# Molecular tectonics — Use of urethanes and ureas derived from tetraphenylmethane and tetraphenylsilane to build porous chiral hydrogenbonded networks<sup>1</sup>

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Abstract: Tetraphenylmethane, tetraphenylsilane, and simple derivatives with substituents that do not engage in hydrogen bonding typically crystallize as close-packed structures with essentially no space available for the inclusion of guests. In contrast, derivatives with hydrogen-bonding groups are known to favor the formation of open networks that include significant amounts of guests. To explore this phenomenon, we synthesized six new derivatives **5a–5e** and **6a** of tetraphenylmethane and tetraphenylsilane with urethane and urea groups at the para positions, crystallized the compounds, and determined their structures by X-ray crystallography. As expected, all six compounds crystallize to form porous three-dimensional hydrogen-bonded networks. In the case of tetraurea **5e**, 66% of the volume of the crystals is accessible to guests, and guests can be exchanged in single crystals without loss of crystallinity. Of special note are: (*i*) the use of tetrakis(4-isocyanatophenyl)methane (**1f**) as a precursor for making enantiomerically pure tetraurethanes and tetraureas, including compounds **5b**, **5c**; and (*ii*) their subsequent crystallization to give porous chiral hydrogenbonded networks. Such materials promise to include chiral guests enantioselectively and to be useful in the separation of racemates, asymmetric catalysis, and other applications.

*Key words:* crystal engineering, molecular tectonics, hydrogen bonding, networks, porosity, urethanes, ureas, tetraphenylmethane, tetraphenylsilane.

**Résumé :** Le tétraphénylméthane, le tétraphénylsilane et leurs dérivés simples ne portant pas de substituants pouvant participer à des liaisons hydrogène cristallisent généralement sous la forme de structures compactes dans lesquelles il n'y a pas de place disponible pour l'inclusion de molécules invitées. Par contraste, il est bien connu que les dérivés comportant des groupes pouvant donner lieu à des liaisons hydrogène favorisent la formation de réseaux ouverts qui peuvent inclure des quantités importantes de molécules invitées. Dans le but d'étudier ce phénomène, on a réalisé la synthèse de six nouveaux dérivés, **5a–5e** et **6a**, du tétraphénylméthane et du tétraphénylsilane portant des groupes uréthane et urée en position para qui ont été cristallisés et dont on a déterminé la structure par diffraction des rayons X. Tel que prévu, les six composés cristallisent en formant des réseaux poreux tridimensionnels reliés par des ponts hydrogène. Dans le cas de la tétraurée **5e**, 66 % du volume des cristaux est disponible pour des molécules invitées et les invités peuvent être échangés dans les cristaux uniques sans perte de cristallinité. Il est particulièrement important de noter: (*i*) qu'il est possible d'utiliser le tétrakis(4-isocyanatophényl)-méthane (**1f**) comme précurseur dans la synthèse de tétrauréthanes et de tétraurées énantiomèrement pures, y compris les composés **5b**, **5c** et (*ii*) qu'il est possible de les cristalliser subséquemment pour donner des réseaux chiraux poreux reliés par des ponts hydrogène. Des tels produits pourraient inclure énantiosélectivement des molécules invitées chirales et ainsi être utilisés dans la séparation de racémates, en catalyse asymétrique ou dans d'autres applications.

*Mots clés :* ingénierie cristalline, tectonique moléculaire, liaison hydrogène, réseaux, porosité, uréthanes, urées, tétraphénylméthane, tétraphénylsilane.

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# Introduction

No reliable method yet exists for predicting the detailed structure of molecular crystals (1-4), and the relationship

between the structure of crystals and their physical properties remains poorly understood. For these reasons, attempts to control molecular crystallization and to engineer crystals for specific applications remain largely empirical activities.

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Dedicated with respect and affection to Professor Ed Piers.

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<sup>1</sup>This article is part of a Special Issue dedicated to Professor Ed Piers. <sup>2</sup>Corresponding author (e-mail: wuest@chimie.umontreal.ca). As a result, crystal engineering offers exceptional challenges and opportunities, and it has become one of the most exciting areas in contemporary science (5).

In a recent review (1), Dunitz identifies a strategy for directing molecular crystallization that has played a key role in bringing crystal engineering to the forefront of science: "...computational methods for predicting crystal structures of organic compounds cannot yet be regarded as reliable. From a more qualitative and descriptive viewpoint has come the notion that certain groupings in organic molecules exercise attractive intermolecular interactions and so guide the molecules into distinctive patterns in their crystal structures...This indeed has become one of the tenets of crystal engineering. The prime example of a structure directing interaction is, of course, the hydrogen bond."

This strategy can be used to design molecules to serve as subunits for the programmed construction of particular crystalline networks. This can be achieved by incorporating carefully oriented arrays of sticky sites that interact intermolecularly according to reliable motifs. Such molecules have been called tectons (6), a term derived from the Greek word for builder, and molecular tectonics refers to the strategy of building supramolecular structures from tectonic subunits (6, 7).

Tectons have arrays of sticky sites that direct intermolecular association, linked to cores that orient the sticky sites and introduce other desirable molecular features. In favorable cases, the oriented sticky sites play a dominant role in association and place each tecton in a predetermined position relative to its neighbors. Normally, tectons cannot form structures that pack efficiently and simultaneously obey the imperatives of strong directional interactions, so open molecular networks are favored, with significant space for the inclusion of guests. Many different sticky sites and cores can be used, giving molecular tectonics wide scope as a strategy for creating ordered materials with unique properties. In particular, we have recently made hydrogen-bonded molecular crystals that (i) can be engineered with sub-nanometric precision (8); (ii) use at least 75% of their volume to include guests, which can be exchanged without loss of crystallinity (9); (iii) can be deformed by at least 30% without loss of crystallinity (10); and (iv) react with external agents to give single crystals of new compounds with retention of the original crystalline architecture (11, 12).<sup>3</sup>

Invaluable basic information about molecular tectonics can be acquired through systematic comparison of structures built from tectons with a fixed core and variable sticky sites, or with fixed sticky sites and variable cores. In such studies, relatively rigid cores are beneficial because they facilitate comparison by minimizing polymorphism due to multiple conformations. The tetraphenylmethyl core (1a) and its tetraphenylsilyl analogue 2a are particularly attractive choices, and various tectons with simple hydrogen-bonding sites attached to these cores have been used in crystal engineering (8, 13–16). Tetraphenylmethane and tetraphenylsilane crystallize to form isomorphous close-packed structures held together by multiple phenyl-phenyl embraces (17, 18), and simple derivatives with substituents that do not engage in hydrogen bonding also typically form close-packed structures (19–29). In contrast, 4-substituted derivatives with simple hydrogenbonding groups, including tetraphenols **1b** and **2b** (13), tetraboronic acids **1c** and **2c** (8), and other compounds (15, 16), are known to favor open networks that include significant amounts of guests. Even derivatives with substituents that form relatively weak C-H···O hydrogen bonds, such as tetrakis(4-nitrophenyl)methane (**1d**) (14), can form open networks.

To explore the scope of this phenomenon, help identify its origins, and test its potential for creating ordered materials with new properties, we have extended our study of tectons derived from tetraphenylmethane and tetraphenylsilane to include new 4-substituted derivatives bearing urethane and urea groups, which have been used previously in crystal engineering because they self-associate reliably in the solid state to form hydrogen-bonded chains **3** and **4** (30–37). In this paper, we show how such compounds can be made and used to generate networks that are both porous and chiral.

# **Results and discussion**

# Synthesis of urethanes and ureas derived from tetraphenylmethane and tetraphenylsilane

Tetrakis(4-nitrophenyl)methane (1d) (38) was reduced by an improved procedure (H<sub>2</sub>/Pd/C, THF) to provide a 99% yield of the known tetrakis(4-aminophenyl)methane (1e) (16, 38, 39). Subsequent reaction of tetramine 1e with triphosgene and triethylamine gave tetrakis(4-isocyanatophenyl)methane (1f) in 97% yield. The analogous isothiocyanate 1g was obtained in 89% yield by the reaction of tetramine 1e with thiophosgene and triethylamine. Heating tetra(isocyanate) 1f with alcohols and amines then gave the corresponding urethanes and ureas. In this way, urethanes 5a, 5b and ureas 5c, 5d were prepared from ethanol, (R)-2-butanol, (S)-2-butylamine, and (S)- $\alpha$ -methylbenzylamine in yields of 83%, 78%, 99%, and 99%, respectively. Treatment of tetra(isocyanate) 1f with aqueous ammonia at 25 °C gave simple urea 5e in 92% yield. For comparison with tetraurethane 5a, analogue 6a with a tetraphenylsilyl core was prepared in 18% yield by Pd-catalyzed coupling of tetrakis(4-bromophenyl)silane (2d) (40) with ethyl carbamate (41).

# Structure of tetrakis(4-isothiocyanatophenyl)methane (1g)

Tetra(isothiocyanate) 1g was crystallized from CHCl<sub>3</sub>– hexane, and its structure was determined by X-ray diffraction (Table 1, Fig. 1).<sup>4</sup> Like most other simple derivatives of tetraphenylmethane and tetraphenylsilane (17–29), compound 1g forms a close-packed structure without included guests. This observation confirms that molecules with a

<sup>&</sup>lt;sup>3</sup>For citations of other recent studies of the engineering of hydrogen-bonded molecular crystals, see refs. 8–12.

<sup>&</sup>lt;sup>4</sup>Supplementary data may be purchased from the Directory of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www/nrc.ca/cisti/irm/unpub\_e.shtml for information on ordering electronically). CCDC 221549–221554 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033; or e-mail: deposit@ccdc.cam.ac.uk).



close structural relationship to tectons 5a-5e, but without an ability to self-associate by hydrogen bonding, are not predisposed to form inclusion compounds.

## Analysis of hydrogen-bonded networks formed by crystallization of tetraurethane 5a and the analogous silane 6a

Tecton **5a** crystallized from THF-pentane in the tetragonal space group *I*-4 as an inclusion compound of welldefined composition **5a**·2THF (Table 1).<sup>4</sup> The structure is shown in Figs. 2 and 3. The tectons can be divided into two equal populations (Fig. 2), one that donates single hydrogen bonds to four symmetrically oriented neighbors, and the other that accepts hydrogen bonds from four symmetrically oriented neighbors and simultaneously donates hydrogen bonds to four molecules of THF. Connecting the tetrahedral centers of hydrogen-bonded tectons defines a diamondoid network (42) with an alternating hydrogen bond donor–acceptor arrangement, in which each node is surrounded by four belonging to the other population. The network is held



Compound	1g	5a•2THF	6a·2dioxane
Formula	C <sub>29</sub> H <sub>16</sub> N <sub>4</sub> S <sub>4</sub>	C <sub>45</sub> H <sub>56</sub> N <sub>4</sub> O <sub>10</sub>	C44H56N4O12Si
Fw	548.74	812.94	861.02
<i>F</i> (000)	1128	1736	916
Crystal system	Monoclinic	Tetragonal	Tetragonal
Space group	$P2_1/n$	<i>I</i> -4	$P4_2/n$
a (Å)	11.6490(1)	24.9135(8)	17.7781(2)
b (Å)	11.4547(1)	24.9135(8)	17.7781(2)
<i>c</i> (Å)	20.5132(1)	7.1597(2)	7.1904(1)
α (°)	90	90	90
β (°)	95.890(1)	90	90
γ (°)	90	90	90
Volume (Å <sup>3</sup> )	2722.75(4)	4443.9(2)	2272.60(5)
Ζ	4	4	2
Density (g/cm <sup>3</sup> )	1.339	1.215	1.258
Temperature (K)	293(2)	293(2)	293(2)
$R_1$	0.0609	0.0688	0.0724
$wR_2$	0.1810	0.1795	0.2160
GoF	1.056	1.008	1.024
Porosity (%)	0	29	0

Table 1. Crystallographic data for compounds 1g, 5a·2THF, and

**Fig. 2.** Representation of the structure of crystals of tetraurethane **5a** grown from THF–pentane, showing a central tecton (dark gray) that donates single hydrogen bonds to four neighboring tectons (light gray). Each neighbor accepts single hydrogen bonds from three other tectons and donates hydrogen bonds to the guests (THF). Hydrogen bonds appear as broken lines.

**6a**·2dioxane.<sup>4</sup>



**Fig. 3.** View along the *c* axis of the network constructed from tetraurethane **5a** showing a  $2 \times 2 \times 4$  array of unit cells. Guests are omitted, and atoms are shown as spheres of van der Waals radii to reveal the cross sections of the channels. Atoms of hydrogen appear in white, atoms of carbon in light gray, atoms of oxygen in gray, and atoms of nitrogen in dark gray.



together by only four hydrogen bonds per tecton. The average distance between the tetrahedral centers of hydrogenbonded neighbors defines an intertectonic separation of 12.6 Å, which is too small to permit interpenetration (43, 44). Approximately 29% of the volume of crystals of tecton **5a** is available for including guests,<sup>5</sup> which occupy parallel channels that lie along the *c* axis and have cross sections measuring nearly  $11 \times 3 \text{ Å}^2$  (Fig. 3).<sup>6</sup> Close examination of the channels reveals that each is helical and chiral, with equal numbers of helices of opposite handedness (Fig. 4).<sup>7</sup>

Crystallization of tetraboronic acid 1c and the analogous silane 2c under similar conditions is known to produce isostructural hydrogen-bonded networks (8). Replacing the central C—C bonds in compound 1c with longer Si—C bonds in analogue 2c results in a rational expansion of the network, with predictable control of geometry on the sub-nanometric scale. To further test the ability of molecular tectonics to control crystallization with this degree of precision, we compared the structure of tetraurethane 5a with that formed by the corresponding silane 6a. Tecton 6a crystallized from dioxane–pentane in the tetragonal space group  $P4_2/n$  as an inclusion compound with the composition 6a·2 dioxane **Fig. 4.** Stereoscopic representation of the parallel helical channels defined by the network constructed from tetraurethane **5a**. The image shows a  $1 \times 1 \times 4$  array of unit cells viewed with the *c* axis horizontal. 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 centre of a sphere of diameter 3 Å as it rolls over the surface of the ordered network.<sup>7</sup>



(Table 1).<sup>4</sup> The structure is shown in Figs. 5 and 6. Each tecton donates four hydrogen bonds to four neighboring molecules of dioxane, and each molecule of dioxane accepts two hydrogen bonds from different tectons, thereby creating a diamondoid network (42) in which dioxane is an essential structural component (Fig. 5). The average Si···Si distance between closest pairs of tectons within the network is 16.6 Å, which is large enough to permit sixfold interpenetration (Fig. 6) (43, 44). This fills the available volume completely, giving a close-packed structure containing only tecton **6a** and molecules of dioxane that are an integral part of the network.

The observed structures of tectons **5a** and **6a** are largely consistent with the emerging principles of molecular tectonics. In particular, both compounds crystallize as expected to form open hydrogen-bonded diamondoid networks that incorporate solvent. Unexpectedly, the networks are not isostructural, but it is important to note that tecton **5a** was crystallized from THF-pentane and tecton **6a** from dioxanehexane. We subsequently found that tecton **5a** can also be crystallized from dioxane and tecton **6a** from THF. However, we elected not to study these new structures further because those already solved did not show exceptional porosity.

## Porous chiral hydrogen-bonded networks formed by crystallization of enantiomerically pure tetraurethane 5b and tetraurea 5c

Exciting opportunities for constructing new types of porous molecular networks are created by using enantiomerically pure tectons such as analogues **5b–5d** of tetraurethane **5a**. The principles of molecular tectonics suggest that crystallization of these analogues should produce porous hydrogen-bonded networks, as observed in the case of tecton **5a**. However, these new networks will be chiral and may therefore be able to include chiral guests enantio-

<sup>&</sup>lt;sup>5</sup>The percentage of volume accessible to guests was estimated by the PLATON program (45, 46), using standard parameters (9, 13).

<sup>&</sup>lt;sup>6</sup>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 (i) they measure the cross section at the most narrow constriction, and (ii) they systematically underestimate the sizes of channels that are not uniform and linear.

<sup>&</sup>lt;sup>7</sup>Representations of channels were generated by the Cavities option in the programs ATOMS Version 5.1 (Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663; www.shapesoftware.com). We are grateful to Eric Dowty of Shape Software for integrating this capacity in ATOMS at our suggestion.

Fig. 5. View of part of the structure of crystals of tetraurethane 6a grown from dioxane-pentane, showing two tectons linked by hydrogen bonds donated to an intervening molecule of dioxane. Hydrogen bonds appear as broken lines.



Fig. 6. Representation of the sixfold interpenetrated diamondoid networks generated by association of tetraurethane **6a** with dioxane. In this drawing, the central silicon atom of each tetraurethane lies at the intersection of solid lines that represent hydrogen bonding to four neighbors via intervening molecules of dioxane. Independent networks are shown in different shades of gray.



selectively. Such behavior would illustrate a key advantage of using molecules to make porous materials for applications in separation and catalysis, rather than using inorganic analogues such as zeolites. Specifically, creating asymmetric environments within supramolecular materials can be achieved by simple modifications of the individual molecular components, whereas very few zeolites are inherently chiral (47–49). As result, an important goal in crystal engineering is to devise molecules that form porous chiral hydrogen-bonded networks and then to use the resulting materials for the enantioselective inclusion and exchange of guests. However, few successes have been reported so far (50–58).

Enantiomerically pure tetraurethane 5b crystallized from THF-pentane in the tetragonal space group  $I4_1$  as an inclusion compound of approximate composition 5b-2 pentane (Table 2).<sup>4,8</sup> As shown in Fig. 7, each tecton forms a total of eight hydrogen bonds with four symmetrically oriented neighbors, and each urethane group serves simultaneously as a donor and acceptor of hydrogen bonds. This defines a diamondoid network (42) in which the average intertectonic distance between the tetrahedral centers of neighbors is 9.73 Å. No interpenetration is observed (43, 44), and 16% of the volume remains available for including guests.<sup>5</sup> Despite intensive effort, we were unable to grow crystals of tecton 5b suitable for X-ray diffraction when we used racemic solvents such as  $(\pm)$ -2-bromobutane,  $(\pm)$ -2-chloropentane, and  $(\pm)$ -2methyltetrahydrofuran, so we were unable to examine the enantioselectivity of inclusion.

Crystals of the analogous enantiomerically pure tetraurea 5c were obtained by allowing dioxane to diffuse into solutions in HCOOH. X-ray crystallography established that tecton 5c crystallized under these conditions in the tetragonal space group  $I4_1$  as an inclusion compound of welldefined composition 5c·2HCOOH (Table 2).<sup>4</sup> Selfassociation of tetraurea 5c produces a hydrogen-bonded diamondoid network (42) isostructural to the one generated by the analogous tetraurethane 5b (Fig. 8). Each tecton forms a total of 16 hydrogen bonds with four symmetrically oriented neighbors, and each urea group serves simultaneously as a double donor and double acceptor of hydrogen bonds. No interpenetration is observed (43, 44), and 17% of the volume remains available for including guests.<sup>5</sup> Unfortunately, we were unable to grow crystals of tecton 5c suitable for X-ray diffraction from racemic solvents, so we were not able to confirm that inclusion is enantioselective.

 $<sup>^{8}</sup>$  The composition was estimated by X-ray crystallography and by  $^{1}$ H NMR spectroscopy of dissolved samples. The amount of any H<sub>2</sub>O included could not be determined accurately.

				5e·2DMSO·5dioxane after
Compound	5b·2Pentane	<b>5с</b> •2НСО <sub>2</sub> Н	5e·2DMSO·5 dioxane	exchange with THF
Formula	C55H80N4O8	C <sub>47</sub> H <sub>62</sub> N <sub>8</sub> O <sub>12</sub>	C <sub>53</sub> H <sub>80</sub> N <sub>8</sub> O <sub>16</sub> S <sub>2</sub>	
Fw	925.23	931.05	1149.37	
<i>F</i> (000)	2008	1864	2456	
Crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space group	<i>I</i> 4 <sub>1</sub>	<i>I</i> 4 <sub>1</sub>	$P-42_{1}c$	$P-42_{1}c$
a = b (Å)	17.7201(6)	17.2392(3)	17.281(2)	17.184(8)
<i>c</i> (Å)	16.0845(7)	17.3495(3)	20.591(2)	20.838(2)
Volume (Å <sup>3</sup> )	5050.6(3)	5156.1(2)	6149(1)	6152(87)
Ζ	4	4	4	
Density (g/cm <sup>3</sup> )	1.217	1.12	1.242	
Temperature (K)	293(2)	293(2)	223(2)	223(2)
$R_1$	0,1022	0,1089	0.0989	
$wR_2$	0,2888	0.3059	0.2721	
GoF	1,038	1.265	1.249	
Flack Parameter	0.1(18)	-0.2(3)	0.14(10)	
Porosity (%)	16	17	66	—

**Table 2.** Crystallographic data for compounds **5b**·2pentane, **5c**·2HCO<sub>2</sub>H, **5e**·2DMSO·5dioxane, and **5e** after replacement of dioxane by THF.<sup>4</sup>

**Fig. 7.** Representation of the structure of crystals of tetraurethane **5b** grown from THF–pentane, showing a tecton (dark gray) hydrogen-bonded to one of four neighbors (light gray). The illustrated neighbor is equivalent by symmetry to three others, which are omitted for clarity. Hydrogen bonds appear as broken lines, and guests are omitted for clarity. Each urethane group serves simultaneously as a donor and acceptor of hydrogen bonds.



# Porous hydrogen-bonded network formed by crystallization of tetraurea 5e

Tetraurea **5e** crystallized from DMSO-dioxane in the tetragonal space group  $P-42_1c$  as an inclusion compound with the approximate composition **5e**·2DMSO·5dioxane (Table 2).<sup>4,8</sup> The composition of the crystals indicated immediately that a large fraction of the volume is accessible to

guests. As shown in Fig. 9, each tecton forms hydrogen bonds with six neighboring tectons (Fig. 9*a*). Two neighbors that lie along the *c* axis on opposite sides of the central tecton are equivalent by symmetry, and each accepts four hydrogen bonds from the central tecton (Fig. 9*b*). The other four neighbors form a second symmetry-equivalent set, and each donates two hydrogen bonds to the central tecton **Fig. 8.** Representation of the structure of crystals of tetraurea 5c grown from HCOOH–dioxane, showing a tecton (dark gray) hydrogen-bonded to one of four neighbors (light gray). The illustrated neighbor is equivalent by symmetry to three others, which are not shown. Hydrogen bonds appear as broken lines, and guests are omitted for clarity. Each urea group serves simultaneously as a double donor and double acceptor of hydrogen bonds.



(Fig. 9*c*). In addition, part of the N—H bonds not used in intertectonic hydrogen bonding remain available for interacting with included DMSO. Each tecton therefore participates in a total of 16 hydrogen bonds with neighboring tectons. Joining the tetrahedral centers of the tectons defines the approximately octahedral 6-connected network shown in Fig. 9*d*. The average intertectonic distances are 10.30 Å in the *c* direction and 12.22 Å in the *a* and *b* directions.

No interpenetration is observed (43, 44), and approximately 66% of the volume of crystals of tecton **5e** remains available for the inclusion of guests,<sup>5</sup> which occupy interconnected channels. The porosity is unusually high, and it far exceeds the fraction of volume (normally about 30%) that is considered to remain unfilled in normal molecular crystals because of inefficient packing (59). The most significant channels are aligned with the *ab* diagonal and have cross sections measuring approximately  $5.7 \times 6.3$  Å<sup>2</sup> at the narrowest points (Fig. 10).<sup>6</sup> The surface shown in Fig. 11 further defines the shape and complex interconnectivity of the channels.<sup>7</sup>

The network built from tecton **5e** is very porous, the interior of crystals is made accessible by significant interconnected channels, and high structural integrity is ensured by the formation of 16 hydrogen bonds per tecton. As a result, guests can be exchanged in single crystals without loss of crystallinity. For example, single crystals of estimated composition **5e**·2DMSO·5dioxane and approximate dimensions 1 mm  $\times$  1 mm  $\times$  5 mm were suspended in THF at 25 °C for

24 h. Subsequent analysis of recovered samples by <sup>1</sup>H NMR spectroscopy in solution showed complete replacement of dioxane by THF. The recovered samples remained transparent, showed no morphological changes visible by optical microscopy, and continued to diffract. Study of single exchanged crystals by X-ray diffraction showed little variation in the unit cell parameters (Table 2), suggesting that the network undergoes little distortion.

# Conclusions

Our studies of tetraurethanes and tetraureas 5a-5e and 6a confirm that (*i*) tetraphenylmethane and tetraphenylsilane are effective cores for constructing molecules of value in crystal engineering, and (*ii*) substituting these cores with hydrogenbonding groups produces tectons that crystallize predictably to give open three-dimensional networks that can include significant amounts of guests. Of special note is the observation that enantiomerically pure tectons such as tetraurethane **5b** and tetraurea **5c** can be made conveniently from tetra-(isocyanate) **1f** and crystallize to give porous chiral networks. Such molecular materials have unique properties that promise to make them useful in enantioselective catalysis, the resolution of racemates, and other applications.

## Experimental

Tetrahydrofuran (THF) was dried by distillation from the

**Fig. 9.** (a) View of the structure of crystals of tetraurea **5e** grown from DMSO-dioxane showing a central tecton (dark gray) and its six hydrogen-bonded neighbors. Four of the neighbors (light gray) define a set equivalent by symmetry, and two others (gray) define a second set. All atoms are shown as spheres of van der Waals radii, and guests are omitted for clarity. (b) Hydrogen bonding between the central tecton (dark gray) and the set of two symmetry-equivalent neighbors (gray). Hydrogen bondis appear as broken lines. (c) Hydrogen bonding between the central tecton (dark gray) and the set of four symmetry-equivalent neighbors (light gray). Hydrogen bondis appear as broken lines. (d) Representation of the 6-connected network defined by joining the central carbon atom of each tecton with the centres of the set of six neighbors shown in Fig. 1a.







sodium ketyl of benzophenone. Xantphos (60) and tetrakis-(4-bromophenyl)silane (**2d**) (40) were synthesized according to known procedures. All other reagents were commercial products that were used without further purification.

## Tetrakis(4-aminophenyl)methane (1e) (16, 38, 39)

A suspension of tetrakis(4-nitrophenyl)methane (1d, 4.10 g, 8.19 mmol) (38) and 10% Pd/C (410 mg) in THF (300 mL) was stirred for 70 h in a Parr reactor at 25  $^{\circ}$ C un-

(d)



der H<sub>2</sub> (1200 kPa). The resulting mixture was filtered through Celite<sup>®</sup>, and volatiles were removed by evaporation under reduced pressure. The residue was triturated with CHCl<sub>3</sub> and washed with CH<sub>3</sub>OH to afford tetrakis(4-aminophenyl)methane (**1e**, 3.09 g, 8.12 mmol, 99%) (16, 38, 39) as a colorless solid that was used without further purification. A sample of analytical purity was obtained by crystallization from ethanol–water to afford small colorless crystals; mp 319 °C (lit. (16) mp 331 °C, lit. (38) mp 319 to

**Fig. 10.** View along the *ab* diagonal of the network constructed from tetraurea **5e** showing a  $2 \times 2 \times 2$  array of unit cells. Guests are omitted, and atoms are shown as spheres of van der Waals radii to reveal the cross sections of the channels. Atoms of hydrogen appear in white, atoms of carbon in light gray, atoms of oxygen in gray, and atoms of nitrogen in dark gray.



320 °C, lit. (39) mp 318 °C). IR (KBr) (cm<sup>-1</sup>): 3396, 3171, 3026, 1610, 1507, 1271, 1183, 860, 829, 813, 578. <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ) & 6.69 (d, <sup>3</sup>J = 8.5 Hz, 8H), 6.40 (d, <sup>3</sup>J = 8.5 Hz, 8H), 4.86 (s, 8H). <sup>13</sup>C NMR (75 MHz, DMSO- $d_6$ ) & 145.7, 135.9, 131.4, 112.6, 61.1. MAB-HR-MS (N<sub>2</sub>) calcd. for C<sub>25</sub>H<sub>24</sub>N<sub>4</sub> *m/e*: 380.20097; found: 380.200966. Anal. calcd. for C<sub>25</sub>H<sub>24</sub>N<sub>4</sub>: C 78.92, H 6.36, N 14.73; found: C 78.65, H 6.33, N 14.23.

## Tetrakis(4-isocyanatophenyl)methane (1f)

A solution of triphosgene (1.39 g, 4.68 mmol) in dry THF (10 mL) was added dropwise to a stirred solution of tetrakis-(4-aminophenyl)methane (**1e**, 1.19 g, 3.13 mmol) and triethylamine (3.49 mL, 25.0 mmol) in dry THF (60 mL) at -78 °C under N<sub>2</sub>. The mixture was then warmed to 0 °C during 2 h, and insoluble solids were removed by filtration through Celite<sup>®</sup>. Volatiles were removed by evaporation under reduced pressure to give tetrakis(4-isocyanatophenyl) methane (**1f**, 1.48 g, 3.05 mmol, 97%) as a colorless solid that was used without further purification. A sample of analytical purity was obtained by sublimation (130 °C/0.1 mm Hg (1 mm Hg = 133.322 Pa)), mp 53 to 54 °C (softening). IR (KBr) (cm<sup>-1</sup>): 2260, 1604, 1574, 1519, 1109, 1016, 822, 563. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.10 (d, <sup>3</sup>J = 8.9 Hz, 8H), 7.00 (d, <sup>3</sup>J = 8.9 Hz, 8H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 143.6, 132.0, 131.8, 125.1, 124.4, 63.7. FAB-HR-MS (3-nitrobenzyl alcohol) calcd. for C<sub>29</sub>H<sub>16</sub>N<sub>4</sub>O<sub>4</sub> *m/e*: 484.117155; found: 484.116508.

#### Tetrakis(4-isothiocyanatophenyl)methane (1g)

Thiophosgene (0.264 mL, 3.46 mmol) was added dropwise to a stirred solution of tetrakis(4-aminophenyl) methane (1e, 300 mg, 0.788 mmol) and triethylamine (0.880 mL, 6.31 mmol) in dry THF (25 mL) at -10 °C under N<sub>2</sub>. The resulting mixture was then warmed to 25 °C during 1 h. Water was added, and the mixture was extracted twice with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, and volatiles were removed by evaporation under reduced pressure. The residual solid was purified by flash chromatography (silica,  $CH_2Cl_2$  (30%) – hexane (70%),  $R_f$ 0.59) to provide tetrakis(4-isothiocyanatophenyl) methane (1g, 386 mg, 0.703 mmol, 89%) as a colorless solid, mp 203 to 204 °C. IR (KBr) (cm<sup>-1</sup>): 2200–2000 (bs), 1496, 932, 817. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.15 (d, <sup>3</sup>J = 8.9 Hz, 8H), 7.10 (d,  ${}^{3}J$  = 8.9 Hz, 8H).  ${}^{13}C$  NMR (100 MHz, CDCl<sub>3</sub>) δ: 144.4, 136.4, 131.8, 130.1, 125.6, 64.2. FAB-MS (3nitrobenzyl alcohol) m/e: 548. Anal. calcd. for C<sub>29</sub>H<sub>16</sub>N<sub>4</sub>S<sub>4</sub>: C 63.48, H 2.94, N 10.21; found: C 63.33, H 2.81, N 10.05.

### **Tetraurethane 5a**

A solution of tetrakis(4-isocyanatophenyl)methane (1f, 315 mg, 0.650 mmol) in absolute ethanol (15 mL) was heated at reflux for 1 h. Volatiles were then removed by evaporation under reduced pressure, and the residual solid was purified by flash chromatography (silica, CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> (50%) – hexane (50%),  $R_f (0.50)$  to afford tetraurethane 5a (360 mg, 0.538 mmol, 83%) as a colorless solid, mp 223 to 224 °C. IR (KBr) (cm<sup>-1</sup>): 3292, 2980, 1729, 1597, 1535, 1412, 1317, 1297, 1221, 1113, 1063, 872, 811. <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ )  $\delta$ : 9.59 (s, 4H), 7.33 (d, <sup>3</sup>J = 8.4 Hz, 8H), 6.98 (d,  ${}^{3}J$  = 8.4 Hz, 8H), 4.09 (q,  ${}^{3}J$  = 6.5 Hz, 8H) 1.22 (t,  ${}^{3}J$  = 6.5 Hz, 12H).  ${}^{13}C$  NMR (100 MHz, DMSO- $d_{6}$ ) δ: 153.5, 140.7, 136.8, 130.5, 117.4, 62.3, 60.0, 14.4. FAB-HR-MS (3-nitrobenzyl alcohol) calcd. for C<sub>37</sub>H<sub>40</sub>N<sub>4</sub>O<sub>8</sub> m/e: 668.28461: found: 668.28410. Anal. calcd. for C37H40N4O8·H2O: C 64.71, H 6.16, N 8.16; found: C 65.11, H 6.16, N 8.00.

#### **Tetraurethane 5b**

(*R*)-2-Butanol (0.66 mL, 7.2 mmol) was added to a stirred solution of tetrakis(4-isocyanatophenyl)methane (**1f**, 440 mg, 0.908 mmol) in dry THF (5 mL), and the mixture was heated at reflux for 1 h. Volatiles were then removed by evaporation under reduced pressure, and the residual solid was purified by flash chromatography (silica, CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> (30%) – hexane (70%), *R<sub>f</sub>* 0.43) to provide tetraurethane **5b** (553 mg, 0.708 mmol, 78%) as a colorless solid, mp 273 °C.  $[\alpha]_D = -21^\circ$  (*c* 0.30 in ethanol). IR (KBr) (cm<sup>-1</sup>): 3311, 2974, 2936, 2879, 1705, 1600, 1528, 1409, 1379, 1321, 1296, 1228, 1127, 1054, 826, 771, 530. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) & 7.25 (d, <sup>3</sup>*J* = 8.7 Hz, 8H), 7.10 (d, <sup>3</sup>*J* = 8.7 Hz, 8H), 6.54 (s, 4H), 4.84 (m, 4H), 1.61 (m, 8H), 1.26 (d, <sup>3</sup>*J* =

**Fig. 11.** Stereoscopic representation of the interconnected channels within the network constructed from tetraurea **5e**. The image shows a  $2 \times 2 \times 1$  array of unit cells viewed along the *c* axis. 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 centre of a sphere of diameter 3.5 Å as it rolls over the surface of the ordered network.<sup>7</sup>



6.3 Hz, 12H), 0.94 (t,  ${}^{3}J$  = 7.4 Hz, 12H).  ${}^{13}C$  NMR (100 MHz, CDCl<sub>3</sub>) & 153.7, 141.9, 136.2, 131.7, 117.7, 73.4, 63.1, 29.2, 19.9, 9.9. FAB-MS (3-nitrobenzyl alcohol) *m/e*: 780.1. Anal. calcd. for C<sub>45</sub>H<sub>56</sub>N<sub>4</sub>O<sub>8</sub>: C 69.21, H 7.23, N 7.17; found: C 69.21, H 7.31, N 7.18.

## **Tetraurea 5c**

(S)-2-Butylamine (261 mg, 3.57 mmol) was added to a stirred solution of tetrakis(4-isocyanatophenyl)methane (1f, 392 mg, 0.809 mmol) in dry THF (20 mL), and the mixture was heated at reflux for 1 h. Hexane was then added, and the resulting precipitate was separated by filtration and washed with  $CHCl_3$  and then hexane to afford tetraurea 5c (622 mg, 0.800 mmol, 99%) as a beige solid. A sample of analytical purity was obtained by crystallization from HCOOHdioxane to afford pale orange crystals, mp > 330 °C.  $[\alpha]_{D}$  =  $+22^{\circ}$  (c 1.00 in DMF). IR (KBr) (cm<sup>-1</sup>): 3330, 2965, 2931, 2875, 1653, 1595, 1541, 1508, 1316, 1228, 816. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 8.27 (s, 4H), 7.23 (d,  ${}^{3}J$  = 8.8 Hz, 8H), 6.90 (d,  ${}^{3}J = 8.8$  Hz, 8H), 5.92 (d,  ${}^{3}J = 8.1$  Hz, 4H), 3.57 (m, 4H), 1.39 (m, 8H), 1.04 (d,  ${}^{3}J$  = 6.6 Hz, 12H), 0.85 (t,  ${}^{3}J = 7.4$  Hz, 12H).  ${}^{13}C$  NMR (100 MHz, DMSO- $d_{6}$ )  $\delta$ : 154.8, 139.6, 138.1, 130.6, 116.5, 62.0, 46.0, 29.3, 20.7, 10.2. FAB-HR-MS (3-nitrobenzyl alcohol) calcd. for  $C_{45}H_{60}N_8O_4 + H m/e: 777.481578;$  found: 777.484089. Anal. calcd. for C45H60 N8O4·3.5H2O: C 64.34, H 8.04, N 13.34; found: C 64.22, H 7.84, N 13.73.

### Tetraurea 5d

A procedure similar to the one used to synthesize tetraurea **5c** converted tetrakis(4-isocyanatophenyl)methane (**1f**, 125 mg, 0.258 mmol) and (*S*)- $\alpha$ -methylbenzylamine (0.166 mL, 1.30 mmol) into tetraurea **5d** (248 mg, 0.256 mmol, 99%), which was isolated as a colorless solid. A sample of analytical purity was obtained by crystallization from CH<sub>3</sub>OH, mp 262 to 263 °C. [ $\alpha$ ]<sub>D</sub> = -116° (*c* 0.30 in ethanol). IR (KBr) (cm<sup>-1</sup>): 3400, 1677, 1596, 1506, 1407, 1319, 1292, 1238, 1115, 821. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) & 8.36 (s, 4H), 7.31 (m, 16H), 7.22 (m, 12H), 6.88 (d, <sup>3</sup>*J* = 8.7 Hz, 8H), 6.56 (d, <sup>3</sup>*J* = 7.6 Hz, 4H), 4.79 (dq, <sup>3</sup>*J* = 7.6, 6.9 Hz, 4H), 1.36 (d, <sup>3</sup>*J* = 6.9 Hz, 12H). <sup>13</sup>C NMR



(75 MHz, DMSO- $d_6$ ) & 154.4, 145.2, 139.7, 137.9, 130.7, 128.3, 126.6, 125.8, 116.6, 62.1, 48.6, 23.1. FAB-MS (3-nitrobenzyl alcohol) *m/e*: 969. Anal. calcd. for C<sub>61</sub>H<sub>60</sub>N<sub>8</sub>O<sub>4</sub>: C 75.60, H 6.24, N 11.56; found: C 75.26, H 6.37, N 11.39.

### Tetraurea 5e

Aqueous NH<sub>3</sub> (28%, 5 mL) was added to a stirred solution of tetrakis(4-isocyanatophenyl)methane (1f, 480 mg, 0.991 mmol) in dry THF (20 mL), and the resulting mixture was stirred for 1 h. Volatiles were then removed by evaporation under reduced pressure, and the residual solid was washed with water and crystallized from 2-methoxyethanol-THF to provide tetraurea 5e (501 mg, 0.907 mmol, 92%) as a colorless solid, mp > 330 °C. IR (KBr) (cm<sup>-1</sup>): 3500–3000 (bs), 1666, 1588, 1532, 1509, 1410, 1344, 816. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 8.49 (s, 4H), 7.26 (d,  ${}^{3}J$  = 8.7 Hz, 8H), 6.93 (d,  ${}^{3}J$  = 8.7 Hz, 8H), 5.80 (s, 8H).  ${}^{13}C$  NMR (100 MHz, DMSO-d<sub>6</sub>) δ: 156.1, 139.9, 138.1, 130.6, 116.9, 62.2. FAB-HR-MS (3-nitrobenzyl alcohol) calcd. for C<sub>29</sub>H<sub>28</sub>N<sub>8</sub>O<sub>4</sub> m/e: 552.223352; found: 552.225072. Anal. calcd. for C<sub>29</sub>H<sub>28</sub>N<sub>8</sub>O<sub>4</sub>·1.5H<sub>2</sub>O: C 60.09, H 5.39; found: C 59.91, H 5.96.

## **Tetraurethane 6a**

Deoxygenated dioxane (10 mL) was added to a deoxygenated mixture of tetrakis(4-bromophenyl)silane (2d, 652 mg, 1.00 mmol) (40), Pd(OOCCH<sub>3</sub>)<sub>2</sub> (45.0 mg, 0.200 mmol), Xantphos (180 mg, 0.311 mmol) (60), Cs<sub>2</sub>CO<sub>3</sub> (1.70 g, 5.22 mmol), and ethyl carbamate (392 mg, 4.40 mmol). The resulting mixture was stirred at reflux for 48 h under N<sub>2</sub> and then filtered through Celite<sup>®</sup>. Volatiles were removed by evaporation under reduced pressure, and the residual solid was purified by flash chromatography (silica, CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> (40%) – hexane (60%),  $R_f$  0.25) to give tetraurethane 6a (125 mg, 0.183 mmol, 18%) as a colorless solid, mp 138 to 139 °C. IR (KBr) (cm<sup>-1</sup>): 3500-3300, 2980, 2928, 1707, 1596, 1519, 1396, 1319, 1222, 1062, 824, 685, 536. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ: 9.74 (s, 4H), 7.49 (d,  ${}^{3}J = 8.3$  Hz, 8H), 7.33 (d,  ${}^{3}J = 8.3$  Hz, 8H), 4.12 (q,  ${}^{3}J =$ 7.1 Hz, 8H), 1.24 (t,  ${}^{3}J$  = 7.1 Hz, 12H).  ${}^{13}C$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$ : 153.5, 140.6, 136.4, 127.2, 117.7, 60.2, 14.5.

FAB-HR-MS	(3-nitrobenzyl	alcohol)	calcd.	for
$\mathrm{C}_{36}\mathrm{H}_{40}\mathrm{N}_{4}\mathrm{O}_{8}\mathrm{Si}$	<i>m/e</i> : 684.261543;	found: 684.2	260943.	

## X-ray crystallographic studies

The structures were solved by direct methods using SHELXS-97 (61) and refined with SHELXL-97 (62). All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were placed in ideal positions and refined as riding atoms.

### Crystallization of compounds 1g, 5a-5e, and 6a

Single crystals of tetra(isothiocyanate) **1g** suitable for analysis by X-ray diffraction were grown from  $CHCl_3$ -hexane. Crystals of tetraurethanes **5a** and **6a** were obtained by slow diffusion of pentane into solutions in THF or dioxane at 25 °C. Crystals of tetraurethane **5b** were grown by slow diffusion of pentane into a solution in dioxane at 25 °C. Crystals of tetraurea **5c** were obtained by slow diffusion of dioxane into a solution in HCOOH at 25 °C. Crystals of tetraurea **5e** were grown by slow diffusion of dioxane into a solution in DMSO at 25 °C.

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