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Construction of extended networks with a trimeric pyrazole synthon†

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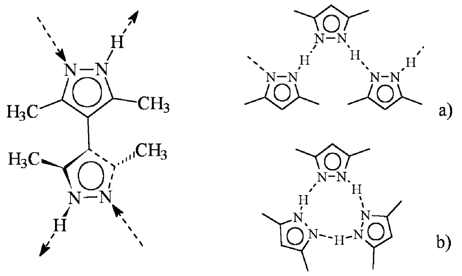
A H-bonded pyrazole trimeric motif drives the self-association of bifunctional tetramethyl-4,4′-bipyrazole, yielding highly interpenetrated 3D frameworks and allowing the engineering by design of a novel supramolecular isomer.

Crystal polymorphism[1] is a fundamental problem of crystal engineering, with many aspects poorly understood. In particular, it makes delineation of what structural information is required for prediction and design of materials difficult. This phenomenon is particularly characteristic for conformationally flexible molecules with multiple binding sites.[2,3] Diversity of crystal patterns by aggregation of self-complementary species is also particularly prevalent. This can occur when two self-complementary binding sites (for example, hydrogen bond donor and acceptor sites, *cf.* H_2O; side donor atoms and unsaturated coordination positions of metal atoms, *cf.* AlF_3)[4] are both available within a single molecular frame and generation of superstructures is feasible by just very simple self-association processes.



Scheme 1 The Me_4bpz tecton and the synthons for 3D supramolecular isomers: a) the catemer in the α- and β-forms, b) the trimer in the structure of the γ-polymorph.

In the realm of organic compounds these observations could be directly applied to the self-assembly behavior of 3,3′,5,5′-tetramethyl-substituted 4,4′-bipyrazole (Me_4bpz), which was recently introduced as a multi-purpose tecton for supramolecular synthesis.[5,6] The relationship of two Me_4bpz polymorphs,[5] both of which are built by simple N–H···N interconnection of all available H-bond donor (NH) and acceptor (N) sites, parallels that of the diamond and lonsdaleite topologies[4,7] and may indicate the existence of an even larger number of polytypes. An even more important aspect for the prediction of novel polymorphs and the realizing of their structure is the Me_4bpz network generated in the chloroform solvate **1**.‡ It demonstrates for the first time the utility of the H-bonded self-assembly of pyrazole oligomers as supramolecular synthons for developing of network solids in which the connectivity of the net point would originate in the nuclearity of the pyrazole pattern (di-, tri- and tetramers are known).[8] The 3D three-connected net in **1** is assembled employing the paradigmatic trimeric pyrazole motif (Fig. 1) and has chiral (10,3)-a (or $SrSi_2$) topology[4,7] in which carbon–carbon bonds link pyrazole trimers (Fig. 2, 3). This is illustrative of a general crystal engineering approach as the present 3D architecture is derived from 0D trimers of the corresponding monofunctional prototype, 3,5-dimethylpyrazole.[8] Though four identical nets (two pairs of opposite chirality) interpenetrate,[9] the resulting structure is very

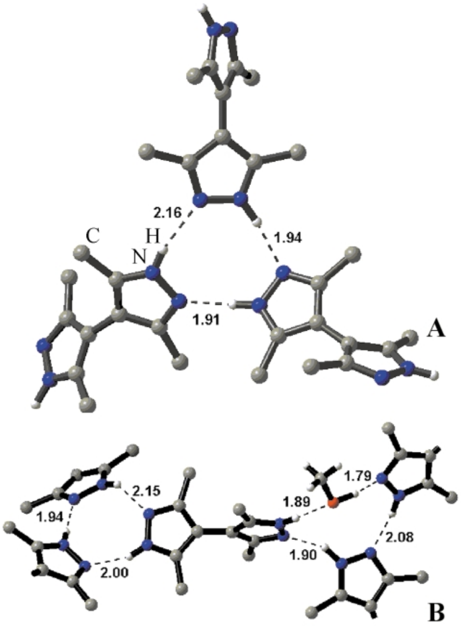


Fig. 1 The trimeric pyrazole motif that dominates self-association of Me_4bpz in structures **1** and **2** (A), and how a small molecule may be immobilized within this connectivity by H-bonding (structure **3**) (B).

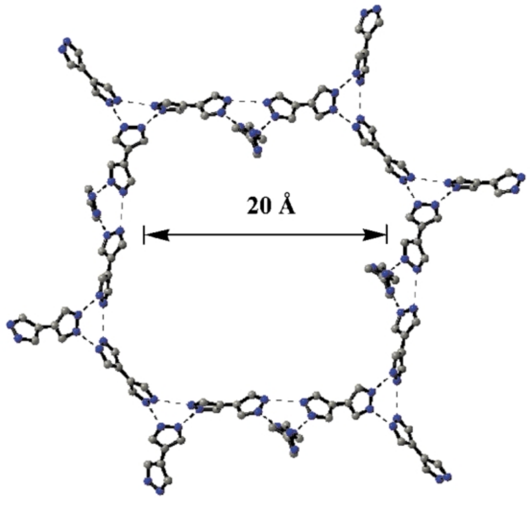


Fig. 2 The shortest circuit of the bipyrazolyl networks in structures **1** and **2**, which includes ten nodes (pyrazole trimers).

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† Electronic supplementary information (ESI) available: details for preparations, solvent-dependent polymorphism and pseudopolymorphism of the compound, crystal structure determination and refinement . See http://www.rsc.org/suppdata/cc/b2/b212540d/

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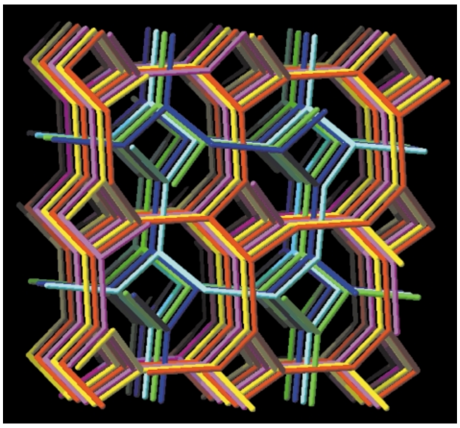

Fig. 3 The interpenetration of six nets of (10,3)-a topology (the nodes are the pyrazole trimers) in the structure of γ-Me_4bpz **2**. Elimination of one enanthiomeric pair (for example, red and blue) gives the four-fold interpenetrated ensemble seen in structure **1**.

open and occupies only 58.4% of the space,[10] with chloroform molecules enclathrated inside the holes.§

Following this scheme, the further incorporation of identical networks may eliminate the remaining crystal volume, and it was interesting to explore whether the space tiling is possible entirely by interpenetration of such 3D bipyrazole nets, *i.e.* does an additional polymorph exist and how it may be rationally designed? A five-fold interpenetrated system inherently generates molecular cages for housing of unwelcome guests from the solution, while the roughly estimated density (using the crystal data for **1**) for a six-fold ensemble is 1.19 g cm^{-3}, which exceeds by 8% that of the most dense of reported polymorphs. For this reason, the extra pressure obtained by synthesis under hydrothermal conditions was at least one of the important factors for successful engineering of a new γ-polymorphic form **2**, which is the densest of existing modifications (1.155 vs. 1.068 and 1.109 g cm^{-3}).[5] Nucleation and crystal growth were also strongly influenced by additional, presumably templating, factors as crystallization of γ-Me_4bpz requires catalytic amounts of metal ions in the solution.‡

The structure of γ-polymorph **2** completely retains the supramolecular motif observed for **1** and is supported by interpenetration of six identical (10,3)-a nets (three pairs of opposite handedness, Fig. 3). Dense packing of the nets is facilitated by a certain flexibility of tecton and synthon as may be seen from a comparison of **1** and **2**. Firstly, the interplanar angles within the frames of the twisted Me_4bpz molecules are slightly narrover (av. 55.0 **2** *vs.* 60.3° **1**) and thus the molecules adopt more a compact conformation. Secondly, the pyrazole trimers are somewhat expanded, as reflected by weaker hydrogen bonding (av. N···N 2.91 for **2** *vs.* 2.84 Å for **1**). This presumably provides for a certain minimization of the density and may possess an evident chemical significance for further modification of the structure.

Expansion of the trimer without alteration of the network connectivity may be reached with incorporation of suitable H-bond donating/accepting molecules within the cyclic structure. The methanol solvate 3Me_4bpz·MeOH **3** is clearly related to the parent structure of γ-Me_4bpz: six identical (10,3)-a nets interpenetrate. In this case half of the nodes are the same pyrazole trimer (av. N···N 2.86 Å), while the other half exist as trimers expanded by incorporation of methanol, NH···OH···N (Fig. 1, B), which lowers the crystallographic symmetry of the network, but has no appreciable impact on the overall supramolecular structure.

We believe that the fascinating supramolecular isomerism and polymorphism of structurally simple bipyrazole and related new self-complementary molecules are significant as they clearly outline prospects for "one-component supramolecular synthesis" relying on relatively strong intermolecular forces that can be easily understood and measured. Our results suggest wider possibilities for crystal design employing the trimeric pyrazole synthon, with direct access to a large number of 3D three-connected frameworks. The study also demonstrates control over the degree of network interpenetration and provides the first examples of six-fold interpenetrated (10,3)-a topologies, as well as for catemer/trimer supramolecular isomerism of pyrazoles.

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Notes and references

‡ Crystallization of Me_4bpz from commercial chloroform (1% EtOH) provides the solvate $Me_4bpz\cdot CHCl_3$ **1**, instead of α-Me_4bpz from absolute chloroform. Compound **1** is unstable under solution and decomposes in air within seconds. Solvate 3Me_4bpz·MeOH **3** was prepared from anhydrous methanol. For crystallization of γ-polymorph **2**, 0.190 g (1 mmol) Me_4bpz, 0.003 g (0.01 mmol) $Ni(NO_3)_2\cdot 6H_2O$ and 5 ml water, in a teflon vessel, were placed in a steel bomb, heated to 180 °C for 10 h and then cooled to r.t. over the period of 72 h. This afforded prisms of γ-Me_4bpz, instead of $Me_4bpz\cdot H_2O$ in the absence of metal, and of $Me_4bpz\cdot 0.5H_2O$ from water under ambient conditions. 5 mol% ZnO has the same effect on recrystallization of the compound, while cobalt and nickel acetates were inactive. We suggest that solvated complex ions of the type $M(Me_4bpz)_3^{2+}$ and $M(Me_4bpz)_4^{2+}$ possess the same shape and size as corresponding bipyrazole tri- and tetramers and are able to act as templates for nucleation and crystal growth.

§ Crystallographic measurements were made using IPDS Stoe and SMART CCD Siemens diffractometers (Mo-Kα, λ = 0.71073 Å). *Crystal data:*For $Me_4bpz\cdot CHCl_3$ **1**: $C_{11}H_{15}Cl_3N_4$, M = 309.62, tetragonal, space group $I4_1/a$ (no. 88), 173 K, a = 29.196(2), c = 22.406(2) Å, U = 19099(3) Å^3, Z = 48, μ = 5.65 cm^{-1}, θ_{max} 26.0°, 5091 unique data, $R1$ = 0.127 that is influenced by disordering of the solvent.

For γ-Me_4bpz **2**: $C_{10}H_{14}N_4$, M = 190.25, tetragonal, space group $I4_1cd$ (no. 110), 223 K, a = 27.619(3), c = 8.603(1) Å, U = 6563(1) Å^3, Z = 24, μ = 0.74 cm^{-1}, θ_{max} 28.3°, 2960 unique data, $R1$ = 0.046.

For 3Me_4bpz·MeOH **3**: $C_{31}H_{46}N_{12}O$, M = 602.80, orthorhombic, space group $Pbca$ (no. 61), 173 K, a = 26.183(1), b = 9.6386(4), c = 27.420(2) Å, U = 6919.7(7) Å^3, Z = 8, μ = 0.75 cm^{-1}, θ_{max} 25.9°, 5770 unique data, $R1$ = 0.047. CCDC 200495–200497. See http://www.rsc.org/suppdata/cc/b2/b212540d/ for crystallographic files in CIF or other electronic format.

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