from a Mixture. To study the feasibility of having a manifestation of a tautomeric switch in liquid crystalline behavior, we studied mixtures of phthalhydrazides and compounds that we expected would induce a lactim–lactam to lactam–lactam transformation. For example, a 1:1 mixture of Phthal**8** and compound **8** shows a columnar hexagonal phase above 90 °C. In contrast to the columns of pure Phthal**8**, the columns in the mixture are rectilinear with the disks normal to the axis. It is difficult to determine with certainty if the new columnar phase is due to a lactam–lactam tetrameric aggregate (pathway A in Figure 9) or if compound **8** inserts into the columnar framework of pure Phthal**8** (pathway B in Figure 9), modifying its supramolecular organization.

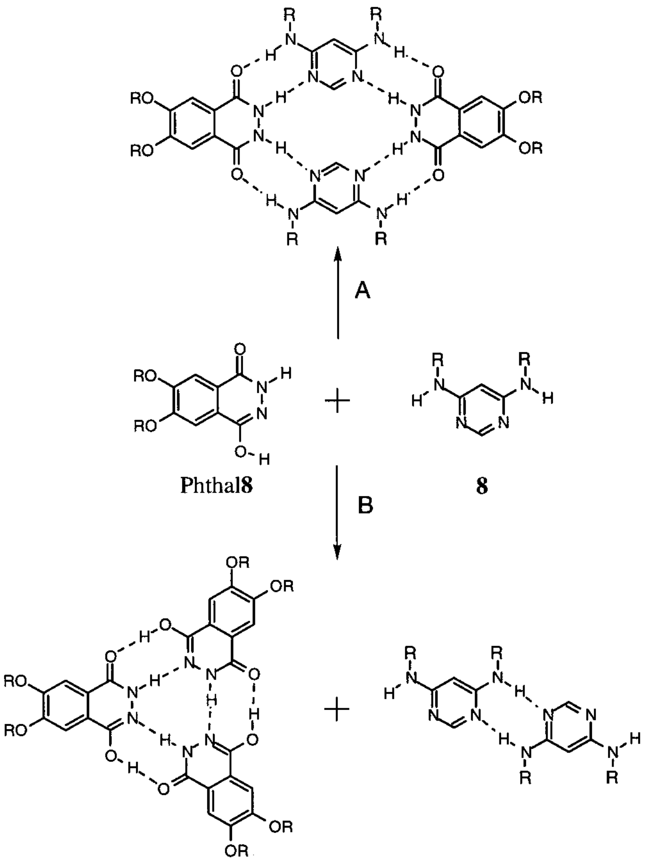

Figure 9. Generation of a columnar mesophase from a mixture of Phthal**8** and compound **8** (R = octyl).

It would be desirable to have a high contrast between the two different phases created by two different tautomeric forms (a discotic to a smectic change, for example). This has not been attained so far.[44]

Conclusions

NMR and SEC analysis are consistent with the self-assembly of phthalhydrazides into lactim–lactam trimeric disks of high stability. With suitable substituents these trimers can stack in the bulk to form thermotropic columnar phases.

Columnar discotic phases have received much attention in the area of one-dimensional transport of energy, charge, or ions.[45] The lactim–lactam trimeric entities are self-assembled disks generating discotic phases that may join established systems based on preformed disks (i.e., triphenylenes[46] and phthalocyanines[47]) in helping to elucidate of the relationship between supramolecular architecture and transport properties.

The ease in which the heterocyclic molecular recognition pattern is synthesized from *o*-phthalate diesters makes phthalhydrazides ideal candidates for their incorporation into supramolecular polymeric systems (i.e., for the synthesis of polymeric hydrogen-bonded discotic liquid crystals) and into

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[42] *International Tables for Crystallography*, 4th ed.; Kluwer Academic Publishers: London, 1995.

[43] The molecular volume of Phthal**8** in the columnar state was measured by dilatometry as a function of temperature: V (Å^3) = 631.94$_{\pm 0.02}$ + 0.4448$_{\pm 0.0002}T$ (°C). The molecular volumes of Phthal**12** and Phthal**16** in the columnar state were deduced from that of Phthal**8** by adding the volume of the appropriate number of methylene groups: VCH2 (Å^3) = 26.56 + 0.0202T (°C). See: Guillon, D.; Skoulios, A.; Benattar, J. *J. Phys.* **1986**, *47*, 133.

[44] An example of a lactam–lactam supermolecule in the phthalhydrazide system is found in the crystal structure of 6,7-dimethoxy-2,3-dihydrophthalazine-1,4-dione. The structure consists of infinite lactam–lactam hydrogen-bonded ribbons. Suárez, M.; Lehn, J.-M.; de Cian, A.; Fischer, J. Unpublished result.

[45] (a) See ref 2, Chapter 8. (b) van Nostrum, C. F.; Nolte, R. J. M. *Chem. Commun.* **1996**, 2385.

[46] Etchegoin, P. *Phys. Rev. A* **1997,** *56* (1, Part B), 538.

[47] Hanack, M.; Lang, M. *Adv. Mater.* **1994**, *6*, 819.

complex hydrogen bonded entities of interest as supramolecular materials.[1a,2,17,18]

The ability of the phthalhydrazide to tautomerize might also be harnessed for the design of adaptive supermolecules that respond to their environment.

Experimental Section

General. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity 400. SEC analysis was performed with a 7.8 × 300 mm styrene−divinylbenzene copolymer column (Waters Styragel HR 3; MW range 500−30 000) coupled with a Waters differential refractometer and a PD200 dual-angle laser light scattering detector or a Hitachi L-4000H UV detector by using a Hitachi L-6000 pump. DSC analysis was performed on a Perkin-Elmer DSC Series 7. Polarizing microscopy observations were performed on a Nikon Optiphot-2 microscope equipped with a Mettler hot-stage and a 10× objective. X-ray diffraction analysis was performed with a Guinier-type focusing camera equipped with an INEL CPS-120 curved position-sensitive detector and a modified INSTEC hot stage. Molar volumes were measured as a function of temperature with a homemade computer-driven dilatometer. Elemental analysis and DSC analysis were performed by the microanalysis laboratory of the University of Illinois. Melting points were measured on a Thomas-Hoover melting point apparatus and are uncorrected.

All solvents and reagents were obtained from commercial sources and used without further purification, unless otherwise noted. The following compounds were prepared by literature procedures and shown to have the expected physical and spectral properties: 4,5-dihydroxyphthalic acid dimethyl ester (**1**),[48] 3,5-bis((3,5-di-*tert*-butylphenyl)methoxy)benzyl bromide (**2**),[49] and 2,3,6,7,10,11-hexahydroxytriphenylene.[50]

General Procedure for the Dialkylation of 1. Preparation of 4,5-(diG$_1$)Phthalic Acid Dimethyl Ester (3). A 50-mL round-bottomed flask equipped with a magnetic stir bar, reflux condenser, addition funnel, and N_2 inlet was charged with 0.050 g (0.22 mmol) of 4,5-dihydroxyphthalic acid dimethyl ester (**1**), 0.401 g of 3,5-bis((3,5-di-*tert*-butylphenyl)methoxy)benzyl bromide (**2**) (0.66 mmol), 0.213 g of K_2CO_3 (1.54 mmol), 0.045 g of 18-crown-6 (0.17 mmol), 0.039 g of NaI (0.026 mmol), and 25 mL of 2-butanone. The reaction mixture was purged (via a syringe) with N_2 for 1 h and then heated at reflux for 48 h. After this time, the reaction was cooled, the solvent evaporated in vacuo, and the residue dissolved with 100 mL of methylene chloride. The organic phase was washed with aqueous saturated solution of NH_4Cl (25 mL), water (25 mL), and brine (25 mL). The organic layer was dried over $MgSO_{4\,(anh)}$, concentrated, and purified by flash column chromatography on silica (hexanes−ethyl acetate, 9:1) to afford 0.18 g (64%) of **3** as a white solid: mp =121−123 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 7.45−7.40 (m, 6H), 7.30 (d, 8H; J = 17 Hz), 6.87 (d, 4H; J = 2.2 Hz), 6.60 (t, 2H, J = 2.2 Hz), 5.27 (s, 4H), 4.97 (s, 8H), 3.81 (s, 6H), 1.28 (s, 72H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 167.7, 160.4, 150.9, 150.4, 138.4, 135.6, 125.5, 122.3, 122.2, 114.1, 105.9, 101.7, 71.0, 70.9, 52.5, 34.8, 31.4. Anal. Calcd for $C_{84}H_{110}O_{10}$: C, 78.83; H, 8.66. Found: C, 78.73; H, 8.61.

General Procedure for the Synthesis of Phthalhydrazides from Dimethyl Esters. Preparation of 6,7-(diG$_1$)-2,3-Dihydrophthalazine-1,4-dione (4). A screw vial was charged with 0.050 g of compound **3** (0.039 mmol), 250 μL of anhydrous hydrazine, and 2 mL of dioxane. The vial was sealed and heated at 90 °C for 48 h. The reaction mixture was cooled to room temperature, the solvent evaporated in vacuo, and the residue purified via column chromatography on silica (methylene chloride−ethyl acetate, 8:2) to afford 0.033 g (67%) of **4** as a solid: mp = 132−134 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 13.76 (s, 1H), 12.44 (s, 1H), 7.72 (s, 2H), 7.35 (s, 4H), 7.22 (d, 8H; J = 1.5 Hz), 6.79 (d, 4H, J = 1.8 Hz); 6.57 (s, 2H), 5.30 (s, 4H), 4.91(s, 8H), 1.28 (s, 72H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 160.4, 157.5, 150.3, 150.9, 138.0, 135.7, 122.3, 122.2, 122.0, 107.5, 105.8, 101.9, 71.0, 70.9, 34.8, 31.4. MALDI calcd for $C_{82}H_{106}N_2O_8$ 1270.74 (M + Na) and 1286.86 (M + K), found 1271 and 1287, respectively. Anal. Calcd for $C_{82}H_{106}N_2O_8$: C, 78.93; H, 8.56; N, 2.25. Found: C, 78.76; H, 8.56, N, 2.31.

2,3,6,7,10,11-Hexa(G$_1$)triphenylene Dendrimer 7. A 50-mL round-bottomed flask equipped with a magnetic stir bar, reflux condenser, and N_2 inlet was charged with 0.050 g (0.15 mmol) of 2,3,6,7,10,11-hexahydroxytriphenylene, 1.032 g (1.69 mmol) of 3,5-bis((3,5-di-*tert*-butylphenyl)methoxy)benzyl bromide (**2**), 0.435 g of K_2CO_3 (3.15 mmol), 0.095 g of 18 crown-6 (0.36 mmol), 0.080 g of NaI (0.54 mmol), and 30 mL of 2-butanone. The reaction mixture was refluxed for 48 h, after which the reaction was cooled, the solvent evaporated in vacuo, and the residue dissolved with 100 mL of methylene chloride. The organic phase was washed with water (50 mL), NH_4Cl (50 mL), water (50 mL), and brine (50 mL). It was then dried over $MgSO_{4(anh)}$ and concentrated. The residue was purified via column chromatography (hexanes−ethyl acetate, 9:1) and chromatotron (hexanes−ethyl acetate: gradient) to afford 0.400 g (77%) of **7** as a solid: mp = 105 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.88 (s, 6H), 7.34 (t, 12H; J = 1.7 Hz), 7,18 (d, 24H; J = 1.7 Hz), 6.90 (d, 12H; J = 2.2 Hz), 6.59 (t, 6H; J = 2 Hz), 5.30 (s, 12H), 4.9 (s, 24H), 1.26 (s, 216H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 160.4, 150.85, 148.7, 139.6, 135.7, 123.8, 122.3, 122.1, 108.2, 106.2, 101.7, 71.6, 70.9, 34.8, 31.4. MALDI calcd for $C_{240}H_{312}O_{18}$ 3508.10 (M + Na), found 3509. Anal. Calcd for $C_{240}H_{312}O_{18}$: C, 82.64; H, 9.17. Found: C, 82.55; H, 9.03.

6,7-Bis(octyloxy)-2,3-dihydrophthalazine-1,4-dione (Phthal8). This compound was prepared via the general procedure for the synthesis of phthalhydrazides as described above. It was purified by recrystallization from dioxane and acetic acid. MP: see Table 2. ^{1}H NMR (400 MHz, CDCl$_3$): δ 13.8 (s, 1H), 12.6 (s, 1H), 7.52 (s,2H), 4.14 (t, 4H; J = 6.6 Hz), 1.94−1.82 (m, 4H), 1.58−1.43 (m, 4H), 1.43−1.20 (m, 16H), 0.88 (t, 6H; J = 5.4 Hz). ^{13}C NMR (100 MHz, CDCl$_3$): δ 157.1, 153.0, 121.1, 105.9, 69.0, 31.9, 29.5, 29.3, 29.0, 26.0, 22.7, 14.1. HRFAB calcd for $C_{24}H_{38}N_2O_4$ 419.290983, found 419.291100. Anal. Calcd for $C_{24}H_{38}N_2O_4$: C, 68.87; H, 9.15; N, 6.69. Found: C, 68.90; H, 9.33; N, 6.73.

6,7-Bis(dodecyloxy)-2,3-dihydrophthalazine-1,4-dione (Phthal12). This compound was prepared via the general procedure for the synthesis of phthalhydrazides as described above. It was purified by recrystallization from dioxane and acetone. MP: see Table 2. ^{1}H NMR (400 MHz, CDCl$_3$): δ 13.7 (s, 1H), 12.4 (s, 1H), 7.46 (s,2H), 4.10 (t, 4H; J = 6.6 Hz), 1.94−1.82 (m, 4H), 1.58−1.43 (m, 4H), 1.43−1.20 (m, 36H), 0.88 (t, 6H; J = 5.4 Hz). ^{13}C NMR (100 MHz, CDCl$_3$): δ 157.04, 152.93, 121.11, 105.78, 68.89, 31.97, 29.81, 29.78, 29.75, 29.65, 29.43, 29.10, 26.08, 22.71, 14.12. HRFAB calcd for $C_{32}H_{54}N_2O_4$ 531.416184, found 531.414575. Anal. Calcd for $C_{32}H_{54}N_2O_4$: C, 72.41; H, 10.25; N, 5.28. Found: C, 72.49; H, 10.17; N, 5.31.

6,7-Bis(hexadecyloxy)-2,3-dihydrophthalazine-1,4-dione (Phthal16). This compound was prepared via the general procedure for the synthesis of phthalhydrazides as described above. It was purified by recrystallization from dioxane. MP: see Table 2. ^{1}H NMR (400 MHz, CDCl$_3$): δ 13.7 (s, 1H), 12.4 (s, 1H), 7.45 (s,2H), 4.10 (t, 4H; J = 6.6 Hz), 1.94−1.82 (m, 4H), 1.58−1.43 (m, 4H), 1.43−1.20 (m, 50H), 0.88 (t, 6H; J = 5.4 Hz). HRFAB calcd for $C_{40}H_{70}N_2O_4$ 643.541384, found 643.541308. Anal. Calcd for $C_{40}H_{70}N_2O_4$: C, 74.72; H, 10.97; N, 4.36. Found: C, 74.65; H, 10.67; N, 4.60.

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