

Molecular Tectonics. Construction of Porous Hydrogen-Bonded Networks from Bisketals of Pentaerythritol

Hélène Sauriat-Dorizon, Thierry Maris, and James D. Wuest*

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

Gary D. Enright

Steacie Institute for Molecular Sciences, National Research Council, Ottawa, Ontario K1A 0R6, Canada

wuest@chimie.umontreal.ca

Received July 31, 2002

2,4,8,10-Tetraoxaspiro[5,5]undecanes tetrasubstituted at the 3 and 9 positions with groups incorporating diaminotriazines can be used for the construction of extensively hydrogen-bonded networks by the strategy of molecular tectonics. Four such compounds, tectons **1–4**, were made by short and efficient syntheses involving bisketalization of pentaerythritol and subsequent reactions. Unlike tectons typically used in previous studies, compounds **1–4** are flexible and chiral, and they orient four sticky diaminotriazine groups in a distorted tetrahedral geometry. Tecton **1** crystallizes from DMF/toluene as an inclusion compound of approximate composition $1 \cdot 8\text{DMF} \cdot x\text{H}_2\text{O}$. In the resulting structure, each tecton participates in a total of 16 hydrogen bonds. Eight of these bonds involve four principal neighbors, and the tectons linked in this way define a distorted diamondoid network. Despite 8-fold interpenetration, 60% of the volume of the network is available for including guests. The guests are disordered and occupy parallel helical channels that have cross sections of approximately $11 \times 12 \text{ \AA}^2$ at the narrowest points. These channels provide access to the interior of the crystals and permit guests to be exchanged quantitatively without loss of crystallinity. It is noteworthy that tecton **1**, despite its flexibility, small size, and structural simplicity, is apparently unable to find a periodic three-dimensional structure in which the dictates of hydrogen bonding and close packing are satisfied simultaneously.

Introduction

Molecular tectonics is a useful strategy for creating new ordered structures by design.^{1–4} It is based on the association of special molecules, called tectons, that interact strongly with their neighbors in well-defined ways. Tectons can be considered to consist of peripheral sticky sites that direct molecular association, as well as cores that hold the sticky sites in particular orientations. Together, these features help tectons control how their neighbors are positioned, despite the competing effects of other intermolecular interactions that are weaker and less specific. When association is controlled by multiple directional interactions, close molecular packing is not

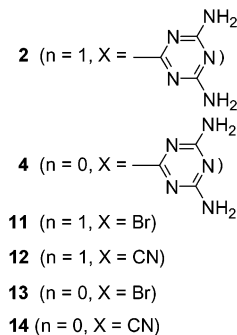
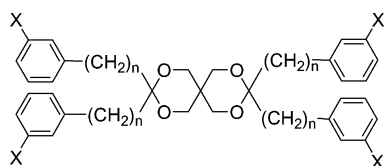
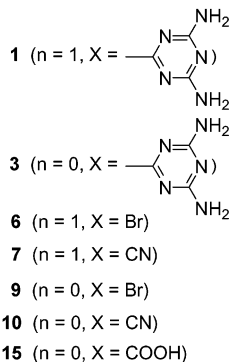
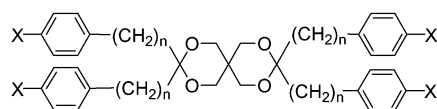
normally favored; instead, open networks are formed, with significant space available for the inclusion of guests. Because both sticky sites and cores can be varied widely, molecular tectonics has significant potential for creating new porous ordered materials.

Nominally tetrahedral cores derived from tetraphenylmethane and tetraphenylsilane have been employed extensively in molecular tectonics, as well as in other areas of chemistry, because they have relatively rigid structures with simple, well-defined geometries.⁵ For example, derivatives of tetraphenylmethane and tetraphenylsilane have been designed to incorporate tetrahedrally directed sites for hydrogen bonding so that association produces diamondoid networks or related three-dimensional, four-connected structures.^{1,2,6} In contrast, little attention has been given to tectons with conformationally flexible cores, chiral structures,⁴ and distorted tetrahedral geometries, which may tend to favor alternative architectures. In this paper, we show that tectons **1–4**, which have flexible chiral 2,4,8,10-tetraoxaspiro[5,5]undecyl cores, can be synthesized efficiently from pentaerythritol by bisketalization. The presence of four diaminotriazine groups ensures extensive intermolecular hydrogen bonding, and the groups are held in highly distorted tetrahedral orientations by the spirobi-

* Author to whom correspondence should be addressed.

(1) Brunet, P.; Demers, E.; Maris, T.; Enright, G. D.; Wuest, J. D. Submitted for publication. Malek, N.; Simard, M.; Maris, T.; Wuest, J. D. Submitted for publication. Saied, O.; Maris, T.; Wuest, J. D. Submitted for publication. Fournier, J.-H.; Maris, T.; Wuest, J. D.; Guo, W.; Galoppini, E. Submitted for publication. Vaillancourt, L.; Simard, M.; Wuest, J. D. *J. Org. Chem.* **1998**, *63*, 9746. Su, D.; Wang, X.; Simard, M.; Wuest, J. D. *Supramol. 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.

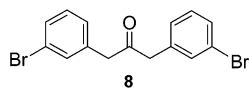
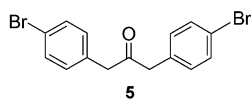
(2) Brunet, P.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1997**, *119*, 2737.



cyclic cores. We have found that tecton **1** crystallizes to form an open hydrogen-bonded network with large helical channels that provide significant space for the inclusion of guests.

Results and Discussion

Syntheses of Tectons 1–4. Tecton **1** was prepared in three steps in 53% overall yield from pentaerythritol and the known ketone **5**,⁷ which we obtained in 68% yield by the self-condensation of 4-bromophenylacetic acid, induced by DCC and DMAP.⁸ Ketalization of compound **5** with pentaerythritol gave an 86% yield of tetrabromide **6**, which was converted into the corresponding tetranitrile **7** in 69% yield by treatment with CuCN in hot DMF.⁹ Heating tetranitrile **7** with dicyandiamide and KOH in 2-methoxyethanol then afforded diaminotriazine **1** in 90% yield.¹⁰



Meta-substituted isomer **2** was synthesized similarly in 35% overall yield from pentaerythritol and 1,3-bis(3-bromophenyl)-2-propanone (**8**), which was made in 81% yield from 3-bromophenylacetic acid by the same method

that provided analogue **5**.⁸ In a similar way, tecton **3** was prepared in 53% overall yield from pentaerythritol and 4,4'-dibromobenzophenone, and meta-substituted analogue **4** was obtained in 58% overall yield from pentaerythritol and 3,3'-dibromobenzophenone.¹¹ The syntheses of compounds **1–4** show that relatively complex tectons can be prepared rapidly and efficiently from inexpensive precursors.

Intermediate tetrabromides and tetranitriles **6–7**, **9–10**, and **11–14** prepared in the course of these syntheses are also useful precursors for making other new derivatives of 2,4,8,10-tetraoxaspiro[5,5]undecane with applications in molecular tectonics or in other fields of chemistry. For example, tetralithiation of tetrabromide **9**, followed by the addition of CO₂ and acidification, gave a 74% yield of tetracarboxylic acid **15**. Coordination to

(3) For other recent studies of hydrogen-bonded supramolecular networks, see: Holman, K. T.; Pivovar, A. M.; Swift, J. A.; Ward, M. D. *Acc. Chem. Res.* **2001**, *34*, 107. Kuduva, S. S.; Bläser, D.; Boese, R.; Desiraju, G. R. *J. Org. Chem.* **2001**, *66*, 1621. Atwood, J. L.; Barbour, L. J.; Ness, T. J.; Raston, C. L.; Raston, P. L. *J. Am. Chem. Soc.* **2001**, *123*, 7192. Ranganathan, D.; Samant, M. P.; Karle, I. L. *J. Am. Chem. Soc.* **2001**, *123*, 5619. Mak, T. C. W.; Xue, F. *J. Am. Chem. Soc.* **2000**, *122*, 9860. Sharma, C. V. K.; Clearfield, A. *J. Am. Chem. Soc.* **2000**, *122*, 4394. Corbin, P. S.; Zimmerman, S. C. *J. Am. Chem. Soc.* **2000**, *122*, 3779. Cantrill, S. J.; Pease, A. R.; Stoddart, J. F. *J. Chem. Soc., Dalton Trans.* **2000**, 3715. Batchelor, E.; Klinowski, J.; Jones, W. J. *Mater. Chem.* **2000**, *10*, 839. Videnova-Adrabsinska, V.; Janeczko, E. *J. Mater. Chem.* **2000**, *10*, 555. Akazome, M.; Suzuki, S.; Shimizu, Y.; Henmi, K.; Ogura, K. *J. Org. Chem.* **2000**, *65*, 6917. Baumeister, B.; Matile, S. *J. Chem. Soc., Chem. Commun.* **2000**, 913. Chowdhry, M. M.; Mingos, D. M. P.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3495. Gong, B.; Zheng, C.; Skrzypczak-Jankun, E.; Zhu, J. *Org. Lett.* **2000**, *2*, 3273. Krische, M. J.; Lehn, J.-M.; Kyritsakas, N.; Fischer, J.; Wegelius, E. K.; Rissanen, K. *Tetrahedron* **2000**, *56*, 6701. Aakeröy, C. B.; Beatty, A. M.; Nieuwenhuysen, M.; Zou, M. *Tetrahedron* **2000**, *56*, 6693. Kobayashi, K.; Shirasaka, T.; Horn, E.; Furukawa, N. *Tetrahedron Lett.* **2000**, *41*, 89. Dahal, S.; Goldberg, I. *J. Phys. Org. Chem.* **2000**, *13*, 382. Bishop, R.; Craig, D. C.; Dance, I. G.; Scudder, M. L.; Ung, A. T. *J. Struct. Chem.* **1999**, *40*, 663. Fuchs, K.; Bauer, T.; Thomann, R.; Wang, C.; Friedrich, C.; Mühlhaupt, R. *Macromolecules* **1999**, *32*, 8404. Karle, I. L.; Ranganathan, D.; Kurur, S. *J. Am. Chem. Soc.* **1999**, *121*, 7156. Chin, D. N.; Palmore, G. T. R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1999**, *121*, 2115. Hanessian, S.; Saladino, R.; Margarita, R.; Simard, M. *Chem. Eur. J.* **1999**, *5*, 2169. Biradha, K.; Dennis, D.; MacKinnon, V. A.; Sharma, C. V. K.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 11894. Schauer, C. L.; Matwey, E.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 10245. Lambert, J. B.; Zhao, Y.; Stern, C. L. *J. Phys. Org. Chem.* **1997**, *10*, 229. Félix, O.; Hosseini, M. W.; De Cian, A.; Fischer, J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 102. Adam, K. R.; Atkinson, I. M.; Davis, R. L.; Lindoy, L. F.; Mahinay, M. S.; McCool, B. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1997**, 467. Schwiebert, K. E.; Chin, D. N.; MacDonald, J. C.; Whitesides, G. M. *J. Am. Chem. Soc.* **1996**, *118*, 4018. Kinbara, K.; Hashimoto, Y.; Sukegawa, M.; Nohira, H.; Saigo, K. *J. Am. Chem. Soc.* **1996**, *118*, 3441. 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. Hollingsworth, M. D.; Brown, M. E.; Hillier, A. C.; Santarsiero, B. D.; Chaney, J. D. *Science* **1996**, *273*, 1355. Kolotuchin, S. V.; Fenlon, E. E.; Wilson, S. R.; Loweth, C. J.; Zimmerman, S. C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2654. Lawrence, D. S.; Jiang, T.; Levett, M. *Chem. Rev.* **1995**, *95*, 2229. Ermer, O.; Eling, A. *J. Chem. Soc., Perkin Trans. 2* **1994**, 925. Venkataraman, D.; Lee, S.; Zhang, J.; Moore, J. S. *Nature* **1994**, *371*, 591.

(4) Holý, P.; Závada, J.; Císarová, I.; Podlaha, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 381.

(5) Fournier, J.-H.; Wang, X.; Wuest, J. D. Submitted for publication.

(6) For a review of diamondoid hydrogen-bonded networks, see: Zaworotko, M. J. *J. Chem. Soc. Rev.* **1994**, *23*, 283.

(7) Zaugg, H.; Rapala, R. T.; Leffler, M. T. *J. Am. Chem. Soc.* **1948**, *70*, 3224.

(8) Bhandari, S.; Ray, S. *Synth. Commun.* **1998**, *28*, 765.

(9) Ellis, G. P.; Romney-Alexander, T. M. *Chem. Rev.* **1987**, *87*, 779.

(10) Simons, J. K.; Saxton, M. R. *Organic Syntheses*, Wiley: New York, 1963; Collect. Vol. IV, p 78.

(11) Vögtle, F.; Alfter, F.; Nieger, M.; Steckhan, E.; Mavili, S. *Chem. Ber.* **1991**, *124*, 897.

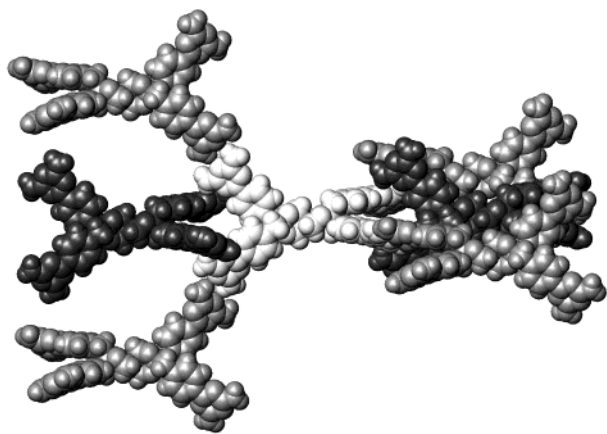


FIGURE 1. Representation of a central molecule of tecton **1** (white) surrounded by its six hydrogen-bonded neighbors. Two hydrogen bonds are formed with each of the four neighbors shown in light gray, creating motifs of type **16**, and four hydrogen bonds are formed with each of the two neighbors shown in dark gray, creating distorted motifs of type **18**. In this view, the *c* axis is horizontal.

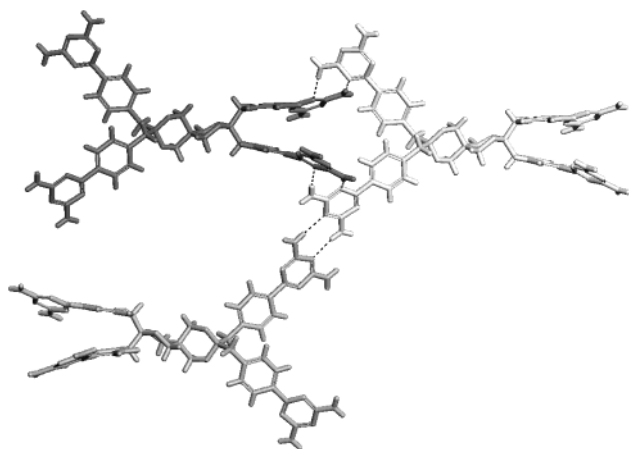
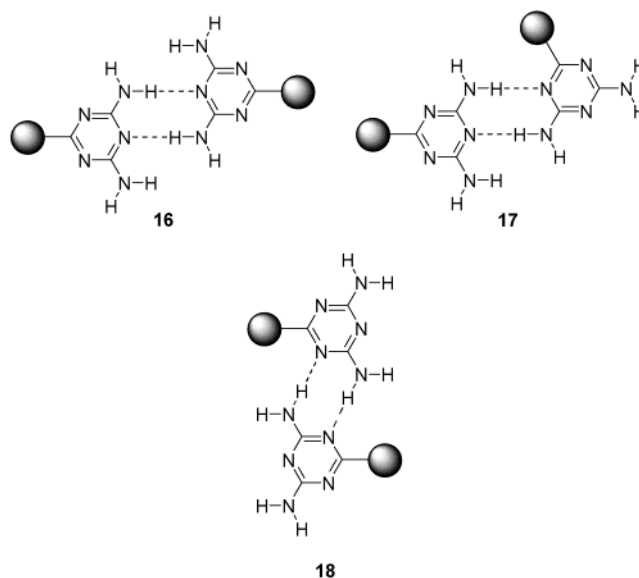


FIGURE 2. Detailed view of a molecule of tecton **1** (white) with two of its six hydrogen-bonded neighbors. The one shown in light gray forms two hydrogen bonds with the tecton shown in white, creating motifs of type **16**, and the dark gray neighbor forms a total of four hydrogen bonds with the white tecton, creating distorted motifs of type **18**. In this view, the *c* axis is horizontal, and hydrogen bonds appear as broken lines.

metals or self-association by hydrogen bonding of the carboxyl groups should yield extended networks.

Structure of the Hydrogen-Bonded Network Built from Tecton 1. Despite varied attempts to crystallize tectons **1–4** and **15**, crystals suitable for X-ray diffraction could only be grown from compound **1**. Crystallization from DMF/toluene gave an inclusion compound of approximate composition $1 \cdot 10\text{DMF} \cdot x\text{H}_2\text{O}$,¹² and its structure was determined by X-ray crystallography. Views of the structure are shown in Figures 1–5. The tectons self-associate by hydrogen bonding of diaminotriazine groups, as expected, to form an open three-dimensional network with significant space for both interpenetration and the

inclusion of guests.¹³ Each tecton forms hydrogen bonds with six neighbors, creating the assembly shown in Figures 1 and 2. Four neighbors (light gray) each form two hydrogen bonds with the central tecton (white). These intertectonic contacts each involve two interacting diaminotriazines that are approximately coplanar and hydrogen bond in the manner represented by structure **16**. This motif is frequently observed in the structures of other 2,4-diaminotriazines.² Motif **16** involves the more accessible N-3/N-3' nitrogen atoms and is therefore expected to be more stable than the alternative N-3/N-1' and N-1/N-1' motifs **17** and **18**.



Formation of the N-3/N-3' motif **16** alone does not fully exploit the ability of diaminotriazines to form hydrogen bonds, so the central tecton in the assembly shown in Figure 1 also forms four hydrogen bonds with each of two other symmetrically oriented neighbors (dark gray). These additional interactions correspond to the less favored N-1/N-1' motif **18**. Evidence that these interactions (motif **18**) are weaker than those linking the central tecton to the four neighbors shown in light gray (motif **16**) is provided by comparing the average planes of the interacting diaminotriazine rings. In the interactions corresponding to motif **16**, the angle is only 9.1°, whereas in those corresponding to motif **18**, it is 55.9°. However, the average hydrogen-bonded N...N distances of type **16** observed in the structure (3.033(6) Å) are not significantly shorter than the average of those of type **18** (3.034(6) Å). Nevertheless, each tecton can be considered to have four principal hydrogen-bonded neighbors (planar motif **16**) and two secondary neighbors (distorted motif **18**).

As shown in structures **16–18**, each diaminotriazine incorporates two $-\text{NH}_2$ groups, which can in principle donate a total of four hydrogen bonds, and three heterocyclic nitrogen atoms (N-1, N-3, and N-5), which can accept a total of three hydrogen bonds. Each molecule of tecton **1** can therefore participate in a maximum of 28 normal hydrogen bonds. Of this number, 16 are used to construct the observed supramolecular network by com-

(12) Compositions were estimated by X-ray crystallography and ¹H NMR spectroscopy of dissolved samples. The amount of H₂O included, if any, could not be determined accurately by these methods.

(13) For discussions of interpenetration in networks, see: Batten, S. R. *Cryst. Eng. Commun.* **2001**, *18*, 1. Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460.

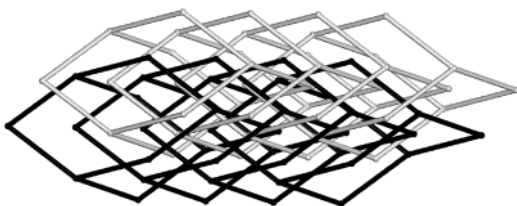


FIGURE 3. Representation of the interpenetrated diamondoid networks generated by tecton **1**. In this drawing, the tectons lie at the intersections of solid lines that represent their interactions with four neighbors by hydrogen bonding according to motif **16**. One system of 4-fold interpenetrated networks is shown in light gray and the other in dark gray. In this view, the *c* axis is horizontal.

bined formation of the N-3/N-3' motif **16** and the N-1/N-1' motif **18**. Hydrogen-bonding sites not used for this purpose are available for interacting with included guests. Other types of interactions, such as intermolecular π - π stacking, do not appear to play a major role in determining the observed supramolecular architecture.

The network defined by tectons that interact according to motif **16** has a distorted diamondoid geometry in which the central spirocyclic carbon atom of each tecton is separated from the corresponding atoms of its four principal hydrogen-bonded neighbors by approximately 25.5 Å.⁶ Because of this large separation, the network is open enough to permit extensive interpenetration, as shown in Figure 3.¹³ The interpenetration can be described as 8-fold, with successive networks related by a displacement along the *c* glide plane. As a result, there are two independent systems of 4-fold interpenetrated diamondoid networks, each aligned with the *c* axis. In the assembly shown in Figure 1, the central tecton (white) and its four principal neighbors (light gray) belong to one network, and the two other neighbors (dark gray) belong to an adjacent network in the same system of 4-fold interpenetration.

Despite multiple interpenetration, the network built from tecton **1** retains very significant volume for the inclusion of guests. The guests were found to be highly disordered and could not be located precisely, but the volume available for their inclusion defines large channels aligned with the *c* axis. The cross sections of these channels measure approximately 11×12 Å² at the narrowest points and are a prominent feature of Figure 4.¹⁴ The channels themselves are represented by the surface shown in Figure 5.¹⁵ This view establishes that the channels are parallel and roughly cylindrical, with no significant interconnections.

Overall, 60% of the volume of crystals of tecton **1** is available for including guests.^{16,17} This value is much

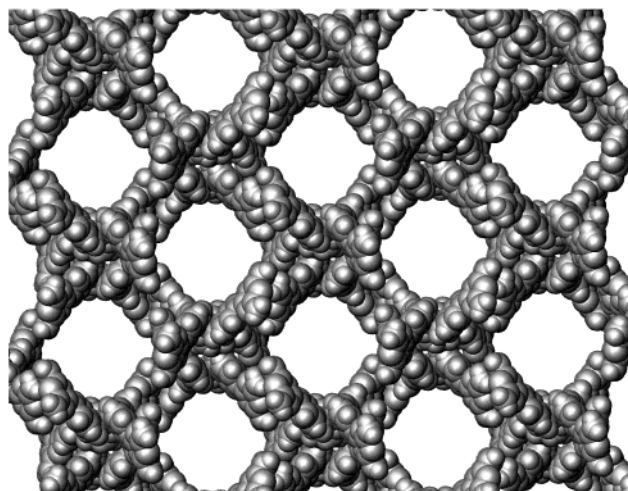


FIGURE 4. View along the *c* axis of the network constructed from tecton **1** showing a $3 \times 3 \times 2$ array of unit cells. Disordered guests are omitted, and atoms are shown as spheres of van der Waals radii in order to reveal the cross sections of channels.

larger than the percentage of unused space created in normal molecular crystals by imperfect packing, which is typically close to 30%.¹⁸ In fact, the percentage of available volume in crystals of tecton **1** even exceeds that occupied by water and other guests in many protein crystals, despite the larger, more complex, and more irregular shapes of proteins.¹⁹ Previous work has established that one way in which tectons differ from normal molecules is that their inherent tendency to form strong directional interactions is typically incompatible with efficient molecular packing. As a result, tectonic association is predisposed to favor the formation of networks in which significant space is available for guests. The behavior of tecton **1** is fully consistent with these generalizations, and the percentage of available volume is similar to that of the most porous analogues studied so far.¹⁻⁴ This observation is noteworthy, because tecton **1** incorporates numerous elements of conformational flexibility, associated primarily with the 2,4,8,10-tetraoxaspiro[5,5]undecyl core²⁰ and the benzylic substituents at positions 3 and 9. Even though tecton **1** is flexible, small, and structurally simple, it is nevertheless apparently unable to find a periodic three-dimensional structure in which the dictates of hydrogen bonding and close packing are satisfied simultaneously.

Exchange of Guests. In the observed network, each tecton participates in a total of 16 hydrogen bonds with its neighbors to form a robust, well-ordered structure, whereas the guests are disordered, potentially mobile, and located in large channels that provide a possible route of escape from inside the crystal. Consequently, guests can be exchanged without loss of crystallinity, as observed in other tectonic materials.^{1,2} For example,

(14) The dimensions of a channel in a particular direction correspond to the cross section of an imaginary cylinder that could be passed through the hypothetical open network in the given direction in contact with the van der Waals surface. Such values are inherently conservative because (1) they measure the cross section at the most narrow constriction and (2) they systematically underestimate the sizes of channels that are not uniform and linear.

(15) Representations of channels were generated by the Cavities option in the program ATOMS (ATOMS, Version 5.1; Shape Software: 521 Hidden Valley Road, Kingsport, TN 37663; www.shape-software.com). We are grateful to Eric Dowty of Shape Software for integrating this capacity in ATOMS at our suggestion.

(16) The percentage of volume accessible to guests was estimated by the PLATON program.¹⁷

(17) Spek, A. L. *PLATON*, A Multipurpose Crystallographic Tool; Utrecht University: Utrecht, The Netherlands, 2001. van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194.

(18) Kitaigorodskii, A. I. *Organic Chemical Crystallography*; Consultants Bureau: New York, 1961.

(19) Quillin, M. L.; Matthews, B. W. *Acta Crystallogr.* **2000**, *D56*, 791. Andersson, K. M.; Hovmöller, S. *Acta Crystallogr.* **2000**, *D56*, 789.

(20) Mager, S.; Horn, M.; Grosu, I.; Bogdan, M. *Monatsh. Chem.* **1989**, *120*, 735.

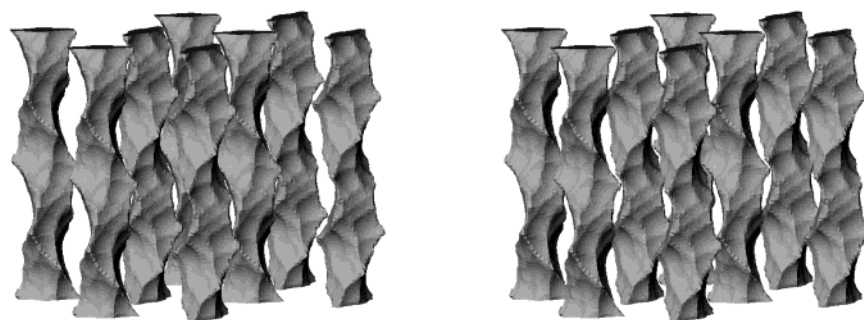


FIGURE 5. Stereoscopic representation of the parallel helical channels defined by the network constructed from tecton **1**. The image shows a $2 \times 2 \times 2$ array of unit cells viewed with the c axis vertical. The outsides of the channels appear in light gray, and dark gray is used to show where the channels are cut by the boundaries of the array. The surface of the channels is defined by the possible loci of the center of a sphere of diameter 6 Å as it rolls over the surface of the ordered tectonic network.¹⁵

single crystals of estimated composition $\mathbf{1} \cdot 10\text{DMF} \cdot x\text{H}_2\text{O}$ and approximate dimensions $1 \times 1 \times 1 \text{ mm}^3$ were exposed to excess $\text{CH}_3\text{COOC}_2\text{H}_5$ at 25 °C for 12 h. The recovered sample remained transparent and morphologically unchanged, continued to diffract, and showed closely similar unit cell parameters when studied by single-crystal X-ray diffraction. However, analysis by ^1H NMR spectroscopy of dissolved samples established that the initial guest, DMF, had been replaced quantitatively by $\text{CH}_3\text{COOC}_2\text{H}_5$ to give new crystals of approximate composition $\mathbf{1} \cdot 10\text{CH}_3\text{COOC}_2\text{H}_5 \cdot y\text{H}_2\text{O}$.¹² In such exchanges, a preference for polar guests is observed, presumably because the surfaces of the channels incorporate aromatic rings, heteroatoms, and multiple sites for hydrogen bonding.

Chirality of Tecton 1. Like other 2,4,8,10-tetraoxaspiro[5,5]undecanes, tecton **1** adopts a chiral chair–chair conformation.²⁰ The observed crystal structure consists of equal numbers of the two enantiomeric conformations of the basic spirocyclic core. Close examination of the channels (Figure 5) reveals that each is helical and chiral, but equal numbers of helices of opposite handedness are present. As a result, crystals of tecton **1** grown by the method described are not suitable for enantioselective inclusion.

Conclusions

Detailed prediction of the structures of molecular crystals remains impossible,²¹ but the strategy of molecular tectonics gives chemists a broadly effective tool for building new structures in which particular features can be incorporated by design. Our observations extend the scope of the strategy by confirming that it can be used to construct robust hydrogen-bonded networks with predictable properties of porosity even when the tectonic subunits are geometrically complex and significantly more flexible than those typically used in previous studies.

Experimental Section

Tetrahydrofuran (THF) was dried by distillation from the sodium ketyl of benzophenone, CH_2Cl_2 was dried by distillation from P_2O_5 , and N,N -dimethylformamide (DMF) was dried by

distillation from CaH_2 . All other reagents were commercial products that were used without further purification.

1,3-Bis(4-bromophenyl)-2-propanone (5).⁷ A solution of dicyclohexylcarbodiimide (15.4 g, 74.6 mmol) and 4-(dimethylamino)pyridine (2.29 g, 18.7 mmol) in CH_2Cl_2 (150 mL) was stirred at 25 °C under dry N_2 and treated dropwise with a solution of 4-bromophenylacetic acid (16.1 g, 74.9 mmol) in CH_2Cl_2 (150 mL). The resulting mixture was stirred at 25 °C for 24 h, and then the precipitated solid was removed by filtration and volatiles were removed from the filtrate by evaporation under reduced pressure. Purification of the residue by flash chromatography (silica, $\text{CH}_3\text{COOC}_2\text{H}_5$ (30%)/hexane (70%)), followed by crystallization from $\text{C}_2\text{H}_5\text{OH}$, gave 1,3-bis(4-bromophenyl)-2-propanone (**5**; 9.32 g, 25.3 mmol, 68%) as a colorless solid: mp 118–120 °C (lit.⁷ mp 116–118 °C); IR (NaCl) 1718 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.46 (d, 4H, $^3J = 8.4$ Hz), 7.02 (d, 4H, $^3J = 8.4$ Hz), 3.69 (s, 4H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 204.2, 132.6, 131.8, 131.2, 121.2, 48.4.

1,3-Bis(3-bromophenyl)-2-propanone (8). The product of an analogous procedure using 3-bromophenylacetic acid (4.02 g, 18.7 mmol) was crystallized from $\text{C}_2\text{H}_5\text{OH}$ to give 1,3-bis(3-bromophenyl)-2-propanone (**8**; 2.80 g, 7.61 mmol, 81%) as a colorless solid: mp 109–111 °C; IR (NaCl) 1719 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.42 (d, 2H, $^3J = 7.9$ Hz), 7.30 (s, 2H), 7.20 (d, 2H, $^3J = 7.8$ Hz), 7.08 (m, 2H), 3.72 (s, 4H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 204.1, 135.7, 132.5, 130.3, 130.2, 122.7, 48.6; MS (FAB, 3-nitrobenzyl alcohol) m/e 369.

3,3,9,9-Tetrakis[(4-bromophenyl)methyl]-2,4,8,10-tetraoxaspiro[5,5]undecane (6). In an apparatus fitted with a Dean–Stark trap, a mixture of 1,3-bis(4-bromophenyl)-2-propanone (**5**; 5.02 g, 13.6 mmol), pentaerythritol (0.920 g, 6.76 mmol), and p -toluenesulfonic acid (0.390 g, 2.26 mmol) in benzene (50 mL) was heated at reflux for 48 h. The resulting mixture was cooled and diluted with CH_2Cl_2 . The solution was extracted with saturated aqueous NaHCO_3 , washed with brine, and dried over Na_2SO_4 . Removal of volatiles by evaporation under reduced pressure left a residue that was purified by crystallization from CHCl_3 /hexane to give 3,3,9,9-tetrakis[(4-bromophenyl)methyl]-2,4,8,10-tetraoxaspiro[5,5]undecane (**6**; 4.83 g, 5.78 mmol, 86%) as a colorless solid: mp 182–183 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.41 (d, 8H, $^3J = 8.3$ Hz), 6.99 (d, 8H, $^3J = 8.3$ Hz), 3.54 (s, 8H), 2.80 (s, 8H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 135.0, 132.3, 131.0, 120.5, 100.2, 63.8, 39.4, 32.8; MS (FAB, 3-nitrobenzyl alcohol) m/e 837. Anal. Calcd for $\text{C}_{35}\text{H}_{32}\text{Br}_4\text{O}_4$: C, 50.27; H, 3.86. Found: C, 49.97; H, 3.79.

3,3,9,9-Tetrakis(4-bromophenyl)-2,4,8,10-tetraoxaspiro[5,5]undecane (9). An analogous procedure was carried out using 4,4'-dibromobenzophenone (3.00 g, 8.82 mmol) and pentaerythritol (0.590 g, 4.33 mmol). The crude product was purified by chromatography (alumina, ether (30%)/hexane (70%)) to give 3,3,9,9-tetrakis(4-bromophenyl)-2,4,8,10-tetraoxaspiro[5,5]undecane (**9**; 2.49 g, 3.19 mmol, 74%) as a colorless solid: mp 219–220 °C; ^1H NMR (300 MHz, CDCl_3) δ

(21) For a discussion, see: Gavezzotti, A. *Acc. Chem. Res.* **1994**, *27*, 309.

7.46 (d, 8H, $^3J = 8.6$ Hz), 7.33 (d, 8H, $^3J = 8.6$ Hz), 3.81 (s, 8H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 140.0, 131.7, 128.0, 122.4, 100.8, 65.1, 32.9; MS (FAB, 3-nitrobenzyl alcohol) m/e 781. Anal. Calcd for $\text{C}_{31}\text{H}_{24}\text{Br}_4\text{O}_4$: C, 47.73; H, 3.10. Found: C, 47.74; H, 2.87.

3,3,9,9-Tetrakis(3-bromophenyl)methyl]-2,4,8,10-tetraoxaspiro[5,5]undecane (11). The product obtained by an analogous procedure using 1,3-bis(3-bromophenyl)-2-propanone (**8**; 1.77 g, 4.81 mmol) and pentaerythritol (0.320 g, 2.35 mmol) was purified by flash chromatography (silica, CH_2Cl_2 (50%)/hexane (50%)) to give 3,3,9,9-tetrakis(3-bromophenyl)methyl]-2,4,8,10-tetraoxaspiro[5,5]undecane (**11**; 1.13 g, 1.35 mmol, 57%) as a colorless solid: mp 108–110 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.39 (m, 4H), 7.31 (m, 4H), 7.17 (m, 4H), (m, 4H), 3.57 (s, 8H), 2.84 (s, 8H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 138.2, 133.5, 129.6, 129.4, 129.3, 121.9, 100.2, 63.7, 39.6, 32.6; MS (FAB, 3-nitrobenzyl alcohol) m/e 837. Anal. Calcd for $\text{C}_{35}\text{H}_{32}\text{Br}_4\text{O}_4$: C, 50.27; H, 3.86. Found: C, 50.03; H, 3.83.

3,3,9,9-Tetrakis(3-bromophenyl)-2,4,8,10-tetraoxaspiro[5,5]undecane (13). An analogous procedure was carried out using 3,3'-dibromobenzophenone (2.55 g, 7.50 mmol)¹¹ and pentaerythritol (0.510 g, 3.75 mmol). The crude product was purified by chromatography (alumina, CH_2Cl_2 (50%)/hexane (50%)) to give 3,3,9,9-tetrakis(3-bromophenyl)-2,4,8,10-tetraoxaspiro[5,5]undecane (**13**; 2.69 g, 3.45 mmol, 92%) as a colorless solid: ^1H NMR (300 MHz, CDCl_3) δ 7.62 (m, 4H), 7.35 (m, 8H), 7.24 (m, 4H), 3.81 (s, 8H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 143.2, 131.4, 130.2, 129.2, 124.9, 122.8, 100.1, 65.2, 33.1. Anal. Calcd for $\text{C}_{31}\text{H}_{24}\text{Br}_4\text{O}_4$: C, 47.73; H, 3.10. Found: C, 47.80; H, 2.90.

3,3,9,9-Tetrakis(4-cyanophenyl)methyl]-2,4,8,10-tetraoxaspiro[5,5]undecane (7). A mixture of 3,3,9,9-tetrakis(4-bromophenyl)methyl]-2,4,8,10-tetraoxaspiro[5,5]undecane (**6**; 2.57 g, 3.07 mmol) and CuCN (1.26 g, 14.1 mmol) in DMF (200 mL) was heated at reflux for 48 h under dry Ar. The resulting mixture was cooled and treated with a 33% aqueous solution of ethylenediamine. The mixture was extracted with CH_2Cl_2 , the extracts were washed thoroughly with 10% aqueous NaCN and water, and the washed extracts were dried over Na_2SO_4 . Removal of volatiles by evaporation under reduced pressure left a residue that was purified by crystallization from $\text{C}_2\text{H}_5\text{OH}$ to give 3,3,9,9-tetrakis(4-cyanophenyl)methyl]-2,4,8,10-tetraoxaspiro[5,5]undecane (**7**; 1.31 g, 2.11 mmol, 69%) as a colorless solid: mp 225–227 °C; IR (NaCl) 2228 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.59 (d, 8H, $^3J = 8.4$ Hz), 7.23 (d, 8H, $^3J = 8.4$ Hz), 3.46 (s, 8H), 2.90 (s, 8H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 141.3, 131.6, 131.3, 129.7, 110.6, 99.9, 63.6, 40.4, 32.0; MS (FAB, 3-nitrobenzyl alcohol) m/e 621; HRMS (electrospray) calcd for $\text{C}_{39}\text{H}_{32}\text{N}_4\text{NaO}_4$ m/e 643.23212, found 643.23212. Anal. Calcd for $\text{C}_{39}\text{H}_{32}\text{N}_4\text{O}_4 \cdot 1\text{H}_2\text{O}$: C, 73.34; H, 5.37; N, 8.77. Found: C, 73.35; H, 5.11; N, 8.24.

3,3,9,9-Tetrakis(4-cyanophenyl)-2,4,8,10-tetraoxaspiro[5,5]undecane (10). An analogous procedure was carried out using 3,3,9,9-tetrakis(4-bromophenyl)-2,4,8,10-tetraoxaspiro[5,5]undecane (**9**; 0.510 g; 0.654 mmol) and CuCN (0.280 g, 3.13 mmol). The crude product was purified by chromatography (alumina, CH_2Cl_2 (50%)/hexane (50%)) to give 3,3,9,9-tetrakis(4-cyanophenyl)-2,4,8,10-tetraoxaspiro[5,5]undecane (**10**; 0.300 g, 0.531 mmol, 81%) as a colorless solid: IR (NaCl) 2231 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) 7.64 (d, 8H, $^3J = 8.5$ Hz), 7.61 (d, 8H, $^3J = 8.5$ Hz), 3.84 (s, 8H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 145.5, 132.9, 126.0, 112.7, 99.8, 65.3, 32.8; MS (FAB, 3-nitrobenzyl alcohol) m/e 565. Anal. Calcd for $\text{C}_{35}\text{H}_{24}\text{N}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$: C, 69.99; H, 4.70; N, 9.33. Found: C, 69.41; H, 3.95; N, 8.78.

3,3,9,9-Tetrakis(3-cyanophenyl)methyl]-2,4,8,10-tetraoxaspiro[5,5]undecane (12). The product obtained by an analogous procedure using 3,3,9,9-tetrakis(3-bromophenyl)methyl]-2,4,8,10-tetraoxaspiro[5,5]undecane (**11**; 1.06 g; 1.27 mmol) was recrystallized from $\text{C}_2\text{H}_5\text{OH}$ to give 3,3,9,9-tetrakis(3-cyanophenyl)methyl]-2,4,8,10-tetraoxaspiro[5,5]undecane (**12**; 0.550 g, 0.886 mmol, 70%) as a colorless solid:

mp 147–149 °C; IR (NaCl) 2230 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.57–7.33 (m, 16H), 3.47 (s, 8H), 2.87 (s, 8H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 137.1, 135.1, 134.0, 130.4, 128.7, 112.0, 99.6, 63.5, 39.7; MS (FAB, 3-nitrobenzyl alcohol) m/e 621; HRMS (electrospray) calcd for $\text{C}_{39}\text{H}_{32}\text{N}_4\text{NaO}_4$ m/e 643.23212, found 643.23153.

3,3,9,9-Tetrakis(3-cyanophenyl)-2,4,8,10-tetraoxaspiro[5,5]undecane (14). An analogous procedure was carried out using 3,3,9,9-tetrakis(3-bromophenyl)-2,4,8,10-tetraoxaspiro[5,5]undecane (**13**; 3.02 g; 3.87 mmol). The crude product was recrystallized from $\text{C}_2\text{H}_5\text{OH}$ to give 3,3,9,9-tetrakis(3-cyanophenyl)-2,4,8,10-tetraoxaspiro[5,5]undecane (**14**; 1.58 g, 2.80 mmol, 72%) as a colorless solid: ^1H NMR (300 MHz, CDCl_3) δ 7.82 (m, 4H), 7.74 (m, 4H), 7.61 (m, 4H), 7.48 (m, 4H), 3.83 (s, 8H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 142.0, 132.1, 130.4, 129.8, 129.7, 118.3, 113.1, 99.7, 65.1, 33.3; MS (FAB, 3-nitrobenzyl alcohol) m/e 565.

Tecton 1. A mixture of 3,3,9,9-tetrakis(4-cyanophenyl)methyl]-2,4,8,10-tetraoxaspiro[5,5]undecane (**7**; 0.30 g, 0.48 mmol), dicyandiamide (0.67 g, 8.0 mmol), and powdered KOH (0.074 g, 1.3 mmol) in 2-methoxyethanol (45 mL) was heated at reflux for 12 h. The resulting mixture was cooled and filtered, and the solid was extracted thoroughly with hot water. The solid was then rinsed with CH_2Cl_2 and dried in vacuo to give tecton **1** (0.41 g, 0.43 mmol, 90%) as a colorless solid: mp >300 °C; ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 8.11 (d, 8H, $^3J = 8.1$ Hz), 7.18 (d, 8H, $^3J = 8.1$ Hz), 6.72 (br s, 16H), 3.60 (s, 8H), 2.95 (s, 8H); ^{13}C NMR (75.4 MHz, $\text{DMSO}-d_6$) δ 170.5, 167.7, 140.3, 135.3, 130.3, 127.4, 100.4, 63.0, 31.4; MS (FAB, 3-nitrobenzyl alcohol) m/e 957. Anal. Calcd for $\text{C}_{47}\text{H}_{48}\text{N}_{20}\text{O}_4 \cdot 4\text{H}_2\text{O}$: C, 54.84; H, 5.49. Found: C, 54.33; H, 5.53.

Tecton 2. An analogous procedure was carried out using 3,3,9,9-tetrakis(3-cyanophenyl)methyl]-2,4,8,10-tetraoxaspiro[5,5]undecane (**12**; 0.43 g, 0.69 mmol) and provided tecton **2** (0.57 g, 0.60 mmol, 87%) as a colorless solid: mp >300 °C; ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 8.10 (d, 4H, $^3J = 7.1$ Hz), 8.02 (m, 4H), 7.35 (m, 4H), 7.28 (m, 4H), 6.79 (br s, 16H), 3.53 (s, 8H), 2.93 (s, 8H); ^{13}C NMR (75.4 MHz, $\text{DMSO}-d_6$) δ 170.5, 167.6, 136.8, 136.6, 133.9, 130.3, 127.9, 126.1, 100.0, 63.0, 31.4; MS (FAB, 3-nitrobenzyl alcohol) m/e 957. Anal. Calcd for $\text{C}_{47}\text{H}_{48}\text{N}_{20}\text{O}_4 \cdot 6\text{H}_2\text{O}$: C, 53.00; H, 5.68; N, 26.30. Found: C, 53.10; H, 5.34; N, 26.82.

Tecton 3. An analogous procedure was carried out using 3,3,9,9-tetrakis(4-cyanophenyl)-2,4,8,10-tetraoxaspiro[5,5]undecane (**10**; 0.18 g, 0.32 mmol) and provided tecton **3** (0.25 g, 0.28 mmol, 88%) as a pale pink solid: mp >300 °C; ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 8.22 (d, 8H, $^3J = 8.4$ Hz), 7.54 (d, 8H, $^3J = 8.4$ Hz), 6.76 (br s, 16H), 3.86 (s, 8H); ^{13}C NMR (75.4 MHz, $\text{DMSO}-d_6$) δ 169.5, 167.2, 133.1, 128.5, 127.3, 126.3, 100.5, 65.0, 33.0; MS (FAB, 3-nitrobenzyl alcohol) m/e 901. Anal. Calcd for $\text{C}_{43}\text{H}_{40}\text{N}_{20}\text{O}_4 \cdot 1.5\text{H}_2\text{O}$: C, 55.66; H, 4.67. Found: C, 55.19; H, 4.56.

Tecton 4. An analogous procedure was carried out using 3,3,9,9-tetrakis(3-cyanophenyl)-2,4,8,10-tetraoxaspiro[5,5]undecane (**14**; 0.17 g, 0.30 mmol) and provided tecton **4** (0.23 g, 0.26 mmol, 87%) as a pale pink solid: mp >300 °C; ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 8.42 (m, 4H), 8.15 (d, 4H, $^3J = 7.5$ Hz), 7.57 (d, 4H, $^3J = 7.5$ Hz), 7.43 (t, 4H, $^3J = 7.5$ Hz), 6.77 (br s, 16H), 3.86 (s, 8H); ^{13}C NMR (75.4 MHz, $\text{DMSO}-d_6$) δ 170.2, 167.7, 142.1, 137.9, 129.1, 128.8, 127.7, 125.1, 101.0, 64.9, 33.0; MS (FAB, 3-nitrobenzyl alcohol) m/e 901. Anal. Calcd for $\text{C}_{43}\text{H}_{40}\text{N}_{20}\text{O}_4 \cdot 6\text{H}_2\text{O}$: C, 51.19; H, 5.19; N, 27.76. Found: C, 51.10; H, 4.72; N, 28.49.

Tecton 15. A solution of 3,3,9,9-tetrakis(4-bromophenyl)-2,4,8,10-tetraoxaspiro[5,5]undecane (**9**; 0.24 g, 0.31 mmol) in THF (10 mL) was stirred at –78 °C under dry Ar and treated dropwise with a solution of butyllithium (0.56 mL, 2.6 M in hexane, 1.5 mmol). After 60 min at –76 °C, gaseous CO_2 was bubbled through the mixture, and the temperature was allowed to rise to 25 °C. After 12 h, volatiles were removed by evaporation under reduced pressure, water was added to the residue, and the pH was adjusted to 1 by acidification with 1

M aqueous HCl. The aqueous phase was extracted with ether, the combined extracts were dried over Na_2SO_4 , and volatiles were removed by evaporation under reduced pressure. The residue was washed successively with hexane and toluene and was then dried in vacuo to give tecton **15** (0.15 g, 0.23 mmol, 74%) as a colorless solid: IR (NaCl) 1694 cm^{-1} ; $^1\text{H NMR}$ (300 MHz, $\text{DMSO}-d_6$) δ 12.8 (bs, 4H), 7.91 (d, 8H, $^3J = 8.4\text{ Hz}$), 7.55 (d, 8H, $^3J = 8.4\text{ Hz}$), 3.81 (s, 8H).

Crystallization of Tecton 1. Tecton **1** (2 mg) was dissolved in DMF (1 mL) at $25\text{ }^\circ\text{C}$, toluene was added until a very slight cloudiness was observed, and a small amount of DMF was added to make the cloudiness disappear. Long colorless plates crystallized as the mixture was allowed to stand undisturbed for 12 h at $25\text{ }^\circ\text{C}$ in a closed vial. Selected crystals were sealed in capillaries with the mother liquors for study by X-ray crystallography.

X-ray Crystallographic Study of Tecton 1. A full sphere of data was collected at 220 K using a Bruker SMART 1000 CCD diffractometer with $\text{Mo K}\alpha$ radiation. Crystals of compound **1** belong to the orthorhombic space group $Pbcn$ with $a = 23.6973(17)\text{ \AA}$, $b = 19.9952(15)\text{ \AA}$, $c = 20.2313(15)\text{ \AA}$, $V = 9586.2(12)\text{ \AA}^3$, $D_{\text{calcd}} = 1.287\text{ g cm}^{-3}$, and $Z = 4$. The structure was solved by direct methods using SHELXS-97 and refined with SHELXL-97.²² An empirical correction (SADABS)²³ was applied to the data to account for absorption and other geometry-dependent effects. All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were placed in ideal positions and refined as riding atoms. The included guests were found to be highly disordered and could not be resolved. The SQUEEZE option of the PLATON program was used to eliminate the contribution of the guests and to give final models based only on the ordered part of the structures.¹⁷

(22) Sheldrick, G. M. *SHELXS-97*, Program for the Solution of Crystal Structures and *SHELXL-97*, Program for the Refinement of Crystal Structures; Universität Göttingen: Göttingen, Germany, 1997.

(23) Sheldrick, G. M. *SADABS*, Bruker Area Detector Absorption Corrections; Bruker AXS Inc.: Madison, WI, 1996.

Full-matrix least-squares refinements on F^2 led to final residuals $R_f = 0.0836$ and $R_w = 0.2426$ for 6277 reflections with $I > 2\sigma(I)$.

Exchange of Guests in Crystals of Tecton 1. Single crystals of estimated composition $1 \cdot 10\text{DMF} \cdot x\text{H}_2\text{O}$ and approximate dimensions $1 \times 1 \times 1\text{ mm}^3$ were grown in the normal manner. The mother liquors were removed by pipet, and the crystals were immediately rinsed several times with $\text{CH}_3\text{COOC}_2\text{H}_5$ and then kept in contact with $\text{CH}_3\text{COOC}_2\text{H}_5$ at $25\text{ }^\circ\text{C}$ for 12 h without stirring. The liquid was removed by pipet, the recovered crystals were washed several times with pentane and dried briefly in air, and their content was determined by $^1\text{H NMR}$ spectroscopy to be approximately $1 \cdot 10\text{CH}_3\text{COOC}_2\text{H}_5 \cdot y\text{H}_2\text{O}$.¹² The unit cell after exchange was found to be orthorhombic with $a = 23.1030(12)\text{ \AA}$, $b = 20.2381(11)\text{ \AA}$, $c = 20.607(10)\text{ \AA}$, and $V = 9635(14)\text{ \AA}^3$.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada, the Ministère de l'Éducation du Québec, and Merck Frosst for financial support. In addition, acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also thank Dr. Michel Simard (Département de Chimie, Université de Montréal) for helping us collect and analyze the crystallographic data used to determine the structure of tecton **1**.

Supporting Information Available: ^1H and ^{13}C NMR spectra of compounds **8**, **11**, and **15**; an ORTEP drawing; and tables of crystallographic data, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for tecton **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO026267T