A novel self-assembled organic tubular structure

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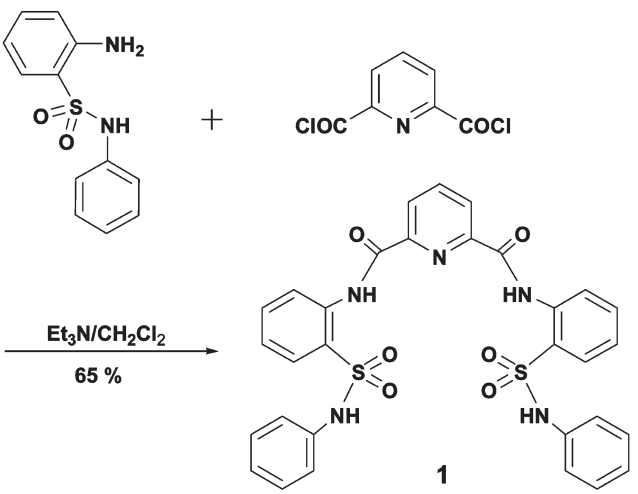
A novel organic tubular structure with the walls consisting of aromatic rings was constructed by the self-assembly of a two-dimensional sheet-like molecule in the solid state.

Synthetic organic nanotubes[1] have been the subject of increased attention because of their potential applications in chemical, biological and material sciences,[2] for example, by acting as ion and small molecule transport systems and closed reaction vessels. So far, a number of approaches to constructing hollow, organic, tubular structures have been reported, the most important of which involves the self-assembly of suitable macrocyclic building blocks to form tubes through non-covalent interactions such as hydrogen bonding and π–π stacking. Examples of such building blocks include cyclic peptides,[3] macrocyclic polyphenethynylenes,[4] bis-urea macrocycles,[5] calix[4]arene derivatives,[6] and others[7] such as porphyrin dendrimers, cyclodextrins, chalcogen-containing cyclic alkynes and alkenes, cyclic oligosaccharides and serinophanes. In contrast, the formation of organic tubular structures by the self-assembly of acyclic molecules has received relatively little attention.[8]

Here we report a novel organic tubular structure, formed by the solid state self-assembly of the two-dimensional sheet-like molecule **1** (Scheme 1). Although a similar strategy (Fig. 1) was adopted for the formation of carbon nanotubes from graphites,[9] until now it had not been used for the construction of tubular organic structures. Moreover, the walls of the tube we present consist of aromatic rings, and the planes of these walls are parallel to the axis of the tube. This is markedly different from other known



Scheme 1 The synthesis of **1**.

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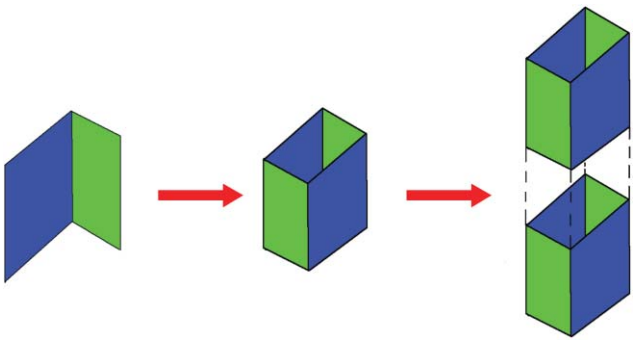

Fig. 1 A schematic representation of a self-assembled tube from a two-dimensional sheet-like building block.

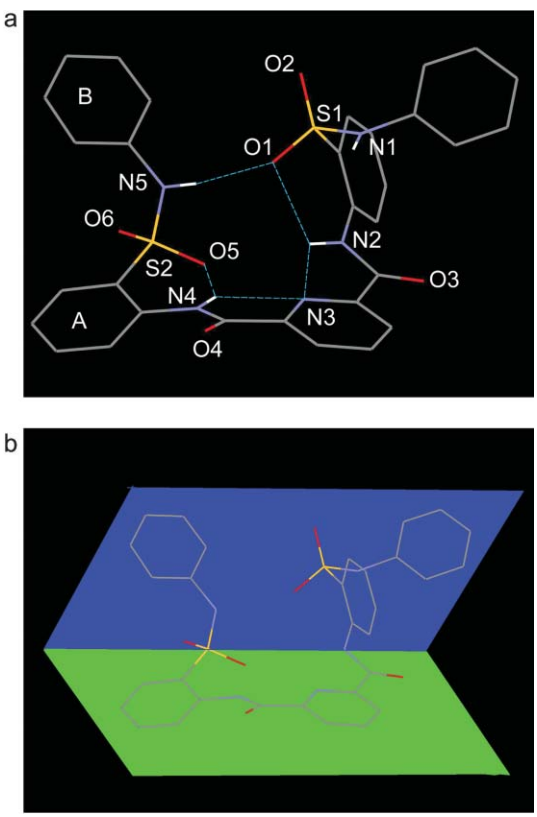

Fig. 2 (a) The crystal structure of **1** and its network of intramolecular hydrogen bonds. Distances (Å): N2–H···O1 2.87, N2–H···N3 2.66, N4–H···O5 2.78, N4–H···N3 2.67, N5–H···O1 2.80. Angles (°): N2–H···O1 116, N2–H···N3 110, N4–H···O5 140, N4–H···N3 111, N5–H···O1 161. Hydrogen atoms not involved in intramolecular hydrogen bonding are omitted for clarity. (b) A schematic representation of the two approximate planes in **1**.

self-assembled organic nanotubes.[3,4] Such a unique structural feature may therefore be of benefit to the recognition and transport of aromatic molecules.

The molecule **1**, based on aromatic sulfonamides, was designed as a building block for the purposes of self-assembly. It was chosen because the sulfonamide group adopts a tetrahedral configuration, contains an S–N bond with a low rotational energy barrier, and is a stronger hydrogen bond donor than amides.† Compound **1** was readily synthesized by the reaction of 2-amino-*N*-phenyl-benzenesulfonamide with pyridine-2,6-dicarbonyl dichloride in the presence of triethylamine (Scheme 1).

Crystals of **1** suitable for X-ray crystallographic analysis were obtained by the slow evaporation of a solution of **1** in $CHCl_3$–CH_3OH.‡ The crystal structure of **1** reveals its two-dimensional sheet-like conformation. As shown in Fig. 2, the first approximate plane consists of the pyridine ring, benzene ring A and atoms S2, N2, N3 and N4. The second approximate plane consists of the terminal benzene ring B and atoms O1, O5, S2, N1, N2 and N5. The dihedral angle between these two approximate planes is 97.8°. The conformation of **1** is stabilized by a network of intramolecular hydrogen bonds with the O1 and O5 of the sulfonamide groups and N3 of the pyridine ring as acceptors. These three-centered hydrogen bonds have the N···O or N···N distances in the range 2.66–2.87 Å.

As shown in Fig. 3, a dimerization of **1** into a tubular structure through the combination of multiple interactions was found. Two kinds of hydrogen bond exist. One is a strong hydrogen bond between HN1 of the sulfonamide group in one molecule and O4 of the carboxiamide group in the second ($d_{N–H···O}$ and $\theta_{N–H···O}$ are 1.99 Å and 168° respectively). The other is a CH···O hydrogen bond between the 3-position proton of the pyridine ring in one molecule and O1 of the sulfonamide group in the second ($d_{C–H···O}$ and $\theta_{C–H···O}$ are 2.54 Å and 161° respectively). A pair of CH···π interactions also exist ($d_{H···\pi}$ = 2.85 Å). The dimer has an approximately rectangular tube shape with a length of ~10.2 Å and a cavity cross-section of ~9.5 × 3.9 Å. The sulfonamide groups in both molecules of the dimer are located at turns of the rectangular tube. The O1 atoms point into the tube and the O2, O5 and O6 atoms point outside of it. The existence of the dimer was also proved by electrospray mass spectroscopy.

Through a pair of CH···O3 hydrogen bonds (of length 2.72 Å) (Fig. 4a), dimers can further associate with each other along the [110] axis to form a supramolecular tubular structure. In this tube,

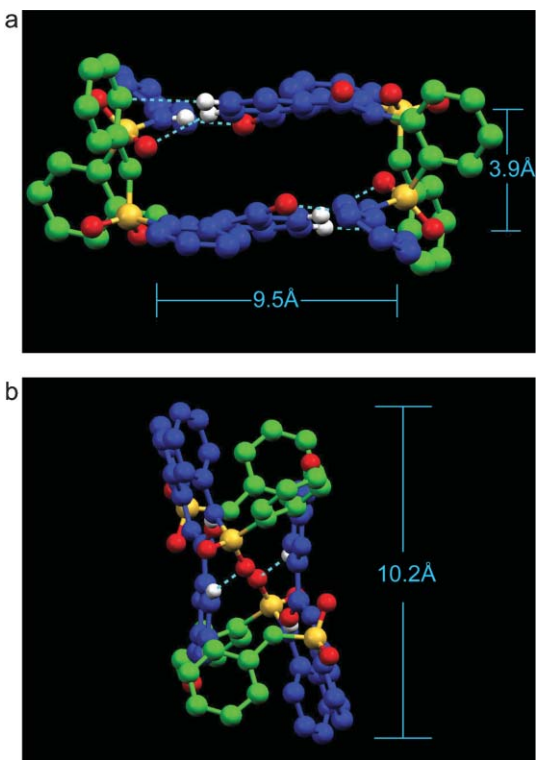

Fig. 3 (a) Top view and (b) side view of the dimer of **1**. Dashed lines show the non-covalent interactions. Hydrogen atoms not involved in interactions are omitted for clarity.

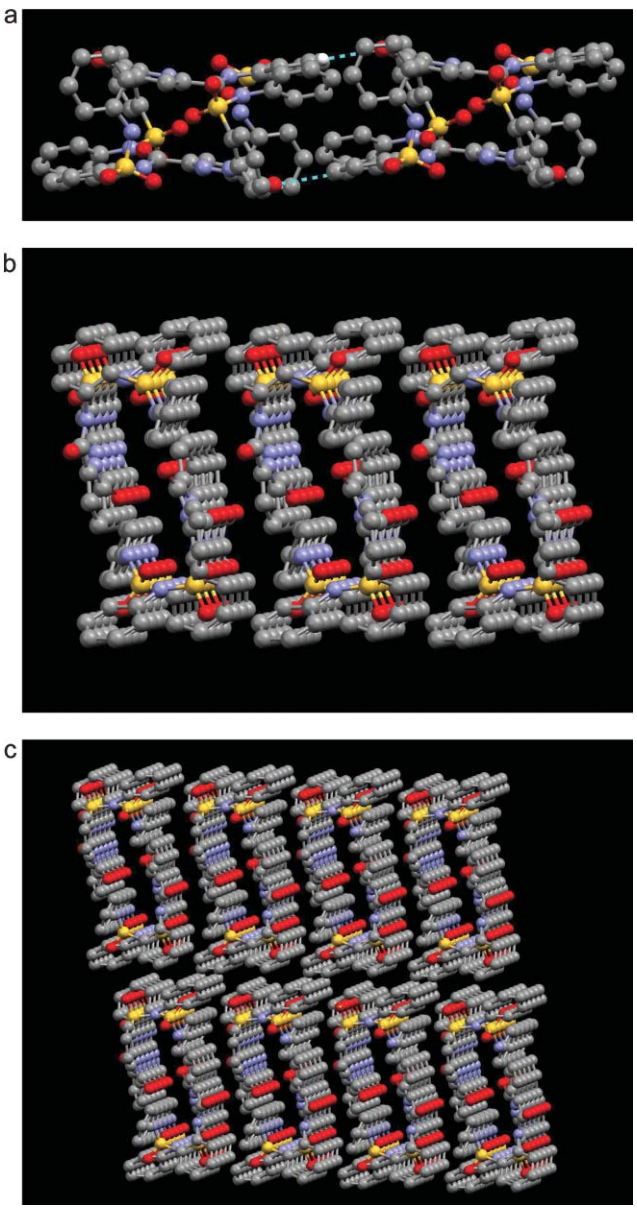

Fig. 4 (a) The assembly of dimers through C–H···O hydrogen bonds (dashed lines) that leads to the formation of infinite tubes. (b) A view of a 2D layer. (c) A view of the 3D structure. Hydrogen atoms not involved in interactions are omitted for clarity.

the walls consist of aromatic ring planes which are either exactly or approximately parallel to the axis of the tube. The planes of the pyridine ring, benzene ring A and another terminal benzene ring (not benzene ring B) in each molecule form the two larger walls. The two smaller walls consist of the planes of the benzene ring B and another benzene ring adjacent to the pyridine ring in each molecule of the dimer. These characteristics may impart on the tube unique structural characteristics, distinct from those of previously reported organic tubes. Additionally, the tubes stack indefinitely along the *a*-axis to form 2D layers (Fig. 4b) through the CH···O2 hydrogen bonds ($d_{C–H···O}$ and $\theta_{C–H···O}$ are 2.43 Å and 140° respectively), and π–π interactions between the adjacent pyridine rings (centroid distance 3.80 Å). The layers can further stack into a 3D structure (Fig. 4c) through CH···O6 hydrogen bonds ($d_{C–H···O}$ and $\theta_{C–H···O}$ are 2.51 Å and 150° respectively) and CH···π interactions (distance 2.84 Å).

In conclusion, we have presented a novel organic tubular structure, formed by the self-assembly of the two-dimensional, sheet-like molecule **1** in the solid state. With the walls consisting of structural features significantly different to those of other reported organic nanotubes—aromatic ring planes, the tube is likely to have unique applications in the recognition and transportation of aromatic molecules. Further studies will endeavour to construct self-assembled organic nanotubes with larger cavities using a similar approach.

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Notes and references

† Synthesis of **1**: A solution of 2,6-pyridinedicarboxylic acid (1 mmol) in $SOCl_2$ (5 mL) was refluxed for 2h and the excess $SOCl_2$ removed under reduced pressure. The acid chloride obtained was dissolved in dry CH_2Cl_2 (10 mL) and added dropwise over 10 min to a solution of 2-amino-*N*-phenyl-benzenesulfonamide (1 mmol) and triethylamine (3 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The mixture was then stirred at rt for 4 h. The organic phase was washed twice with 2M HCl and dried over anhydrous Na_2SO_4. The solvent was removed and the residue purified by flash chromatography (20 : 1, CH_2Cl_2 : ethyl acetate) to give **1** as a white solid (404 mg, 65%). MP: 271–273 °C. δ_H (DMSO-d_6) 11.17 (2H, s), 10.23 (2H, s), 8.36 (3H, s), 8.25 (2H, d, J = 7.8 Hz), 7.82 (2H, d, J = 7.8 Hz), 7.71 (2H, t, J = 7.8 Hz), 7.35 (2H, t, J = 7.7 Hz), 7.02–6.85 (10H, m). δ_C ($CDCl_3$) 162.3, 148.5, 139.6, 135.6, 135.1, 134.5, 130.3, 129.2, 129.0, 126.4, 125.9, 125.1, 124.7, 123.8. *m/z* (MALDI–TOF) 650.1 $[M+Na]^+$. Found: C, 59.33; H, 4.00; N, 11.04. $C_{31}H_{25}N_5O_6S_2$ requires C, 59.32; H, 4.01; N, 11.16%

‡ Crystal data for **1**: Rigaku Raxis Rapid IP diffractometer, Mo–Kα radiation, λ = 0.71073 Å, μ = 0.236 mm^{-1}, T = 293(2) K, $C_{31}H_{25}N_5O_6S_2$, M = 627.68, triclinic, space group P-1, a = 8.2022(3), b = 12.7166(5), c = 15.4752(7) Å, α = 73.8650(10), β = 76.8680(7), γ = 73.036(3)°, V = 1464.21(10) $Å^3$, Z = 2, $\rho_{calc.}$ = 1.424 Mg m^{-3}, 12977 reflections measured, 6307 independent, 4199 used, number of parameters 398, R_{int} = 0.0312, R_1 = 0.0492 ($I > 2\sigma(I)$), wR_2 = 0.1298 (all data). CCDC 263745. See http://www.rsc.org/suppdata/cc/b5/b501941a/ for crystallographic data in CIF or other electronic format.

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