Disruption of the hexagonal networks of trimesic acid (benzene-1,3,5-tricarboxylic acid, TMA) by acetic acid

Ilana Goldberg and Joel Bernstein*

Received (in Austin, TX, USA) 30th June 2006, Accepted 29th August 2006
First published as an Advance Article on the web 24th October 2006
DOI: 10.1039/b609263b

The single crystal X-ray structure of the acetic acid solvate of trimesic acid shows the complete disruption of the hydrogen-bonded hexagonal networks of TMA by bonding to an acetic acid molecule.

Trimesic acid (benzene-1,3,5-tricarboxylic acid, TMA) is a widely studied molecule, in part due the versatile range of solid state compounds it can form. In crystals, this molecule predictably forms hydrogen-bonded hexagonal networks with a variety of supramolecular structural properties such as catenation, interpenetration, polymorphism and inclusion.[1] These hexagonal networks have become of great interest due to their low-density, non-covalent interactions, which have potential applications in designer solids for separations, catalysis and electronic materials.[2] Networks can be unary, containing only TMA, as well as binary, containing TMA linked in an ordered fashion to other molecules. Examples of structures where unary and binary networks are combined in a single structure also exist.[3] The original structure of TMA, which has been termed α-TMA by Herbstein,[3] who also reports the existence of two high-temperature polymorphs, β- and γ-TMA, has a unary hexagonal ("chicken wire") network, formed from the hydrogen bonding of the carboxylic acid groups of TMA in the $R_2^2(8)$ pattern.[3–5] The binary network has been shown to exhibit a preference for the $R_4^4(12)$ pattern with amine groups,[2] while with alcohols is known to form the $R_3^3(10)$ pattern for singly-bridged and the $R_4^4(12)$ pattern for doubly-bridged dimer motifs (Fig. 1).[6] Here, we report the structure of the acetic acid solvate of TMA, where the hexagonal networks along the ac plane are disrupted after every second ring network by the hydrogen bonding from a carboxylic acid group of TMA to an acetic acid in the $R_2^2(8)$ pattern (Fig. 2).

In attempting to prepare hydrogen-bonded co-crystals between 1-naphthylamine and TMA we serendipitously discovered the acetic acid solvate of TMA. Yellow prism-shaped crystals were obtained by making solutions of about 200 mM TMA dissolved in ethanol and roughly 100 mM 1-napththylamine dissolved in chloroform. A layering technique of the solutions, as prescribed by Otter and Neudorfl,[7] was used to obtain the crystals. In a slim vial, 0.5 mL of the TMA solution was layered under 0.5 mL of acetic acid, which was finally layered under 0.5 mL of the 1-naphthylamine solution. The vial was covered by parafilm, in which tiny holes were punched, and placed on a shelf at room temperature. After a few days of diffusion, a precipitate began to form. After a few weeks, single crystals suitable for X-ray structure determination formed under a layer of precipitate.†

The basic structure of this compound is analogous to the α-TMA structure, in that both have six molecules of TMA in the asymmetric unit and both are composed of two sets of three parallel hexagonal networks that are triply-catenated.[3,4] However, both of the hexagonal networks in the α-TMA structure are unary, infinite networks, whereas in the acetic acid solvate, one of these networks is binary and the hydrogen bonding of the TMA molecules is completely disrupted after every second ring formation. This is in contrast to other binary networks of TMA, where the guest molecule forms part of the network and, in effect, changes only the hydrogen bonding pattern in it.[2,6] To the best of our knowledge, no other binary network of TMA has its hydrogen-bonded network disrupted to this degree. In this binary network, the acetic acid molecule is hydrogen-bonded to the O_{48}–C_{48}–$O_{48'}$ carboxylic acid group of the TMA molecule in an $R_2^2(8)$ pattern. The carboxylic acid groups of the TMA molecules are generally rotated out of the plane of the benzene ring by around 5°; however, the carboxylic acid O_{48}–C_{48}–$O_{48'}$ group is rotated out of the plane of the benzene ring by 28.12° to form a hydrogen bond

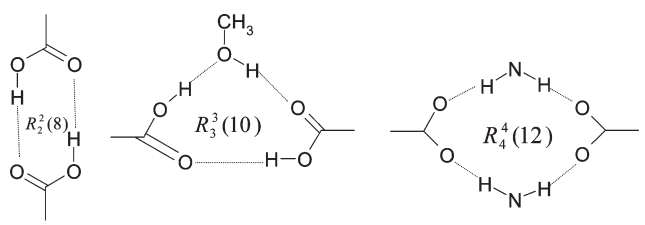

Fig. 1 Hydrogen bonding patterns. Hydrogen bonds are shown with dashed lines.

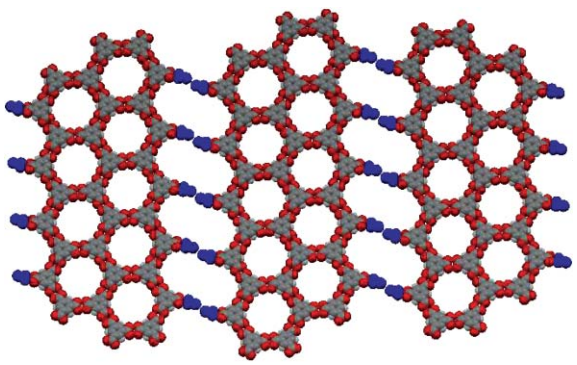

Fig. 2 Space filling model along the ac plane of the binary network showing the disruption of the hexagonal network. Acetic acid molecules disrupting the plane are shown in blue, carbon atoms of the TMA network are show in grey and oxygen atoms are shown in red. All other atoms and molecules have been omitted for clarity.

Department of Chemistry, Ben-Gurion University of the Negev, Be'er Sheva, Israel. E-mail: yoel@bgu.ac.il; Fax: +972 8 6477641; Tel: +972 8 6461187

to the acetic acid molecule in the binary network (estimated standard deviation for the angles of the TMA structure range from 0.05–0.08°). The O···O distances for the hydrogen bonding of the carboxylic acid groups of the TMA molecules range from 2.604 to 2.656 Å in the chicken wire network. However, O···O the distances of a TMA carboxylic acid from an acetic acid molecule are slightly larger, between 2.614 and 2.696 Å (estimated standard deviation ranges from 0.006–0.008 Å). The cavities in the hydrogen-bonded network are 14.3 × 15.4 Å, as estimated by atomic centers, and are comparable with those in the α-TMA structure.[4] The distance between each of the disrupted networks is 3.764 Å, which is significantly longer than any of the O···O distances in the hexagonal network.

The C–O distances for the carboxyl groups of the TMA vary from 1.278 to 1.232 Å. While there is a clear indication that the C–O and the C=O groups can be distinguished, no absolute determination between them can be made.

Acetic acid molecules fill the cavities in the region of the triple catenation. There are two sets of two acetic acid molecules in a $R_2^2(8)$ pattern that are found inside the binary network of TMA rings, and which are highly disordered (Fig. 3). This is not uncommon, as guest molecules contained in tunnels are often disordered at room temperature.[3] The C–O distances for the acetic acid molecules vary from 1.201 to 1.415 Å. Due to the high disorder of the molecules found in the chicken wire structure of the TMA molecules, the C–O and C=O bonds are not distinguishable. However, these values are typical for acetic acid dimers, being approximately 1.3 Å for the C–O and 1.2 Å for the C=O. The O···O distances for the hydrogen bonding of the acetic acid dimers are 2.657 and 2.577 Å—in agreement with expected values.

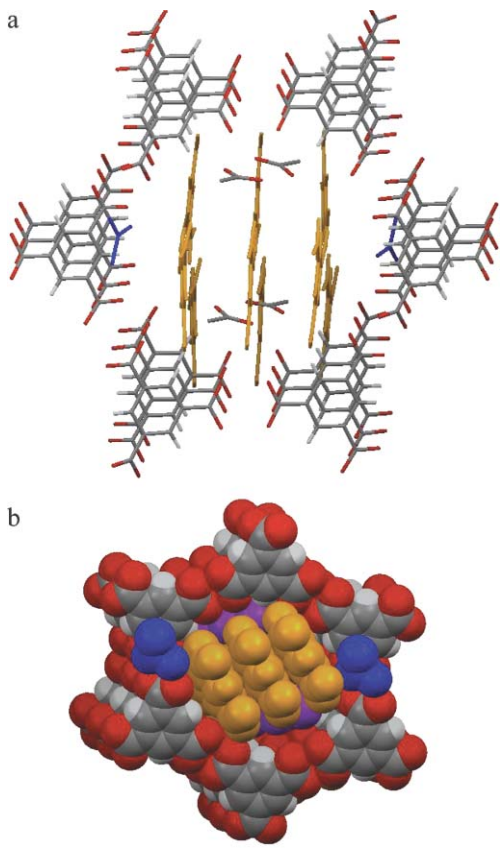

Fig. 3 The complete structure of the acetic acid solvent of TMA. Carbon atoms are shown in dark grey, oxygen atoms are shown in red and hydrogen atoms are shown in light grey for the TMA molecules of the binary network, with acetic acid molecules shown in blue. The unary network of TMA rings is shown in orange. Acetic acid molecules inside the rings of the binary networks: Oxygen is shown in red and carbon is shown in grey for a, and all of these elements are shown in purple for b. a: Wire frame diagram along the plane (40 $\bar{4}$). b: Space filling diagram perpendicular to the plane of the unary network of TMA molecules.

It has been pointed out to us that the $R_2^2(8)$ pattern with two different carboxylic acid molecules is quite rare. In order to confirm this, a search of the Cambridge Structural Database (Conquest v1.8, CCDC, 2006) using the term carboxylic acid and the $R_2^2(8)$ pattern (drawing) was performed. This search yielded 789 hits. Of these 789 hits, 50 structures included two different carboxylic acid groups. Of these 50 structures, 19 exhibited the $R_2^2(8)$ pattern with two different carboxylic acids. However, the first four of these structures included bis(1,1′-binaphthyl-2,2′-dicarbxylic acid) with four different second carboxylic acids (propionic, butyric, acetic and valeric) (CSD Refcodes AJUSED, AJUSIH, AJUSON and AJUSUT). There is another case similar to this in *trans*-dichloro-bis(1′-(diphenylphosphino)ferrocene carboxylic acid-*P*)-platinum(II) acetic acid solvate, where the only difference between the two structures is that the platinum is substituted for a palladium (Refcodes POZVEF and POZVOP). There are seven structures of the same co-crystal of *ortho*-ethoxy-*trans*-cinnamic acid and 2,2′-diethoxy-truxillic acid that do not appear to be polymorphs (Refcodes AWAJOX and AWAJOX06). Interestingly, there are seven structures with two different carboxylic acids that have the $R_2^2(8)$ pattern, in which one of them is acetic acid (Refcodes AJUSON, OGAWUO, POZUEF, POZVOP, SIMPMIN, VEVLOX and ZOZSEM).

I. G. thanks the Fulbright Foundation for a fellowship administered by the United States–Israel Educational Foundation. The research was supported by grant no. 2004118 from the United States–Israel Binational Science Foundation (BSF), Jerusalem, Israel.

Notes and references

† Crystal data: $(C_9O_6H_6)_3C_2O_2H_4$, M = 681.288, triclinic, $P\bar{1}$, a = 15.626(3), b = 16.476(3), c = 16.562(3) Å, α = 118.31(3), β = 117.91(3), γ = 91.61(3)°, U = 3141(1) Å^3, T = 293(2) K, Z = 18 (6 molecules of TMA and 3 molecules of acetic acid in the asymmetric unit), μ(Mo-Kα) = 0.132 mm^{-1}, data were collected in the range 1.48–28.32° (ω scan), 27675 reflections measured, 15566 unique (R_{int} = 0.1051). Final R_1 = 0.0770 ($F_o > 4\sigma(F_o)$) and wR_2 = 0.1970. Disordered solvent molecules are present in the structure.

Crystal data were collected on a Bruker SMART 6 K CCD diffractometer. Programs: Bruker SMART[8] (control), SAINT (integration), Bruker AXS SHELXTL[9–11] (structure solution and refinement), PLATON[12] (to check for higher symmetry) and Mercury (for viewing the molecule and creating diagrams). CCDC 612917. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b609263b

1 C. V. K. Sharma and M. J. Zaworotko, *Chem. Commun.*, 1996, 2655–2656.
2 D. J. Plaut, K. M. Laund and M. D. Ward, *Chem. Commun.*, 2000, 769–770.
3 F. H. Herbstein, *Crystalline Molecular Complexes and Compounds*, Oxford University Press, London, 2005, vol. 1; F. H. Herbstein, *Top. Curr. Chem.*, 1987, **40**, 107–139; F. H. Herbstein, M. Kapon and V. Shteiman, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst.*

Chem., 1978, **34**, 1613–1617; F. H. Herbstein, M. Kapon and G. M. Reisner, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1985, **41**, 348–354.
4 D. Duchamp and R. Marsh, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1969, **25**, 5–19.
5 J. Bernstein, R. E. Davis, L. Shimoni and N. L. Chang, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1555–1575; M. C. Etter, *Acc. Chem. Res.*, 1990, **23**, 120–126.
6 S. H. Dale, M. R. J. Elsegood and S. J. Richards, *Chem. Commun.*, 2004, 1278–1279.
7 E. Otter and J. Neudorfl, *Helv. Chim. Acta*, 2001, **84**, 1268–1312.
8 *SAINT+: release 6.22*, Bruker Analytical Systems, Madison, Wisconsin, USA, 2001.
9 G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997.
10 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.
11 G. M. Sheldrick, *SHELXTL-Plus: release 6.10*, Bruker Analytical Systems, Madison, Wisconsin, USA, 2000.
12 A. L. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, C34.

