Supramolecular Architectures Constructed by Strong Hydrogen Bonds. Crystal Structures of Novel One-Dimensional Polycatenane and Three-Dimensional Interpenetrated Network

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(Received May 21, 2002; CL-020444)

We report novel supramolecular architectures based on flexible benzene-1,3,5-triacetic acid (bta) through strong hydrogen bonds. Partial deprotonated triacid forms a novel one-dimensional (1D) polycatenated chain $(NH_4)_{1.5}[1,3,5\text{-}C_6H_3(CH_2COOH)_{1.5}(CH_2COO)_{1.5}]$ (**1**). While in the case of compound bta·H_2O (**2**) with non-deprotonated triacid, a three-dimensional (3D) interpenetrated network was self-organized by strong O–H···O hydrogen bonds. The conformation of flexible triacid is *cis*, *cis*, *cis* in **1** and *cis*, *trans*, *trans* in **2**.

Hydrogen bonding, one of the most important non-covalent interactions, has been proved to play important roles in the construction and stabilization of molecular structures, and it can provide practicable methods for design of molecules with specific topologies.[1] Especially in the biological system, simple units are organized into aggregates efficiently with intricate functions by non-covalent interactions. A number of hydrogen-bonded aggregates have been obtained by self-organization of organic and organic-inorganic components.[2–4] Among them, there are many recent reports of the utilization of carboxylic acids, e.g. 1,3,5-benzenetricarboxylic acid (btc), 1,4-benzenedicarboxylic acid etc, in crystal engineering due to the hydrogen bonding and coordination ability of carboxylate group.[4] However, most of these acids used in crystal engineering are rigid, i.e. the carboxylate groups attached directly to the central benzene ring. In this paper, we report novel one-dimensional (1D) polycatenene $(NH_4)_{1.5}[1,3,5\text{-}C_6H_3(CH_2COOH)_{1.5}(CH_2COO)_{1.5}]$ (**1**) and three-dimensional (3D) interpenetrated network bta·H_2O (**2**), based on a flexible benzene-1,3,5-triacetic acid (bta) through strong hydrogen bonds. The structural analysis shows that **1** is consisted of ladders and two ladders interpenetrate each other to generate an 1D polycatenated structure. To the best of our knowledge, **1** is the first example of 1D chain-like polycatenane constructed by strong hydrogen bonds, though polycatenaned Cu(I) ladders formed by coordination bonds have been reported.[5]

The crystals of **1** were obtained with yield of ca. 40% by layering method between a solution of bta in acetone and a freshly prepared aqueous solution of $[Ag(NH_3)_2]NO_3$ in DMSO (H_2O : DMSO, 1 : 4 v/v). TGA data of **1** indicate that **1** has thermal stability to ca. 180 °C. Crystallographic studies show that part of the triacid bta were deprotonated and the ammonium ions exist as counter cations.[6] It is interesting that the silver(I) ions are absent in **1**. The anions of partial deprotonated triacid are linked by strong O–H···O hydrogen bonds [O(3)···O(1A) = O(1)···O(3B) = 2.495(1) Å, O(6)···O(6C) = 2.443(3) Å; O(3)–H(10)–O(1A) = O(1)–H(10B)–O(3B) = 177°, O(6)–H(11)–O(6C) = 180.0°] to form an infinite 1D double stranded chains (Figure 1a). It is clear that the H(11) is shared by two carbonyl oxygen atoms [O(6) and O(6C)] with the bond distances of O(6)–H(11)=O(6C)–H(11)=1.2215(10) Å, i.e. the O(6)–H(11)–O(6C) is a symmetric hydrogen bond. While the hydrogen bond O(3)–H(10)···O(1A) is asymmetric with bond lengths of O(3)–H(10) = 1.20(2) Å, H(10)···O(1) = 1.30(2) Å, respectively. Such unusually strong hydrogen bonds are known as low-barrier hydrogen bonds (LBHB) and have been supported by experimental and theoretical data.[7] Every four triacid anions linked by four O–H···O hydrogen bonds form a window with a length (between the centroids of the benzene rings **A** and **B**) of 10.02 Å and a breadth (between the centroids of benzene rings **A** and **C**) of 9.52 Å. The structure of this double stranded chain resembles a ladder made up of edge sharing 40-membered rhombohedra. Similar ladder motif has been reported in Co(II) complex with btc, 2,2′-bipyridine and water ligands.[8]

The remarkable structural feature of **1** is that the large rhombohedra between the rungs of the ladder allow the inclusion of another ladder generating a polycatenated structure as shown in Figure 1b. The dihedral angle of 83 ° between two average planes of polycatenated two ladders implies a near perpendicular interpenetration. The observed 1D polycatenated structure of **1** is stabilized by formation of N–H···O hydrogen bonds due to the presence of ammonium cations. In the asymmetric unit of **1**, the ammonium ion binds to the triacid through three N–H···O hydrogen bonds similar to previously reported parachute-like non-covalent complex obtained by zinc tetrachloride and 1,3,5-tris(1-methylimidazol-2-ylmethyl)-2,4,6-trimethylbenzene through triple N–H···Cl hydrogen bonds.[9] There are two additional N–H···O hydrogen bonds in **1** between the ammonium ion and the carbonyl oxygen atoms of the neighboring ladder.

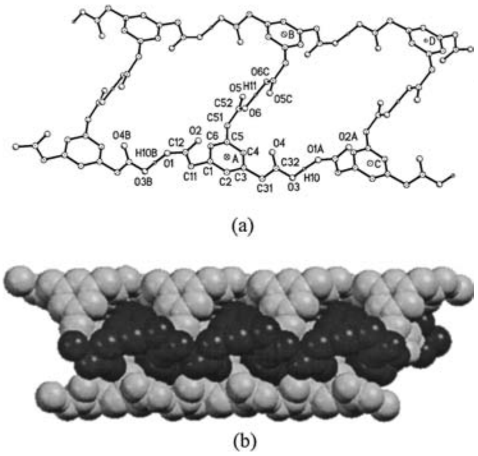
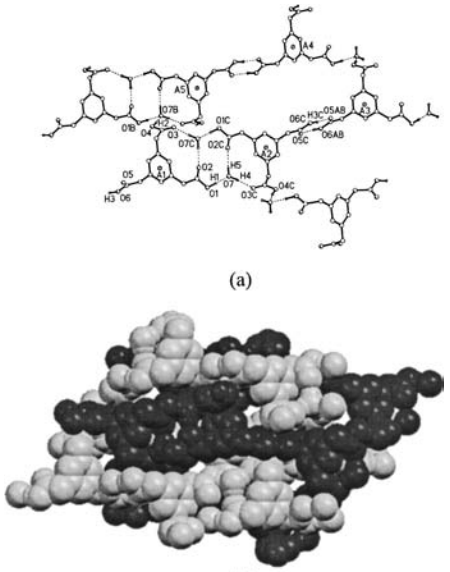


Figure 1. (a) 1D ladder structure of **1**. Hydrogen atoms not involved in hydrogen bonding and ammonium cations were omitted for clarity; (b) space-filling 1D polycatenaned structure of **1**.

The compound **2** was obtained by recrystallization of bta from hot water with yield of 90%.[10] In contrast to the partial deprotonation of bta in **1**, the triacid of bta in **2** is neutral without deprotonation; however, there is one molecule of water per bta participating the formation of hydrogen bonds as illustrated in Figure 2a. TGA data of **2** showed that the water lost around 70 °C and the residue is stable to 260 °C. There are five strong O–H···O hydrogen bonds with distances and angles: O1–O7 = 2.675(3) Å, O1–H1–O7 = 177°; O4–O7B = 2.671(2) Å, O4–H2–O7B = 170°; O6C–O5AB = 2.653(2) Å, O6C–H3C–O5AB = 175°, O7–O3C = 2.728(2) Å, O7–H4–O3C = 170°; O7–O2C = 2.782(2) Å, O7–H5–O2C = 175°. It is noteworthy that each water molecule forms four hydrogen bonds with tetrahedral geometry (e.g. O7B in Figure 2a), two of which serve as donor of the hydrogen bonds with carbonyl and the other two of which act as acceptor of the hydrogen bonds with hydroxyl group of the triacid. These hydrogen bonds link the bta and water molecules to generate a 3D network structure (Figure 2a), where there are small macrocyclic rings formed by water and bta molecules with the benzene rings **A1** and **A2**, and large macrocyclic rings formed by water and bta with the benzene rings **A2**, **A3**, **A4** and **A5** in Figure 2a. The large macrocyclic ring is spacious enough to include another 3D network to produce interpenetrated structure as exhibited in Figure 2b. There are weak π-π interactions between two benzene rings of the interpenetrated network with the nearest distance of 4.4 Å.



(a)

(b)

Figure 2. (a) Hydrogen bonds indicated by dashed lines in **2**; (b) space filling diagram of the 3D interpenetrated network of **2**.

In the compounds **1** and **2**, the triacid bta is flexible because of the presence of methylene group between the central benzene ring and terminal carboxylate group, and can adopt two different conformations, *cis*, *cis*, *cis* and *cis*, *trans*, *trans*, as observed in the 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene.[11] It has been reported that the bta with *cis*, *trans*, *trans* conformation forms 1D ladder-like chains defined by the O–H···O (carbonyl) hydrogen bonds of 8-membered cyclic dimer interactions.[12] However, our compound **2** shows greatly changed hydrogen bonding pattern due to the presence of water molecule although the bta in **2** is also *cis*, *trans*, *trans* conformation. While in the case of **1**, the partially deprotonated bta adopts *cis*, *cis*, *cis* conformations and forms polycatenated ladder-like chains. The number of O–H···O hydrogen bonds in **1** is reduced, yet the strength is greatly enhanced. In addition, partially or fully deprotonated salts of H_3btc invariably react with amines to afford salts with flat hydrogen-bonded sheet structures.[13]

In conclusion, the flexible bta triacid was demonstrated to form 1D polycatenaned ladder and 3D interpenetrated network structures with different conformations for the first time.

We thank the National Nature Science Foundation of China for financial support.

References and Notes

1 a) D. Braga, F. Grepioni, and G. R. Desiraju, *Chem. Rev.*, **98**, 1375 (1998). b) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, **101**, 1629 (2001). c) M. M. Conn and J. Rebek, Jr., *Chem. Rev.*, **97**, 1647 (1997). d) D. S. Lawrence, T. Jiang, and M. Levett, *Chem. Rev.*, **95**, 2229 (1995).

2 a) A. Marsh, M. Silvestri, and J.-M. Lehn, *Chem. Commun.*, **1996**, 1527. b) O. Félix, M. W. Hosseini, A. De Cian, and J. Fischer, *Angew. Chem., Int. Ed. Engl.*, **36**, 102 (1997). c) D. J. Pesak and J. S. Moore, *Angew. Chem., Int. Ed. Engl.*, **36**, 1633 (1997). d) A. Kraft and R. Fröhlich, *Chem. Commun.*, **1998**, 1085. e) O. Ermer and J. Neudörfl, *Chem.—Eur. J.*, **7**, 4961 (2001). f) D. J. Plaut, K. M. Lund, and M. D. Ward, *Chem. Commun.*, **2000**, 769.

3 a) G. M. Whitesides, E. E. Simanek, J. P. Mathlas, C. T. Seto, D. N. Chin, M. Mammen, and D. M. Gordon, *Acc. Chem. Res.*, **28**, 37 (1995). b) P. N. W. Baxter, J.-M. Lehn, J. Fischer, and M.-T. Youinou, *Angew. Chem., Int. Ed. Engl.*, **33**, 2284 (1994).

4 a) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, and O. M. Yaghi, *Acc. Chem. Res.*, **34**, 319 (2001). b) S. V. Kolotuchin, P. A. Thiessen, E. E. Fenlon, S. R. Wilson, C. J. Loweth, and S. C. Zimmerman, *Chem.—Eur. J.*, **5**, 2537 (1999). c) T. J. Prior and M. J. Rosseinsky, *Chem. Commun.*, **2001**, 1222. d) T. J. Prior and M. J. Rosseinsky, *Chem. Commun.*, **2001**, 495. e) R. Liu, K. F. Mok, and S. Valiyaveettil, *New J. Chem.*, **25**, 890 (2001).

5 A. J. Blake, N. R. Champness, A. Khlobystov, D. A. Lemenovskii, W.-S. Li, and M. Schröder, *Chem. Commun.*, **1997**, 2027.

6 The compound bta was prepared according to the method reported in the literature: M. S. Newman, and H. S. Lowrie, *J. Am. Chem. Soc.*, **76**, 6196 (1954). The data collection for **1** and **2** were carried on a Rigaku RAXIS-RAPID Imaging Plate diffractometer by $\omega - 2\theta$ scan techniques using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), $T = 200$ K. The structures were solved by direct methods with SIR92. All non-hydrogen atoms were refined anisotropically by the full-matrix least-square method. All the hydrogen atoms were found from experimental data directly, their position and isotropic thermal parameters were refined. Crystal data for **1**: $C_{12}H_{16.5}N_{1.5}O_6$, $M = 277.77$, monoclinic, space group $I1$ 2/a 1 (#15), $a = 10.0199(4)$, $b = 10.9079(4)$, $c = 23.1238(9)$ Å, $\beta = 89.2880(10)°$, $V = 2527.15(17)$ Å^3, $Z = 8$, $D_{\text{calcd}} = 1.460$ g/cm^3, $\mu = 0.118$ mm^{-1}, $F(000) = 1176$. Total 5481 reflections were collected of which 2896 are independent ($R_{\text{int}} = 0.0284$). The final $R1 = 0.0342$ [$I > 2\sigma(I)$].

7 a) Y. Kato, L. M. Toledo, and J. Rebek, Jr., *J. Am. Chem. Soc.*, **118**, 8575 (1996). b) P. Gilli, V. Bertolasi, V. Ferretti, and G. Gilli, *J. Am. Chem. Soc.*, **116**, 909 (1994). c) M. Garcia-Viloca, A. González-Lafont, and J. M. Lluch, *J. Am. Chem. Soc.*, **119**, 1081 (1997).

8 M. J. Plater, M. R. St. J. Foreman, E. Coronado, C. J. Gómez-García, and A. M. Z. Slawin, *J. Chem. Soc., Dalton Trans.*, **1999**, 4209.

9 W. Y. Sun, J. Xie, T. Okamura, C. K. Huang, and N. Ueyama, *Chem. Commun.*, **2000**, 1429.

10 Crystal data for **2**: $C_{12}H_{14}O_7$, $M = 270.23$, monoclinic, space group $C2/c$, $a = 21.0829(18)$, $b = 8.7082(7)$, $c = 16.8213(18)$ Å, $\beta = 123.185(3)°$, $V = 2584.6(4)$ Å^3, $Z = 8$, $d_c = 1.389$ g/cm^3, $\mu = 0.116$ mm^{-1}, $F(000) = 1136$. Total 5314 reflections were collected of which 2942 are independent ($R_{\text{int}} = 0.0463$). The final $R1 = 0.0408$ [$I > 2\sigma(I)$].

11 a) W. Y. Sun, J. Fan, T. Okamura, J. Xie, K. B. Yu, and N. Ueyama, *Chem.—Eur. J.*, **7**, 2557 (2001). b) H. K. Liu, W. Y. Sun, W. X. Tang, T. Yamamoto, and N. Ueyama, *Inorg. Chem.*, **38**, 6313 (1999).

12 a) L. J. Fitzgerald and R. E. Gerkin, *Acta Crystallogr.*, **C53**, 967 (1997). b) S. R. Batten, *Acta Crystallogr.*, **C54**, 1193 (1998).

13 a) C. V. K. Sharma, C. B. Bauer, R. D. Rogers, and M. J. Zaworotko, *Chem. Commun.*, **1997**, 1559. b) R. E. Melendez, C. V. K. Sharma, M. J. Zaworotko, C. Bauer, and R. D. Rogers, *Angew. Chem., Int. Ed.*, **35**, 2213 (1996).