Molecular Tectonics. Porous Hydrogen-Bonded Networks with Unprecedented Structural Integrity

Philippe Brunet, Michel Simard,[1] and James D. Wuest*

Département de Chimie, Université de Montréal
Montréal, Québec, H3C 3J7 Canada

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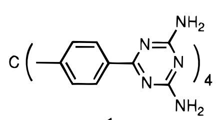
Tectons are molecules whose interactions are dominated by specific attractive forces that induce the assembly of aggregates with controlled geometries, and *molecular tectonics* is the art and science of supramolecular construction using tectonic subunits.[2] We have previously demonstrated that the strategy of molecular tectonics can be used to create predictably ordered three-dimensional networks linked by hydrogen bonds, and we have shown that these networks can have properties similar to those of zeolites and related inorganic materials, including the selective inclusion of guests, potentially large void volumes, and adjustable porosity.[2−4] Hydrogen-bonded networks are considered to be intrinsically less robust than inorganic analogues, which are held together by bonds that are individually much stronger. However, the integrity of hydrogen-bonded networks can in principle be increased by increasing the number or strength of the hydrogen bonds in which each tectonic subunit participates. We have now found that crystallization of tecton **1** generates porous inclusion compounds in which each tecton is held in position by 16 intertectonic hydrogen bonds, thereby creating a three-dimensional network so robust that it remains ordered even when most of the guests are removed.



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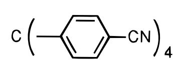

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Tecton **1** was synthesized in 90% yield by treating the known nitrile **2**[5] with dicyandiamide.[6,7] Crystallization was achieved by allowing dioxane to diffuse into solutions of tecton **1** in formic acid. This procedure produced inclusion compounds containing variable ratios of formic acid and dioxane depending on the precise conditions of crystallization; however, X-ray crystallography established that crystals ranging in approximate composition from **1**·10HCOOH to **1**·5dioxane all incorporate the same network and have closely similar unit cell parameters.[8] This indicates that the network is robust enough to be insensitive to the nature of the guests. The structure of inclusion compound **1**·1HCOOH·4dioxane was determined by X-ray crystallography,[9] which revealed that each tecton is linked to eight neighbors by normal hydrogen bonding of the 2,4-diaminotriazine groups.[10] Four of the neighbors lie approximately in the *ab* plane, defining an open lattice constructed from cyclic quartets (Figure 1a). Additional hydrogen bonding in the *c* direction links each tecton to four others (Figure 1b), causing the cyclic quartets to stack with their openings aligned and thereby creating a non-interpenetrating three-dimensional network in which each tecton participates in a total of 16 intertectonic hydrogen bonds. The resulting network defines very prominent channels that are parallel to the *c* axis and 11.8 Å in diameter in the largest dimension.[11] One NH_2 group of each diaminotriazine is not involved in intertectonic hydrogen bonding and instead forms part of the walls of the channels. Enclosed in the channels are partially disordered formic acid and dioxane, which is hydrogen-bonded to the NH_2 groups of the walls (Figure 1c). Together, the guests occupy approximately 42% of the volume of the crystal.[11]

When single crystals of tecton **1** containing both formic acid and dioxane were suspended in pure dioxane or acetonitrile,[13] complete exchange of guests occurred rapidly to produce single crystals of approximate composition **1**·5dioxane or **1**·10CH_3CN.[8] Similarly, suspension of single crystals of inclusion compound **1**·5dioxane in water produced single crystals of approximate composition **1**·21H_2O.[8] In all cases, the samples continued to diffract after exchange, the network remained the same, and the unit cell parameters showed only small changes, presumably in response to minor variations in the effective volume of the guests.[14] These experiments establish that the three-dimensional hydrogen-bonded network generated by tecton**1** behaves as a porous material and is sufficiently robust to remain intact during the exchange of guests.[15]

(1) Laboratoire de Diffraction des Rayons-X, Département de Chimie, Université de Montréal.

(2) Su, D.; Wang, X.; Simard, M.; Wuest, J. D. *Supramolecular Chem.* **1995**, *6*, 171. Wuest, J. D. In *Mesomolecules: From Molecules to Materials*; Mendenhall, G. D., Greenberg, A., Liebman, J. F., Eds.; Chapman & Hall: New York, 1995; p 107. Wang, X.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1994**, *116*, 12119. Simard, M.; Su, D.; Wuest, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 4696.

(3) For other recent studies of inclusion and porosity in hydrogen-bonded networks, see: Yaghi, O. M.; Li, H.; Groy, T. L. *J. Am. Chem. Soc.* **1996**, *118*, 9096. Aoyama, Y.; Endo, K.; Anzai, T.; Yamaguchi, Y.; Sawaki, T.; Kobayashi, K.; Kanehisa, N.; Hashimoto, H.; Kai, Y.; Masuda, H. *J. Am. Chem. Soc.* **1996**, *118*, 5562. Munakata, M.; Wu, L. P.; Yamamoto, M.; Kuroda-Sowa, T.; Maekawa, M. *J. Am. Chem. Soc.* **1996**, *118*, 3117. Hartgerink, J. D.; Granja, J. R.; Milligan, R. A.; Ghadiri, M. R. *J. Am. Chem. Soc.* **1996**, *118*, 43. Zafar, A.; Yang, J.; Geib, S. J.; Hamilton, A. D. *Tetrahedron Lett.* **1996**, *37*, 2327. Kolotuchin, S. V.; Fenlon, E. E.; Wilson, S. R.; Loweth, C. J.; Zimmerman, S. C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2654. Copp, S. B.; Holman, K. T.; Sangster, J. O. S.; Subramanian. S.; Zaworotko, M. J. *J. Chem. Soc., Dalton Trans.* **1995**, 2233. Shibakami, M.; Tamura, M.; Sekiya, A. *J. Am. Chem. Soc.* **1995**, *117*, 4499. Venkataraman, D.; Lee, S.; Zhang, J.; Moore, J. S. *Nature* **1994**, *371*, 591. Hollingsworth, M. D.; Brown, M. E.; Santarsiero, B. D.; Huffman, J. C.; Goss, C. R. *Chem. Mater.* **1994**, *6*, 1227. Ermer, O.; Lindenberg, L. *Helv. Chim. Acta* **1991**, *74*, 825.

(4) Ung, A. T.; Gizachew, D.; Bishop, R.; Scudder, M. L.; Dance, I. G.; Craig, D. C. *J. Am. Chem. Soc.* **1995**, *117*, 8745.

(5) Kirste, B.; Grimm, M.; Kurreck, H. *J. Am. Chem. Soc.* **1989**, *111*, 108. See also: Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546.

(6) The structure assigned to tecton **1** is consistent with its mass, IR, ^1H NMR, and ^{13}C NMR spectra. These data are included in the supporting material.

(7) For related conversions of nitriles into 2,4-diaminotriazines, see: Quirke, J. M. E. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon: Oxford, 1984; Vol. 3, p 457. Smolin, E. M.; Rapoport, L. In *The Chemistry of Heterocyclic Compounds*; Weissberger, A., Ed.; Interscience: New York, 1959; Vol. 13.

(8) The compositions of inclusion compounds were determined by ^1H NMR spectroscopy.

(9) Crystals of inclusion compound **1**·1HCOOH·4dioxane were sealed in a capillary with the mother liquors. They belong to the tetragonal space group $I\bar{4}$ with $a = b = 20.466(8)$ Å, $c = 7.185(2)$ Å, $V = 3010(2)$ Å^3, $D_{calcd} = 1.275$ g cm^{-3}, and $Z = 2$ (molecules of tecton **1**). Data were collected at 293 K, and the structure was refined to $R_F = 0.047$, $R_w = 0.100$ for 1628 reflections with $I > 2\sigma(I)$.

(10) For previous structural studies of aminotriazines and related compounds, see: Beijer, F. H.; Sijbesma, R. P.; Vekemans, J. A. J. M.; Meijer, E. W.; Kooijman, H.; Spek, A. L. *J. Org. Chem.* **1996**, *61*, 6371. Bock, H.; Van, T. T. H.; Solouki, B.; Schödel, H.; Artus, G.; Herdtweck, E.; Herrmann, W. A. *Liebigs Ann.* **1996**, 403. Zerkowski, J. A.; MacDonald, J. C.; Whitesides, G. M. *Chem. Mater.* **1994**, *6*, 1250. Pyrka, G. J.; Pinkerton, A. A. *Acta Crystallogr.* **1992**, *C48*, 91. Schwalbe, C. H.; Williams, G. J. B.; Koetzle, T. F. *Acta Crystallogr.* **1987**, *C43*, 2191. Nahringbauer, I.; Kvick, Å. *Acta Crystallogr.* **1977**, *B33*, 2902. Varghese, J. N.; O'Connell, A. M.; Maslen, E. N. *Acta Crystallogr.* **1977**, *B33*, 2102. Cromer, D. T.; Larson, A. C.; Stewart, R. F. *J. Chem. Phys.* **1976**, *65*, 336. Chao, M.; Schempp, E.; Rosenstein, R. D. *Acta Crystallogr.* **1975**, *B31*, 2922.

(11) The estimated pore sizes correspond to distances between van der Waals surfaces of opposing walls defined by a projection along the channel axis. Volumes occupied by guests were estimated by using the stoichiometry of the inclusion compound, its calculated density, and the density of the pure guest at 25 °C. For comparison, pore sizes in zeolites normally range from approximately 4 to 13 Å, and void volumes are typically less than 50%.[12]

(12) For references, see: Davis, M. E.; Lobo, R. F. *Chem. Mater.* **1992**, *4*, 756.

(13) These experiments used crystals of dimensions that were approximately 0.1 mm × 0.1 mm × 1.5 mm.

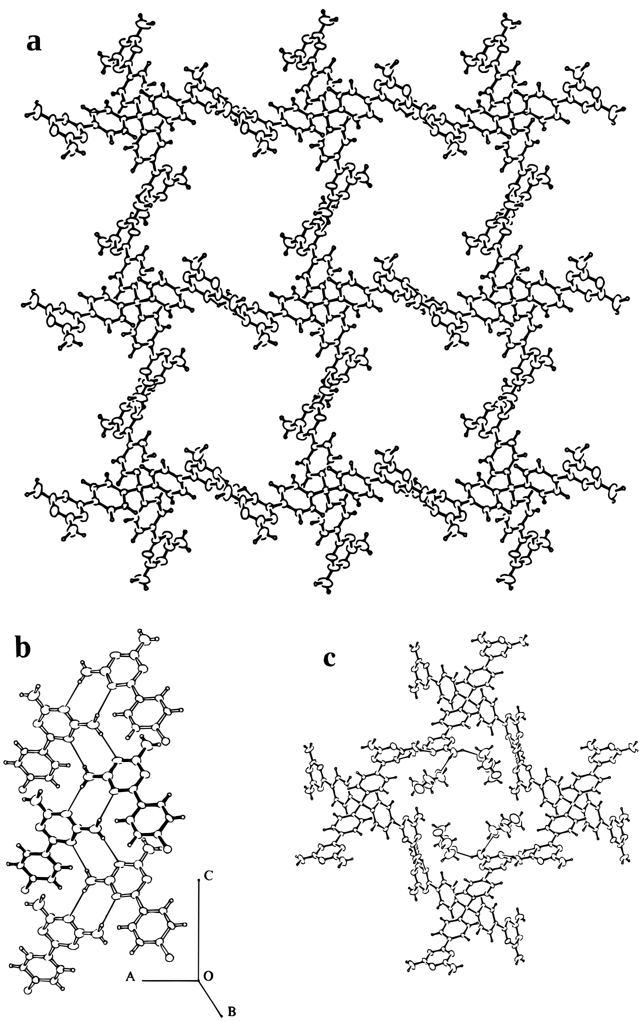

Figure 1. ORTEP views of the three-dimensional hydrogen-bonded network present in crystals of inclusion compound **1**·1HCOOH·4dioxane. In each view, non-hydrogen atoms are represented by ellipsoids corresponding to 40% probability, hydrogen atoms are shown as spheres of arbitrary size, and hydrogen bonds are represented by narrow lines. (a) This view (along *c*) is parallel to the channel axes and shows the cross sections of four adjacent channels. Formic acid and dioxane are omitted for clarity. (b) This view (along *b*) is perpendicular to the channels and shows how their walls are constructed. The arms of two tectons (represented by broad filled lines) are joined by hydrogen bonds to form one side of a cyclic quartet. These tectons are linked by hydrogen bonds in the *c* direction to tectons in adjoining quartets (open lines). (c) This view is parallel to the axis of a single channel and shows the location of the partially disordered dioxane. Disordered formic acid occupies space in the middle of the channel but is omitted for clarity.

Certain zeolites, related porous inorganic solids, and coordination networks are robust enough to withstand the removal of guests and to remain ordered even when they are partially or completely empty.[16] Their striking structural integrity challenges chemists to solve the more difficult problem of devising porous hydrogen-bonded organic analogues that remain ordered during extensive removal of guests.[17] We have now found that the network generated by tecton **1** has this remarkable property. Single crystals of inclusion compound **1**·5dioxane were kept under vacuum (0.1 Torr) at 25 °C and then transferred to a glovebox under dry Ar.[13] Subsequent analysis by ^{1}H NMR spectroscopy revealed that after 3.5, 7.0, 26, and 66 h of exposure to vacuum, the crystals had lost 28, 37, 56, and 63% of the original dioxane. The crystals remained optically transparent and showed uniform extinction when viewed through crossed polarizers, so no conspicuous noncrystalline zones were present. Moreover, the crystals continued to diffract, the space group remained identical, and the unit cell parameters showed a small but systematic and significant contraction.[21] We conclude that the network remains ordered even when most of the guests are removed.

The hydrogen bonds that help direct the association of tecton **1** and related compounds are individually weak (≤7 kcal/mol).[22] Nevertheless, when tectons are oriented in networks by suitably large numbers of hydrogen bonds, their collective effect can approach or even exceed that of strong covalent bonds. As our results have shown, this permits the assembly of porous hydrogen-bonded networks with unprecedented structural integrity. The creation of such networks demonstrates that molecular tectonics is a very powerful strategy for producing ordered materials with useful and unusual properties.

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Supporting Information Available: X-ray crystallographic data for inclusion compound **1**·1HCOOH·4dioxane and IR, ^{1}H NMR, ^{13}C NMR, and mass spectra for tecton **1** (17 pages). See any current masthead page for ordering and Internet access instructions.

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(14) For example, formation of inclusion compound **1**·21H_2O from **1**·5dioxane caused a contraction of the unit cell from $a = b = 20.395(7)$ Å, $c = 7.160(2)$ Å, $V = 2978(2)$ Å^3 (measured at 205 K) to $a = b = 19.412(9)$ Å, $c = 7.166(5)$ Å, $V = 2700(3)$ Å^3 (also measured at 205 K). In both cases, the space group was $I\bar{4}$.

(15) We have established that exchange does not occur by recrystallization because (1) tecton **1** is essentially insoluble in the media used for exchange; (2) the morphology of the crystals is essentially unaffected by exchange; and (3) exchange occurs in minutes and is much faster than initial crystallization of tecton **1**, which takes place during several days.

(16) Barrer, R. M. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1984; Vol. 1, p 191. Venkataraman, D.; Gardner, G. B.; Lee, S.; Moore, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 11600.

(17) Despite intensive study of inclusion, very few molecular substances that form inclusion compounds have been shown to crystallize without guests to form empty networks with the same topology.[4,18,19] Previously known compounds of this type, such as Dianin's compound,[18] are distinctly different from tecton **1** because (1) guests typically occupy only a small fraction of the total volume of the crystals and (2) conspicuous channels are generally absent, so the interiors of the crystals cannot be penetrated unless the lattice is disrupted. In the 6:1 clathrate of Dianin's compound with $CHCl_3$, for example, the guests occupy only 6% of the volume.[11] Furthermore, replacement or removal of guests in clathrates of Dianin's compound occurs only when the network is disrupted by heating, dissolution, or mechanical action.[20]

(18) Abriel, W.; du Bois, A.; Zakrzewski, M.; White, M. A. *Can. J. Chem.* **1990**, *68*, 1352. MacNicol, D. D. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1984; Vol. 2, p 1. Flippen, J. L.; Karle, J.; Karle, I. L. *J. Am. Chem. Soc.* **1970**, *92*, 3749.

(19) Ibragimov, B. T.; Talipov, S. A.; Aripov, T. F. *J. Inclus. Phenom.* **1994**, *17*, 317.

(20) The sorption of gaseous guests by Dianin's compound has been reported, but only when the compound is shaken with steel balls before and during exposure to the guests. Barrer, R. M.; Shanson, V. H. *J. Chem. Soc., Chem. Commun.* **1976**, 333.

(21) Removal of 38% of the guests from inclusion compound **1**·5dioxane caused a contraction of the unit cell from $a = b = 20.395(7)$ Å, $c = 7.160(2)$ Å, $V = 2978(2)$ Å^3 to $a = b = 20.208(12)$ Å, $c = 7.138(15)$ Å, $V = 2915(7)$ Å^3. Removal of 63% caused a further contraction to $a = b = 20.144(10)$ Å, $c = 7.154(7)$ Å, $V = 2903(3)$ Å^3. In all cases, the parameters were measured at 205 K. The systematic contraction is important, because it excludes the possibility that samples from which guests have been partially removed consist of crystalline domains of normal composition **1**·5dioxane and disordered domains with less dioxane. Further removal of guests becomes more difficult as the network becomes more nearly empty.

(22) For discussions of the enthalpies of hydrogen bonds in the solid state, see: Whitesides, G. M.; Simanek, E. E.; Mathias, J. P.; Seto, C. T.; Chin, D. N.; Mammen, M.; Gordon, D. M. *Acc. Chem. Res.* **1995**, *28*, 37. Aakeröy, C. B.; Seddon, K. R. *Chem. Soc. Rev.* **1993**, *22*, 397.