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Interpenetration of distinct 2D and 3D organic networks in the crystal structure of 1,3,5-tris(4-methylbenzoyl)benzene

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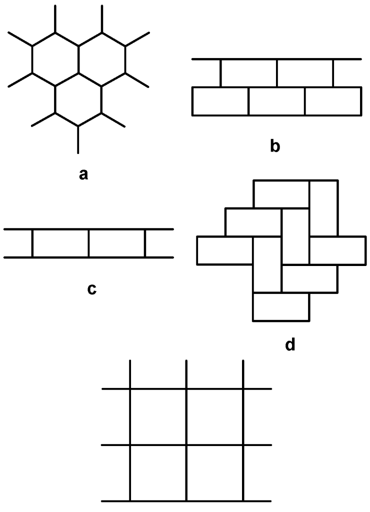
Conformational differences between two independent molecules in the same crystal of the title triaroylbenzene derivative give rise to an interpenetrated structure involving two dimensionally distinct networks—a 2D hexagonal and a 3D α-polonium-type.

The visualization of crystal structures as networks comprised of nodes linked by node connectors has greatly simplified many types of crystal engineering strategies.[1] In particular, net topology has proven invaluable for the rational design and classification of coordination polymers in which metal ions typically serve as nodes and polytopic ligands as node connectors.[2] Purely organic structures can be categorized as discrete networks according to this classification scheme as well; thus facilitating comparison of coordination polymers to organic crystal structures.[3] Often, descriptions of organic structures apply more liberal definitions of node and node connector that encompass abstract constructs such as molecular planes, hydrogen bonds, halogen–halogen interactions and edge-to-face π stacking interactions.

The ability to harness functional group and/or metal–ligand interactions in combination with molecular properties (such as size and shape) in the rational design and construction of specific solid-state supramolecular networks is a principal goal of crystal engineering.[2,4] In turn, it is envisioned that such designed networks may be imbued with pre-selected properties (*e.g.*, magnetic, optical, electronic, porous) through judicious choice of network building blocks. For example, various three- and four-connected building blocks have been employed in the construction of organic and metal–organic networks exhibiting the 2D topologies illustrated in Scheme 1. The honeycomb network (a (6,3) net, Scheme 1a) is encountered in various organic solids such as those incorporating trimesic acid,[5] cyclohexanetricarboxylic acid,[6] and triphenoxy triazenes.[7] Other topologically related three-connected networks such as brick wall (Scheme 1b), ladder (Scheme 1c), and herringbone (Scheme 1d) are less common in organic structures[3,8] but are frequently observed in coordination polymers.[9] The four-connected square grid network illustrated in Scheme 1e (a (4,4) net) represents another frequently observed network structure in both organic and metal–organic systems.[9]

The controlled self-assembly of interpenetrated frameworks in which two or more discrete complementary networks are intertwined *via* mechanical bonds constitutes a higher level of supramolecular design.[2] Interpenetrated networks are relatively common in coordination polymers and much progress has been made in developing approaches for synthesizing metal–organic architectures with predictable interpenetrated topologies.[2,9,10] Less frequently encountered are examples of interpenetration involving topologically non-identical networks.[2,11] In particular, such interpenetration in organic structures is quite rare and to the best of our knowledge there appears to be only one documented example.[12,13] As part of continuing studies exploring the supramolecular chemistry of triaroylbenzene derivatives,[14] we have examined the solid-state structure of 1,3,5-tris(4-methylbenzoyl)benzene and found that this material also self-assembles *via* interpenetration of two non-identical and purely organic networks. Moreover, the interpenetrated networks are not only non-identical, they also are of different dimensionality (*i.e*, 2D and 3D).

Relatively simple triaroylbenzenes have yielded a wealth of structural information relevant to contemporary studies of crystalline network design and engineering. For example, 1,3,5-tris(4-cyanobenzoyl)benzene (**1**) is obtained as a mixture of concomitant conformational polymorphs when recrystallized from acetone–H_2O.[15] In the presence of suitable solvates, however (*e.g.*, EtOAc, $MeNO_2$), **1** forms isostructural inclusion complexes in which the triaroylbenzene adopts a different polymeric network from that exhibited in either of the solvate-free polymorphs.[16] Alternatively, 1,3,5-tris(4-chlorobenzoyl)benzene (**2**) is obtained as a mixture of concomitant polymorphs when recrystallized from numerous solvents and displays no propensity for inclusion complex formation.[17] It appears that conformational flexibility inherent to the triaroylbenzene framework coupled with large numbers of hydrogen bond donor and acceptor sites contributes greatly to the observed polymorphism and enclathrating ability of **1** and **2**.



Scheme 1 Examples of common 2D networks: (a) honeycomb; (b) brick wall; (c) ladder; (d) herringbone; (e) square grid.

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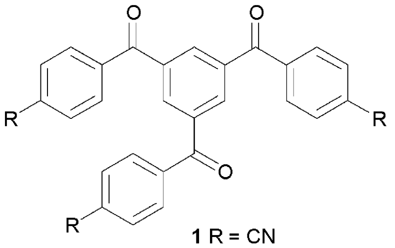

1 R = CN
2 R = Cl
3 R = CH_3

To further explore the solid-state properties of symmetrical triaroylbenzenes, the methyl derivative 1,3,5-tris(4-methylbenzoyl)benzene **3** was synthesized from benzene-1,3,5-tricarbonyl trichloride and toluene in 60% yield *via* Friedel–Crafts acylation.[18] Recrystallization of **3** from benzene afforded single crystals in the rhombohedral space group $R\bar{3}$ with two symmetry independent molecules (**A** and **B**) in the asymmetric unit. Both independent molecules are positioned on three-fold axes and retain their molecular symmetry in the crystal. The two independent molecules observed in the crystal structure of **3** differ in the rotation about the C–C bonds between the methylbenzoyl groups and the central 1,3,5-substituted benzene ring. The torsional angles are 131.3° and 36.5° for molecules **A** and **B**, respectively, and an overlay of the two independent molecules is given in Fig. 1a. The innate conformational differences in **A** and **B** are propagated throughout the crystal as each independent molecule is part of an independent polymeric network.

In the crystal structure, individual molecules of **A** form dimeric Piedfort units[19] with inversion related partners through C–H···O hydrogen bonding[20] involving aryl C–H donors and carbonyl acceptors (2.63 Å, 157.5°). Each Piedfort unit is connected to six symmetry related Piedfort units *via* C–H···O hydrogen bonding between methyl hydrogen donors and carbonyl acceptors as shown in Fig. 2 (2.37 Å, 153.5°, the methyl hydrogens were crystallographically located). Overall, this intermolecular arrangement produces a three-dimensional square grid network (or α-polonium type network) with each Piedfort dimer of **A** acting as a node and C–H···O hydrogen bonds serving as node connectors.

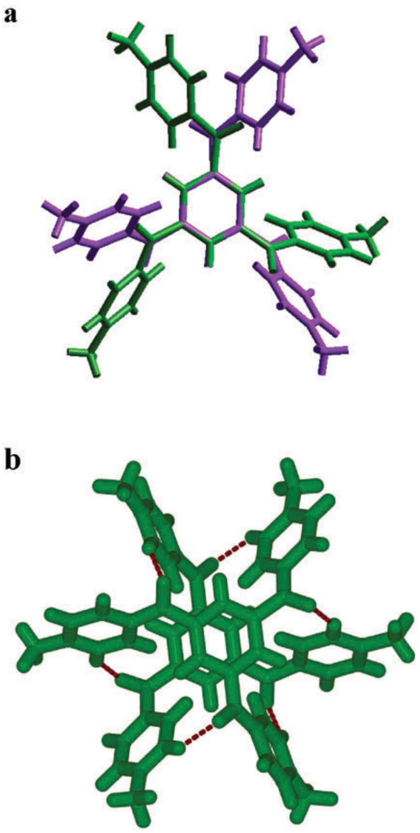

Fig. 1 (a) Overlay of two independent conformations observed in the crystal structure of 3 (molecule **A**—violet; molecule **B**—green). (b) Example of a dimeric Piedfort unit found in the structure of **3**.

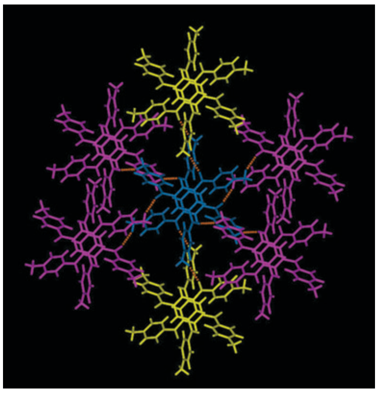

Fig. 2 3D Octahedral (α-Po-like) arrangement of Piedfort nodes in **3**. Central node = blue; "equatorial" nodes = violet; "axial" nodes = yellow. C–H···O hydrogen bonding indicated in orange.

In a similar fashion, each molecule of **B** stacks with an inversion related molecule to also form dimeric Piedfort units mediated by aryl C–H···O hydrogen bonding (2.53 Å, 150.3°). Each molecule in the Piedfort unit is connected to three of its inversion related neighbors (again *via* C–H···O hydrogen bonding –2.58 Å, 144.5°) to form a hexagonal network in the (110) plane as shown in Fig. 3. (It should be noted that for clarity only one layer of the Piedfort dimer array is shown.)

Thus, two distinct networks, a 3D α-Po type and a 2D hexagonal, co-exist in the crystal structure of **3**. Close packing is achieved through interpenetration of these two networks as shown in Fig. 4 (only one layer of each Piedfort unit is depicted). The α-Po network inserts through the 2D holes present in the honeycomb hexagonal framework. The two discrete networks are further connected by additional aryl C–H···O hydrogen bonds (2.68 Å, 160.4°). Interpenetration of two distinct structural motifs is a novel trait, even for coordination polymers.[9,10] As discussed previously, examples of interpenetrated organic networks with different topology are quite rare,[12] and the structure of **3** appears to represent the second documented instance of this phenomenon. The solid-state packing in **3** is further intriguing in that interpenetration involves distinct 2D and 3D networks.[21] This packing arrangement was observed under a number of crystallization conditions and attempts to form inclusion complexes with **3** and

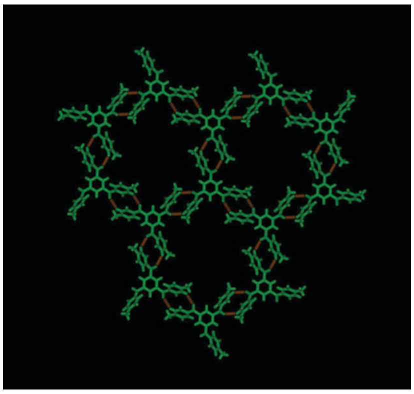

Fig. 3 The honeycomb (2D) pattern of **3** in (110). Only a single Piedfort layer is illustrated for clarity.

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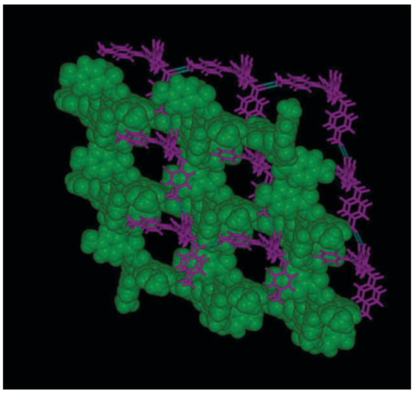

Fig. 4 Interpenetration of a 3D α-Po-type network (violet) and a 2D hexagonal network (green) in **3**. A single layer of each Piedfort unit is shown.

solvates such as benzene, toluene, xylene, DMSO, and nitrobenzene were unsuccessful.

In conclusion, triaroylbenzene **3** provides an interesting example of a trigonal molecule which, upon crystallization, leads to the novel interpenetration of distinct 3D α-Po and 2D hexagonal networks. Different conformations assumed by **3** in the same crystal structure result in the formation of two relatively diverse hydrogen bonding motifs. Close packing of these open hydrogen bonded networks is then achieved through interpenetration. This work highlights the architectural diversity that can be encountered in solid-state structures of conformationally flexible organic molecules while also illustrating the potential topological similarities between organic and metal–organic networks. Studies aimed at further defining the supramolecular chemistry of triaroylbenzenes are ongoing in our laboratory and results will be reported in due course.

Experimental

Synthesis[18]

A solution of benzene-1,3,5-tricarbonyl trichloride (1.33 g, 5 mmol) in toluene was added dropwise to a solution of $AlCl_3$ (2.00 g, 15 mmol) in toluene under an inert atmosphere over 45 minutes. The resulting mixture was stirred at rt for 4 h and then added to ice-cold water. The mixture was extracted with ethyl acetate, washed sequentially with water and brine, and dried over $MgSO_4$. Filtration and evaporation of the solvent afforded the crude product (1.30 g, 60%). Recrystallization of the crude product from benzene afforded colorless crystals of **3** suitable for analysis by X-ray diffractometry. The material prepared in this way exhibited spectral and physical properties (NMR, mp) identical to those previously reported.[22]

Crystal data

Preliminary examination and data collection were performed using a Bruker SMART CCD area detector system single crystal X-ray diffractometer. The SHELXTL-PLUS software package was used for structure solution and refinement.[23] Hydrogens were fixed at idealized geometries and treated isotropically as riding groups.

Rhombohedral, $R\bar{3}$, $a = 21.7465(10)$, $b = 21.7465(10)$, $c = 16.8412(15)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 120°$, $V = 6897.3(8)$ Å^3, $Z = 12$, $D_c = 1.249$ g cm^{-3}, $T = 295$ K, $F(000) = 2736$ $\lambda = 0.71073$ Å , $\mu = 0.080$, $R1 = 0.0544$ for 2557 $F_o > 2\sigma(o)$, $wR = 0.1394$. CCDC reference numbers 244725. See http://www.rsc.org/suppdata/nj/b4/b408481k/ for crystallographic data in .cif or other electronic format.

Acknowledgements

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