A supramolecular assembly of side-by-side polyimidazole tripod coils stabilized by π–π stacking and unique boric acid templated hydrogen bonding interactions†

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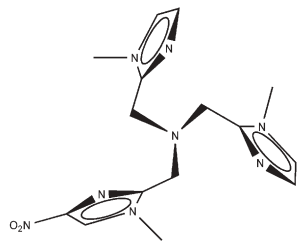
The self assembly of (bis(1-methyl-imidazol-2-yl)methyl)-(1-methyl-4-nitroimidazol-2-yl)methyl)amine and boric acid results in a supramolecular structure containing bundled antiparallel imidazole-boric acid helices and boric acid filled one-dimensional channels.

The self-assembly of molecular species in the solid-state *via* weak non-covalent interactions is a fundamental property of supramolecular chemistry[1] and an important component in the synthesis and manipulation of nanoscale materials.[2] Supramolecular assemblies are often stabilized by hydrogen bonding, hydrophobic, and hydrophilic interactions, π–π stacking, as well as electrostatic interactions between ionic groups.[1–3] In addition, small organic compounds have been utilized as templating agents to form supramolecular structures. For example, Etter[4] and others[5] have shown that the proton donor–acceptor properties of urea are ideal for templating the assembly of 2 and 3D solid-state assemblies. Similarly, the neutral and ionic forms of boric acid stabilize extended solid-state structures with various amines.[6]

In related studies, we have examined the interactions of $B(OH)_3$ with imidazole compounds such as tris(1-methylimidazolyl-2-yl)methyl)amine (tmima),[7a] which produces a supramolecular 2D network of hydrogen bonded $B(OH)_3$ and imidazole molecule sheets containing extended π–π stacking interactions.[7b] As an extension of these studies, we were interested in determining whether boric acid could be used as a templating agent for stabilizing supramolecular assemblies containing 1D channel structures containing imidazoles. Our recent studies[8] have shown that imidazole compounds readily assemble in the solid state generating supramolecular structures with channels that in some cases contain water and organic molecules of crystallization. The 1D hydrated imidazole assemblies have pore structures relevant to biological systems such as aquaporin proteins.[9a] Similar structures may be relevant to the action of chaperone transport of organic molecules through membranes.[9b–c]

With this in mind, we report an example of co-crystallization of $B(OH)_3$ with another polyimidazole compound, (bis(1-methyl-imidazol-2-yl)methyl) (1-methyl-4-nitroimidazol-2-yl)methyl)amine (**1**) (Scheme 1),[10a] designed to alter the hydrogen bonding and π–π stacking network of tmima so as to facilitate stabilization of 1D solid-state assemblies. Vapor diffusion of ether into an ethyl acetate solution of **1** produces colorless crystals of **2**,[10b] which contains a 2:1 nitroimidazole tripod/$B(OH)_3$ ratio. Compound **2** crystallizes with two molecules of the nitroimidazole tripod per $B(OH)_3$ in the asymmetric unit (Fig. 1).‡ Each of the unique imidazole rings has been assigned a letter to assist in the discussion below. All of the imidazole groups are involved in π–π stacking



Scheme 1 Illustration of compound **1**.

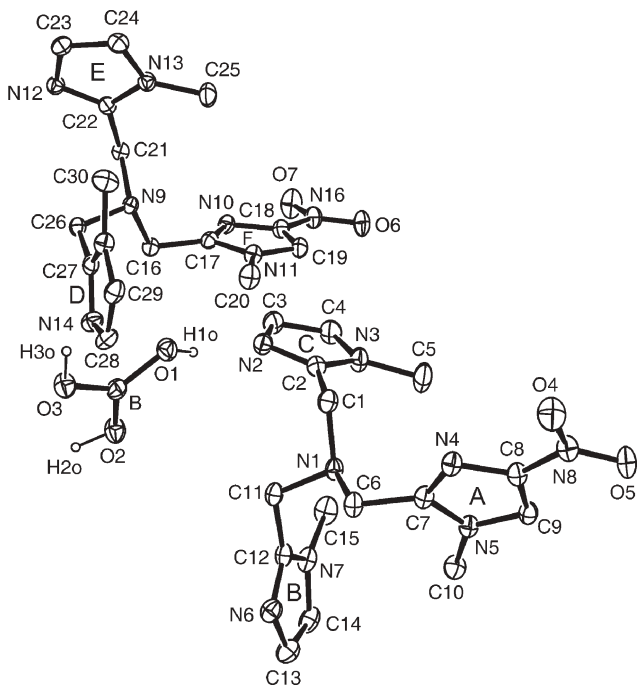


Fig. 1 An ORTEP[11] view of the three molecular components of **2**, shown with 50% probability displacement ellipsoids. All hydrogen atoms except those associated with the boric acid molecules have been omitted for clarity. Each individual imidazole ring has been assigned a letter from A to F.

† Electronic Supplementary Information (ESI) available: synthesis, crystallographic data and intermolecular contacts. See http://www.rsc.org/suppdata/cc/b4/b419040h/

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and three of the six imidazole pendants (C, D and E) are hydrogen bonded to a $B(OH)_3$ molecule. The bond distances and angles of the nitro-imidazole tripods and $B(OH)_3$ are consistent with those reported previously.[7b]

Fig. 2 shows views of the complementary antiparallel one-dimensional coils of **2** that extend along the crystallographic a axis. Also shown is the interlocking arrangement of its side-by-side coiled structure (c and d) stabilized by hydrogen bonding interactions between imidazole and $B(OH)_3$ molecules and π–π stacking between neighboring imidazole groups (see ESI Figs. S1–S5†).

Within each individual helix, two boric acid hydrogen atoms associated with O1 and O3 are strongly hydrogen bonded with nitrogen atoms, N2 and N14, associated with imidazole rings labeled C and D (Fig. 1) resulting in N···O separations of 2.761(2) and 2.808(2) Å and N···H–O angles of 165(2) and 174(2)°, respectively. Also the turn of the coil is stabilized by π–π stacks between nitro functionalized and non-functionalized imidazole rings (A···E and F···C). A slipped[12] π-stack is observed between ring C and the nitro group of ring F as reflected by the closest contact of 3.390 Å (Fig. S1†). A strong parallel π–π interaction occurs between ring E and the nitro group of ring A with a separation of 3.182 Å (Fig. S2†). The two complementary coils interlock forming a one-dimensional side-by-side coiled structure, as illustrated in Fig. 2 (c and d), *via* a third hydrogen bond between O2 of $B(OH)_3$ and the nitrogen atom N12 of ring E with a N···O separation of 2.788(2) Å and an O–H···N angle of 170(2)°. The resulting fusion of the two 1D coils into a larger interlocked structure shown in Fig. 2 (c and d) generates a continuous 1D channel contoured around the $B(OH)_3$ molecules. The boric acid molecules are stacked unsymmetrically in the channel with B–B separations of 7.311 and 8.587 Å. The B–B–B angle between neighboring boron atoms is 167° (Fig. S6†). The widest dimension of the channel is approximately 2.8 × 2.8 $Å^2$; ideally suited to accommodate a boric acid molecule whose molecular radius is 2.573 Å.[14] The narrowest region of the channel is 2.514 Å between N6 (ring B) and H11b of the methylene backbone of the tripod. In addition, Fig. 2 (c and d) also shows the opposing orientation of the nitro groups on the surface of neighboring coils.

Fig. 3 shows the arrangement of the coils bundled in the crystallographic bc plane and the different interactions that zip the individual units together. First, along the crystallographic c axis, adjacent bundles interlock *via* weak slipped π-stacks between the nitro C–N bonds of rings A and F with a separation of 4.111 Å (Fig. S3†). Also the nitro groups are weakly hydrogen bonded to symmetry related imidazole ring hydrogens associated with neighboring helices projected along the crystallographic b axis. The O5···H9″[15] separation between imidazole A rings is 2.542 Å and the O5···H9″–C9″ angle is 143° (Fig. S7†). Similarly, the nitro group of the same A ring is directed towards H24″ of ring E with a O5···H24″ separation of 2.375 Å and an O5···H24″–C24″ angle of 124°. In the same manner, O6″ of ring F is weakly interacting with H19″ of the symmetry related ring F and H4″ of ring C with separations of 2.571 and 2.491 Å and O6···H19″–C19″ and O6···H4″–C4″ angles of 141 and 176°, respectively (Fig. S8†). Comparable C–H···O bond distances and angles between aromatic C–H and nitro oxygen atoms have been observed in other structures.[16]

The supramolecular assembly of the interlocked coils of **2** is further stabilized by strong parallel π–π stacking of the two remaining imidazole rings, B and D, along the crystallographic b axis (Fig. S4–S5†). The separation between ring B and its symmetry related neighbor is 3.426 Å, and a shorter separation of 3.387 Å is observed between symmetry related D rings.

In conclusion, boric acid in the presence of **2** has been shown to effectively template the formation of a supramolecular structure containing 1D channels. The weak non-covalent interactions in **2** are important in supramolecular chemistry and mirror the forces influencing protein–protein associations in membranes and bundled helices and channels[18] used to transport ions, water, glycerol and other small molecules.[9] In fact, Popot *et al.*[19] have noted that the presence of weak van der Waals contacts on the surface of complementary helices, as well as the presence of surface prosthethic groups, favor side-to-side helical association. Therefore, **2** provides a unique glimpse of the effect of weak non-covalent interactions and the potential role of small molecules in templating the organization of supramolecular structures containing 1D channels as opposed to 2D layered structures. This study also supports our recent findings that weak van der Waals interactions involving imidazole compounds can produce supramolecular assemblies containing biologically relevant water channels with novel one-dimensional water structures.[8] Further studies in our lab are exploring the host–guest chemistry and supramolecular properties of other imidazole compounds. We

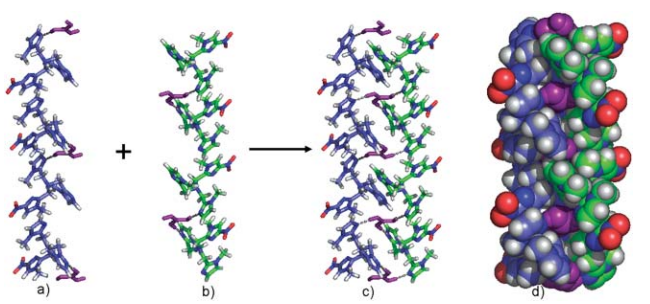

Fig. 2 Views[13] of the complementary antiparallel helices (a and b) of **2**, the capped stick representation (c) and space filling model (d) of the side-by-side coils along the crystallographic a axis.

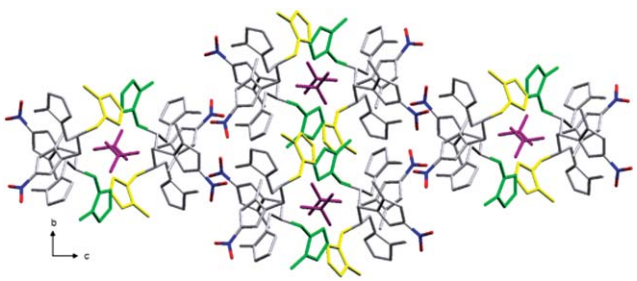

Fig. 3 Packing diagram[17] of **2** projected along the crystallographic bc plane showing the intermolecular hydrogen bonding (Fig. S7–S8†) and parallel π–π stacking interactions between neighboring interlocked coils (Fig. S4–S5†). $B(OH)_3$ are represented in purple, weak π interactions between imidazole nitro groups in blue (N) and red (O), and π–π stacking between imidazole rings B (green) and D (yellow). All hydrogen atoms have been omitted for clarity.

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Notes and references

‡ *Crystal data*. $C_{30}H_{40}N_{16}O_4 \cdot B(OH)_3$ (**2**), M = 750.61, 0.30 × 0.17 × 0.08 mm, monoclinic, space group $P2(1)/n$, a = 15.7997(18), b = 8.2540(9), c = 27.530(3) Å, β = 92.861(2)°, V = 3585.7(7) Å^3, ρ_{calcd} = 1.390 Mg m^{-3}, Z = 4, μ = 0.103 mm^{-1}, $2\theta_{max}$ = 3.04 to 56.60, Mo Kα radiation (λ = 0.71073 Å), T = 100 K, F(000) 1584, total reflections = 29945, independent reflections = 8345 (Rint = 0.027), observed data = 6562 ($I > 2\sigma(I)$), adsorption correction: SADABS (V 2.02).[20] CCDC 239617. See http://www.rsc.org/suppdata/cc/b4/b419040h/ for crystallographic data in CIF or other electronic format.

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10 (*a*) Compound **1** was prepared as described in the ESI section and isolated as a pale yellow oil in 58% yield. IR(film): ν = 1291 and 1503 cm^{-1} (NO_2); ^{1}H NMR ($CDCl_3$): δ = 7.6 (s, 1H, ^{nitro}Im(H5)), 6.9 (s, 2H, Im(H5)), 6.6 (s, 2H, Im(H4)), 3.9 (s, 2H, ^{nitro}Im(CH_2)), 3.8 (s, 4H, Im(CH_2)), 3.3 (s, 6H, Im(N–CH_3)), 3.3 (s, 3H, ^{nitro}Im(N–CH_3)); MS *m*/*z* 345.4 [M + H$^+$]; (b) Compound **2** was crystallized by dissolving 0.2 g (0.58 mmol) of **1** with 17 mg (0.29 mmol) of $B(OH)_3$ in 1 mL of ethyl acetate/methanol (1/1) and ether vapors were allowed to slowly diffuse into the solution.
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