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Enforced Stacking in Crowded Arenes

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Disk-shaped π-surfaces that stack to form columnar structures[1] are prototypes of molecular-scale wires that have an insulating hydrocarbon sheath surrounding a conductive aromatic core.[2] Typically, the strengths of the associations between the molecules, formed through contacts between aromatic surfaces, are weak. Previous schemes to modulate these strengths are based on metal−ligand interactions,[3] π-donor/acceptor pairs,[4] and hydrogen bonds.[5] The study described below considers whether substituents in the 2,4,6-positions can force 1,3,5-triamides into conformations favorable for intermolecular hydrogen bonding.[6] Suprisingly, there are *no* examples of benzene rings with secondary amides at the 1,3,5-positions with any substituents other than hydrogen at the remaining positions.[7] Described below are syntheses of the first members of this new class of molecules (**1a**−**d**) and studies showing that they self-assemble into columns. Their physical properties show that **1d** forms a liquid crystalline phase with its columns perpendicular to the surface and that **1b** forms a highly ordered phase whose columns are parallel to the surface.

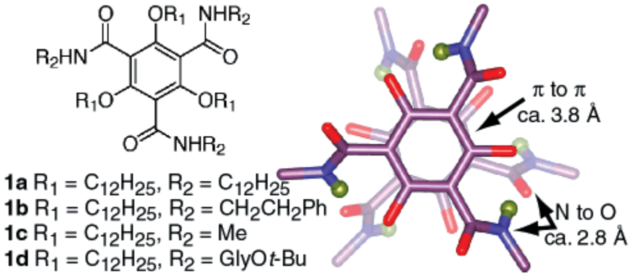
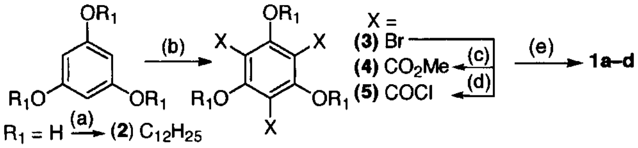


Figure 1. Energy minimized dimeric model. Methyls on the ether oxygens were included in the minimization and removed to clarify the view.

Scheme 1



a (a) K_2CO_3, $C_{12}H_{25}I$, Δ; (b) Br_2, $FeCl_3$, Δ; (c) *i.* t-BuLi; *ii.* $ClCO_2Me$; (d) *i.* NaOH, Δ; *ii.* $SOCl_2$, Δ; (e) $(R_2)NH_2$, Et_3N.

Table 1. Transition Temperatures (°C) and Enthalpies (kJ/mol) for **1a**−**d**

	heating cycle			cooling cycle	
1a	98 (57.1)		294 (35.1)	247 (−5.6)	83 (−39.1)
1b	82 (11.1)	176 (7.6)	232 (4.0)	227 (−3.0)	104 (−7.1)
1c	91 (2.9)		123 (27.4)	107 (−21.3)	
1d	47 (25.0)	85 (6.3)	200 (18.6)	189 (−8.6)	66 (−4.4)

Shown in Figure 1 is the lowest energy[8] dimer of a benzene ring that is alternatingly substituted with methoxyls and methylamides. To relieve steric congestion, the amides twist out of the aromatic plane by ca. 45° allowing three intermolecular hydrogen bonds, while π-surfaces are “in-registration”, stacked 3.8 Å apart. Key to the synthesis of this class of molecules[9] (Scheme 1) was the discovery that 1,3,5-tribromo-2,4,6-tridodecyloxylbenzene (**2**) undergoes a triple lithium/halogen exchange at −78 °C.[10] After quenching with methyl chloroformate, **4** is produced in an unoptimized 30% yield on a 4-g scale. The target structures **1a**−**d** are then synthesized in three steps: saponification, conversion to **5**, and reaction with primary amines (75−81% yield). The synthesis is both expeditious and flexible.

As shown in Table 1, **1a**−**d** undergo an initial thermal transition between 47 and 98 °C. At higher temperatures, both **1a** and **1c** form isotropic liquids. In contrast, **1b** (at 176−232 °C) and **1d** (at 85−200 °C) form another phase before becoming isotropic. Upon cooling the isotropic liquids, **1b** and **1d** undergo phase transitions (**1b**, 3 kJ/mol, and **1d**, 8.6 kJ/mol) with enthalpies similar to those observed for discotic liquid crystals (ca. 1−20 kJ/mol).[1,3−5] Indicative of hydrogen bonds forming in the mesophases,[5f] the N−H stretching frequency of **1b** shifts from 3295 (at 200 °C) to 3361 cm^{-1} (at 250 °C), and for **1d** it shifts from 3282 (at 135 °C) to 3374 cm^{-1} (at 220 °C).

Displayed in Figure 2 is the diffraction pattern of synchrotron radiation (λ = 1.151 Å) by **1b** at 200 °C. The diffractogram is dominated by a single sharp peak at low angle, diagnostic of columnar assemblies.[11] Remarkably, diffraction peaks up to fifth-order are seen that can be indexed to a hexagonal lattice. The diffuse reflection at ca. 4.5 Å arises from the fluidlike packing of side chains.[11] The lateral core-to-core separation[12] is 21 Å—in

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10.1021/ja0104148 CCC: $20.00

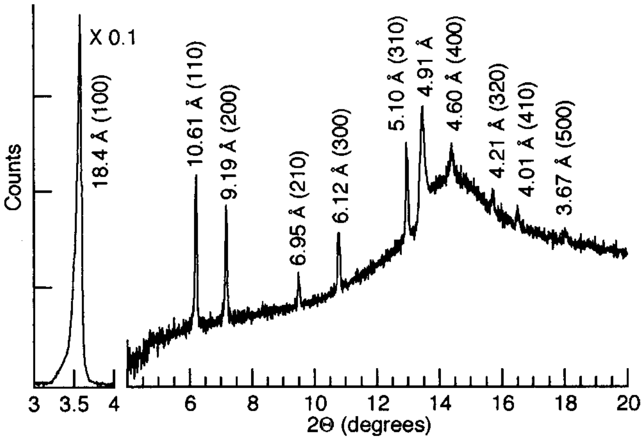

Figure 2. X-ray diffraction from **1b** at 200 °C.

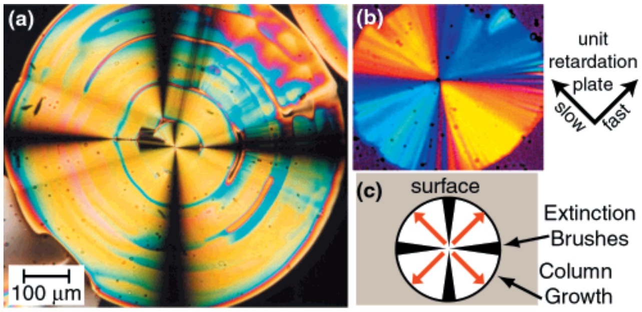

Figure 3. (a) Optical micrograph of **1b** cooled from an isotropic liquid; (b) thinner sample with a unit retardation plate at a 45° angle; and (c) orientation of the columns.

agreement with the ca. 27 Å expected for columns with noninterdigitating, extended side chains. There is one reflection (4.91 Å) that could not be indexed.

The polarized light micrograph of **1b** shown in Figure 3a is seen when samples are cooled from their clearing temperatures. It is uniform over *several hundred micrometers*. The areas of extinction in the pattern are aligned along the polarizer/analyzer axes and are invariant with the sample's rotation (spherulitic domains).[13] A unit retardation plate allows the direction of column growth to be determined.[14] As shown in Figure 3b, the pattern is shifted to yellow along the slow vibration ray of the plate and blue along the fast vibration ray.[14a] The lower index of refraction, and therefore the long axis of the columns,[15] radiates outward from a central defect point to the edge of the pattern (Figure 3c).[13] The pattern is *not* typical of a discotic liquid crystal and may indicate that **1b** forms plastic or soft crystals.

For **1d** the two phases below 85 °C are shown by X-ray diffraction to be crystalline polymorphs.[9] Above 85 °C, a fluid phase develops that is easily aligned by shearing.[16] The diffraction pattern seen at 120 °C (Figure 4a) has reflections that index to a rectangular lattice with parameters a = 38 Å and b = 22 Å. Rectangular packing has been seen in other columnar liquid crystals[17] and results from a distortion of the lattice. For **1d** the lattice deviates by only 1% from hexagonal.[18] This distortion could arise because the side chains are mismatched in size, which frustrates hexagonal packing, or are bulky, which tilts or offsets the subunits.

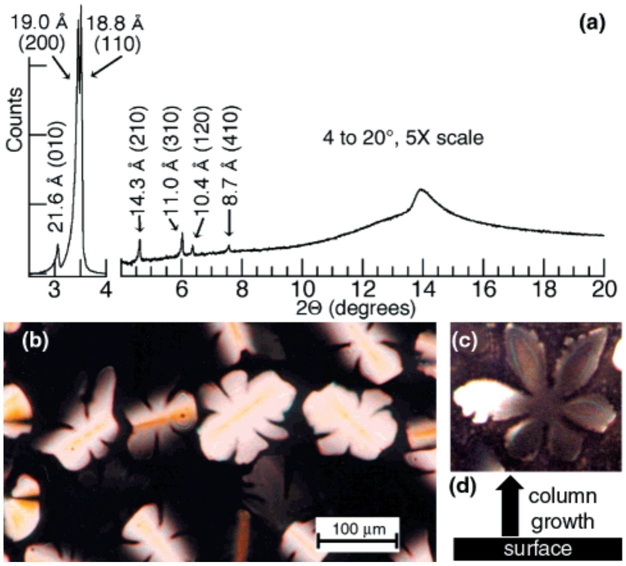

Figure 4. (a) X-ray diffraction of **1d** at 120 °C; (b) polarized light micrograph of **1d** at 180 °C; (c) hexagonal features (2× magnification); and (d) homeotropic alignment.

The birefringent texture of **1d** is shown in Figure 4b. In thicker regions of the sample, linear defects occur, resembling those seen in other homeotropically grown discotic liquid crystals.[19] In thinner regions, the material is weakly birefringent with large areas of blackness. The hexagonal pattern in Figure 4c is diagnostic[19,20] of structures having columnar axes perpendicular to surfaces.[21] Therefore, the orientations of the columns are opposite for **1d** and **1b**. Possibly, the ester-containing side chains act as anchors to the surface.[15b]

The birefringence that develops for **1a**, after supercooling for 47 °C, is similar to that of **1b**. Diffraction from **1a** after it was cooled from an isotropic liquid showed a two-dimensional hexagonal lattice of columns.[9] Diffraction from **1c** at 100 °C, on the heating or the cooling cycle, is consistent with a columnar organization, but a multitude of other peaks indicate a crystalline phase.[9]

In summary, a new class of molecules is put forth that assemble into columnar superstructures whose exteriors are coated with a variety of functional groups. They may have useful properties[22] because each subunit's dipole moment should be amplified when it assembles into stacks.

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Supporting Information Available: Experimental details and X-ray diffraction patterns (**1a**,**c**,**d**) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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