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[28] The chiral effect is sensitive to the precise conditions used, which include the solution pH, the solution flow rate, and the ESI temperature. Under some operating conditions, especially gentle conditions that favor clustering, the discrimination between the homo- and heterochiral systems can be much less pronounced.
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Hydrogen-Bonded Helices in Crystals with Prescribed Organization**

Radu Custelcean and Michael D. Ward*

Self-assembled molecular helices are ubiquitous in nature and can be found in many biologically important macromolecules. It is therefore not surprising that chemists have made significant efforts to introduce helicity in many artificial systems.[1] The inherent chirality present in such spiral structures is generally associated with enantioselectivity[2] or interesting optoelectronic properties.[3] Theoretical[4] and experimental[5] studies have indicated that helical supramolecular networks can affect chiral ordering in crystal lattices.

Molecular helicity can be programmed by judicious selection of elements that are encoded with structural and conformational information designed to enforce intramolecular self-organization in a spiral arrangement. Examples such as helicenes,[6] poly(*m*-phenylene),[7] polyheterocyclic strands,[8] *m*-phenylacetylene oligomers,[9] β-peptides,[10] polyisocyanates,[11] and oligoarylamides[12] elegantly illustrate this concept. The generation of supramolecular helices requires an additional design element, namely, a reliable noncovalent motif that can provide the desired connectivity of the building blocks in a predictable manner. Hydrogen bonds,[13] metal coordination,[14] and $\pi-\pi$ stacking interactions[15] are often utilized in this regard. These design strategies, however, are generally limited to one dimension, coinciding with the helix direction, while the assembly and structure along the remaining two crystal dimensions are difficult to control. The rational construction of new materials with tailored functions and properties, however, requires control of crystal architecture in all three dimensions. Here we report the formation of hydrogen-bonded helices with predictable three-dimensional (3D) organization in the solid state. This study represents a key first step towards the rational design of crystalline, hydrogen-bonded chiral networks with potential applications in enantioselective separation.[16]

We are actively involved in the design of molecular crystals based on the self-assembly of complementary guanidinium and organosulfonate ions, which typically crystallize in a quasihexagonal hydrogen-bonded network (Figure 1a).[17] These 2D layers can be described as consisting of 1D ribbons along a_1. The S···S distance along this axis is nominally identical for all these compounds (7.5 ± 0.2 Å). The ribbons themselves aggregate by hydrogen bonding along the orthogonal direction b_1. The magnitude of b_1 can vary significantly (7.3 – 13 Å) as a result of puckering of the sheet about the hydrogen bonds that connect the ribbons.

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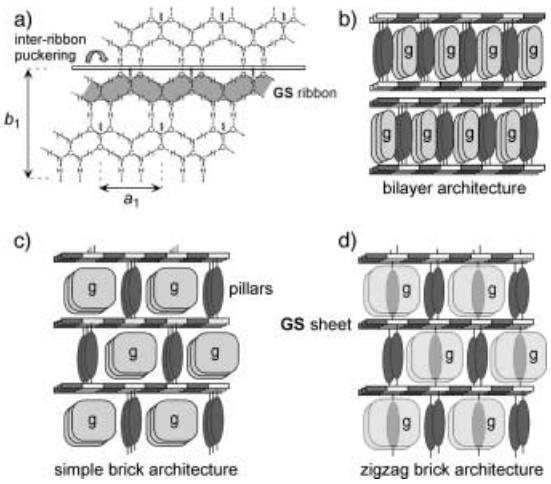
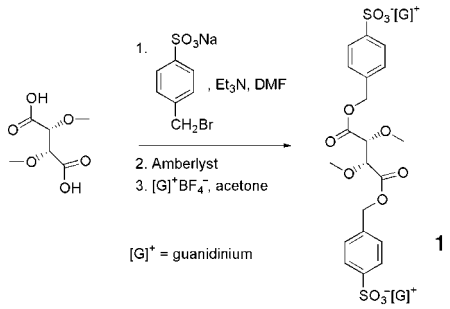


Figure 1. a) Quasihexagonal guanidinium–sulfonate hydrogen-bonding motif of one-dimensional ribbons running along the a_1 direction. The ribbons are linked to each other by hydrogen bonding along b_1 (a_1 and b_1 here represent generic lattice constants). The magnitude of b_1 can vary substantially through inter-ribbon puckering. b) Bilayer architecture. c) Simple brick architecture. d) Zigzag brick architecture. All three architectures contain inclusion cavities that can be occupied by guest molecules (g).

The persistence of the 2D guanidinium–sulfonate (**GS**) motif, observed in over 200 compounds synthesized in our laboratory, simplifies the engineering of these "lamellar" crystals by allowing convenient manipulation of the structure in the third dimension through the choice of the organic substituent. Organodisulfonates can be employed to link the hydrogen-bonded sheets and thereby act as molecular "pillars" that support the formation of either discrete bilayers, in which all the organic groups project from the same side of each sheet (Figure 1b), or continuous "brick" architectures, in which the organic substituents alternate up and down in each sheet (Figure 1c and d). Because of the low density enforced by the quasihexagonal hydrogen-bonding motif, these topologies can produce inclusion cavities that are occupied by guest molecules. The flexibility of the **GS** hydrogen-bonded networks, through puckering and conformational freedom of the pillars, allows self-optimization of host–guest interactions and efficient packing needed for crystallization.

The ability to modify the pillars with retention of the overall crystal architecture facilitates the rational design of functional materials. In this regard, the employment of chiral pillars could afford asymmetric cavities capable of including chiral guests, which in turn could serve as a basis for enantioselective separations. Flexible pillars may be ideal in this regard, as this characteristic would permit the host to mold to a chiral guest while maintaining the persistent lamellar architecture. These concepts prompted us to synthesize the chiral guanidinium disulfonate **1**, starting from the readily accessible, optically pure *O*,*O*′-dimethyl-L-tartaric acid (Scheme 1).

Tartrates have been successfully employed for the synthesis of liquid-crystalline[18] and oligomeric helical materials.[19] Moreover, a search of the Cambridge Structural Database revealed that simple, optically pure tartaric acid derivatives have a propensity to crystallize in the space groups $P2_1$ and $P2_12_12_1$. These compounds contain at least one twofold screw



Scheme 1. Synthesis of **1**.

axis, a symmetry element that favors helical organization. Most of them, however, do not possess functional groups that provide the supramolecular connectivity required for the formation of a continuous helix. Those that do exhibit unpredictable hydrogen-bonding patterns, and this limits their potential for rational assembly.

Molecular modeling[20] indicated that the disulfonate dianion in **1** is extremely flexible, with more than 100 low-energy conformations within 10 kcal mol^{-1}. The most stable conformation (Figure 2a), optimized by DFT at the B3LYP/6-31G* level,[21] has an S···S separation of 18.8 Å and a dihedral angle between the two S–C terminal bonds of 54.4°. This conformational twist, which originates from the two chiral centers in the pillar, provides the structural encoding for helical organization in **1**.

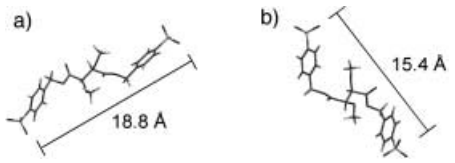


Figure 2. a) Calculated structure (B3LYP/6-31G*) of the organodisulfonate pillar in **1**. b) Structure of the same pillar in the crystalline state.

Crystallization of **1** from methanol/1,4-dioxane afforded single crystals suitable for X-ray diffraction,[22] which revealed the existence of the simple brick architecture (Figure 3c). We surmise that formation of a bilayer framework is prevented by the steric bulk of the pillars which thereby promotes the lower density brick framework. The steric bulk is further reflected by the intermolecular S···S distance along the ribbon direction, which at 8.03 Å is the largest observed value to date for a_1 in guanidinium sulfonates. The **GS** sheets actually display a shifted-ribbon hydrogen-bonding motif, which is a slight variation of the quasihexagonal arrangement that was observed in some other guanidinium mono- and disulfonates.[17]

The pillars in **1** are strongly twisted, with an S–C···C–S dihedral angle of 53.7°, in agreement with the theoretical calculations. Compared to the gas-phase calculated geometry, however, the pillars are significantly more folded in the crystal which results in a shorter S···S separation of 15.4 Å (Figure 2b). This structural "collapse" apparently reflects the tendency for dense packing and a preference to fill the void space of the framework by conformational distortion of the pillars instead of guest inclusion. Hydrogen bonds between

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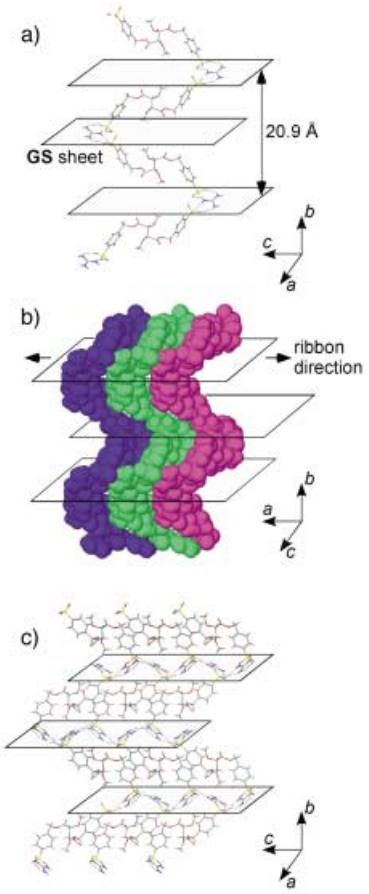
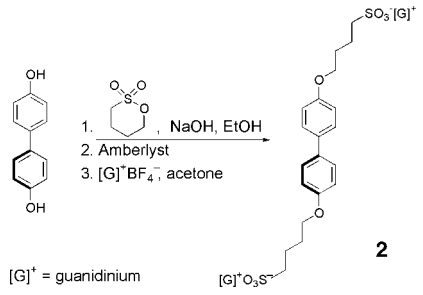


Figure 3. X-ray crystal structure of **1**. a) Self-assembly into the hydrogen-bonded helix. b) Association of helices along the **GS** ribbon (crystallographic *a* direction). c) Formation of the "brick" architecture by hydrogen bonding of helices along the crystallographic *c* direction.

the sulfonate and guanidinium ions generate extended right-handed helices about the twofold crystallographic *b* axis, with a pitch of 20.9 Å (Figure 3a). The intramolecular S–C···C–S twist is augmented by an intermolecular C–S···S–C torsion angle of 97.7° through guanidinium–sulfonate hydrogen bonds. When combined with the flexible backbone of the pillar, the result is a smoothly curved, supramolecular spiral. The helices further associate along the crystallographic *a* direction to generate the typical **GS** ribbons (Figure 3b), and then orthogonally, along the *c* direction, to complete the **GS** sheets and form the familiar 3D brick architecture (Figure 3c). The twisted organic pillars, winding through the crystal and connecting the **GS** sheets, are reminiscent of spiral staircases connecting the floors of a building. It is remarkable that despite the significant conformational twist and flexibility of the pillars, this compound still self-assembles in the brick topology, a crystal architecture found for numerous rigid pillars in this class of molecular materials.

The ability of the **GS** system to generate helical networks was further explored with the guanidinium disulfonate **2** (Scheme 2). Although this compound is not inherently chiral, it can assume chiral conformations upon twisting about the C(Ph)–C(Ph) bond. The flexible butoxy chains were introduced to amplify this conformational twist and promote helical self-organization.



Scheme 2. Synthesis of **2**.

Single-crystal X-ray diffraction[22] on **2** (from MeOH/AcOEt) revealed the formation of supramolecular helices that self-assemble into a "zigzag brick" architecture[17b] (Figure 4). The twist of the biphenyl core induces a S–C···C–S dihedral angle of 49.8° in the 19.3-Å-long pillar, which in combination with the intermolecular C–S···S–C torsion angle of of 21.0° (by hydrogen bonding to guanidinium cations) results in the formation of a helix about the crystallographic *b* axis with a pitch of 18.1 Å. Helices of the

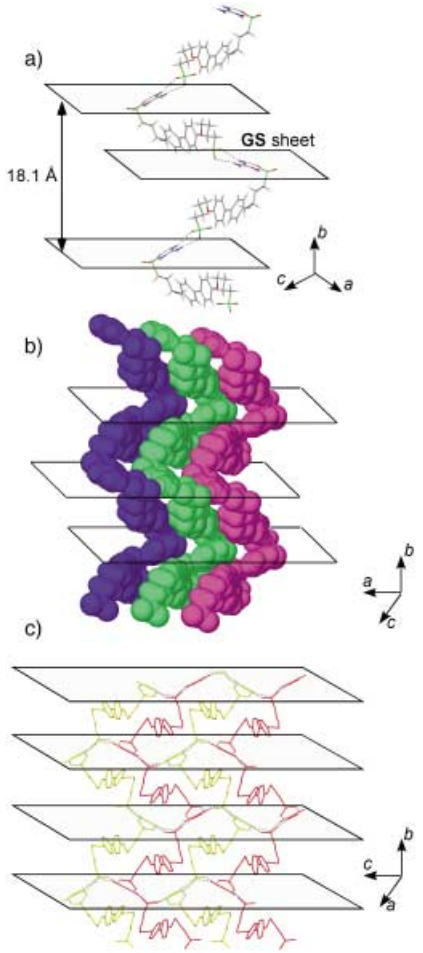


Figure 4. X-ray crystal structure of **2**. a) Self-assembly into the hydrogen-bonded helix. b) Homochiral association of helices along the *a*-axis. c) Formation of the "zigzag brick" architecture by hydrogen bonding of helices along the *c*-axis. Left- (red) and right-handed (yellow) helical domains alternate along *c*, producing a racemic crystal.

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same handedness aggregate through guanidinium–sulfonate hydrogen bonds along the crystallographic *a* axis to generate homochiral domains, as illustrated in Figure 4b. Further association of helical domains with opposite chirality, by hydrogen bonding along *c* (Figure 4c), generates the "zigzag brick" architecture (Figure 1d), in which the pillars alternate up and down along both the *a* and *c* axes that delineate the **GS** sheets.

We have illustrated here a rational approach towards hydrogen-bonded helices with predictable three-dimensional organization in the crystalline state. While other strategies for encoding helicity in self-assembled materials have been reported, this approach offers advanced control of the overall crystal architecture. Though no guests are included in the frameworks described here, the pronounced folding and tilt of the pillars, together with the substantial puckering of the **GS** sheets, suggest the potential for guest inclusion upon conformational expansion of these networks, and the prospect of inclusion-based enantioselective separation.

Experimental Section

1: *O*,*O*′-dimethyl-L-tartaric acid[23] (0.178 g, 1 mmol) was dissolved in anhydrous DMF (1 mL). The resulting solution was cooled in ice, and triethylamine (0.212 g, 2.1 mmol) was added dropwise with stirring under an inert atmosphere. A solution of sodium *p*-bromomethylbenzene sulfonate[24] (0.546 g, 2 mmol) in anhydrous DMF (8 mL) was then added dropwise while stirring the reaction mixture under ice. The solution was warmed to room temperature, and stirred for 3 d under an inert atmosphere. It was subsequently poured over 75 mL of 2-propanol, and the resulting precipitate was collected by filtration, washed well with 2-propanol, then dissolved in 5 mL of deionized water, and passed over Amberlyst 36 ion-exchange resin (Aldrich). After the removal of water in vacuo at 40 °C, the resulting oil was extracted with acetone (10–15 mL) and poured over a solution of 0.3 g guanidinium tetrafluoroborate in 5 mL acetone. The resulting precipitate was filtered and washed with acetone. Yield 0.06 g. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): $\delta = 3.26$ (s, 6H), 4.40 (s, 2H), 5.12 (d, J(H,H) = 12.9 Hz, 2H), 5.25 (d, J(H,H) = 12.6 Hz, 2H), 6.94 (s, 12H), 7.35 (d, J(H,H) = 8.1 Hz, 4H), 7.60 (d, J(H,H) = 8.1, 4H).

2: 4,4′-Biphenol (0.93 g, 5 mmol) and NaOH (0.4 g, 10 mmol) were dissolved in EtOH (40 mL). The resulting solution was added dropwise over 90 min to a vigorously stirred solution of 1,4-butanesultone (2.72 g, 20 mmol) in refluxing EtOH (10 mL). The mixture was refluxed for 44 h with stirring. The resulting precipitate was filtered from the hot solution, washed with EtOH, then with 50 mL of hot MeOH. The obtained white powder was dissolved in minimum amount of deionized water and passed over Amberlyst 36 ion-exchange resin. After the removal of water in vacuo, the resulting solid was dissolved in 85 mL acetone, and a solution of 1.46 g guanidinium tetrafluoroborate in 10 mL acetone was subsequently added. The resulting precipitate was collected by filtration and washed with acetone. Yield 1.4 g. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): $\delta = 1.78$ (m, 8H), 2.61 (t, J(H,H) = 7.2 Hz, 4H), 3.98 (t, J(H,H) = 6.0 Hz, 4H), 6.97 (d, J(H,H) = 6.9 Hz, 4H), 7.06 (s, 12H), 7.51 (d, J(H,H) = 6.9 Hz, 4H).

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[22] A Siemens SMART CCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$) was used for single-crystal X-ray diffraction studies. The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 with the SHELXTL package (Structure Analysis Program 5.1, Brucker AXS, Inc., Madison, WI, **1997**). Absorption corrections were applied with SADABS. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated and placed in idealized positions. Crystal data for **1**: crystal dimensions $0.39 \times 0.22 \times 0.17$ mm; $T = 173$ K; monoclinic, space group $P2_1$; $a = 8.029(2)$ Å, $b = 20.895(5)$ Å, $c = 9.033(3)$ Å, $\beta = 98.312(5)^\circ$, $V = 1499.4(7)$ Å^3, $Z = 2$; $\rho_{calcd} = 1.410$ g cm^{-3}; $2\theta_{max} = 54.0^\circ$; 5805 reflections collected, 2711 unique reflections; 381 parameters; $R_1 = 0.0463$, $wR_2 = 0.0938$ for $I > 2\sigma(I)$; residual electron density: 0.28 e Å^{-3}. Crystal data for **2**: crystal dimensions: $0.39 \times 0.25 \times 0.08$ mm; $T = 173$ K; monoclinic, space group $P2_1/c$; $a = 12.8032(17)$ Å, $b = 18.092(2)$ Å, $c = 12.8969(18)$ Å, $\beta = 91.646(3)^\circ$, $V = 2986.1(7)$ Å^3, $Z = 4$; $\rho_{calcd} = 1.283$ g cm^{-3}; $2\theta_{max} = 54.0^\circ$; 6513 reflections collected, 4120 unique reflections; 343 parameters; $R_1 = 0.0662$, $wR_2 = 0.1269$ for $I > 2\sigma(I)$; residual electron density: 0.55 e Å^{-3}. CCDC-175036 (**1**) and CCDC-175037 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit @ccdc.cam.ac.uk).

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