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Engineering Hydrogen-Bonded Molecular Crystals Built from Derivatives of Hexaphenylbenzene and Related Compounds

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Abstract: Hexakis[4-(2,4-diamino-1,3,5-triazin-6-yl)phenyl]benzene (**4**) incorporates a disc-shaped hexaphenylbenzene core and six peripheral diaminotriazine groups that can engage in hydrogen bonding according to established motifs. Under all conditions examined, compound **4** crystallizes as planned to give closely related noninterpenetrated three-dimensional networks built from sheets in which each molecule has six hydrogen-bonded neighbors. In the structure of compound **4**, the number of hydrogen bonds per molecule and the percentage of volume accessible to guests approach the highest values so far observed in molecular networks. Analogue **5** (which has the same hexaphenylbenzene core but only four diaminotriazine groups at the 1,2,4,5-positions) and analogue **7** (in which the two unsubstituted phenyl groups of compound **5** are replaced by methyl groups) crystallize according to a closely similar pattern. Analogues with flatter pentaphenylbenzene or tetraphenylbenzene cores crystallize differently, underscoring the importance of maintaining a consistent molecular shape in attempts to engineer crystals with predetermined properties.

Introduction

Designing molecules to form crystals with particular structures and properties has become a very active area of research.[3] An especially productive strategy in crystal engineering builds structures from molecules that engage in multiple specific interactions with neighbors.[4−7] Such molecules, which have been called tectons,[8] are well suited for the purposeful construction of new materials. Hydrogen bonds have been widely exploited in this strategy because their strength and directionality tend to favor the formation of crystals in which neighboring molecules are positioned predictably.[9] The resulting structures can be described as networks of molecules connected by hydrogen bonds.

These networks often have a significant degree of openness because efficient packing cannot normally be achieved at the same time that hydrogen bonding is optimized. In such cases, an important percentage of the volume of the resulting crystals can be occupied by included guests. Systematic efforts to increase the openness of the resulting networks have yielded molecular crystals in which as much as 75% of the volume is accessible to guests.[5,6,10,11] Initially, these permeable molecular crystals were exotic curiosities; increasingly, however, they are serving as inspiration for scientists studying subjects of immediate practical importance, such as ways to make new porous materials for selectively storing guests,[12] to make solids react

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(2) Fellow of the Natural Sciences and Engineering Research Council of Canada, 2003−2007.

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(7) For recent overviews of the strategy, see: Wuest, J. D. *Chem. Commun.* **2005**, 5830−5837. Hosseini, M. W. *Acc. Chem. Res.* **2005**, *38*, 313−323.

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(9) For reviews, see: Steiner, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 48−76. Prins, L. J.; Reinhoudt, D. N.; Timmerman, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2382−2426.

(10) We estimate the percentage of volume accessible to guests by using the PLATON program.[11] PLATON calculates the accessible volume by allowing a spherical probe of variable radius to roll over the van der Waals surface of the network. PLATON uses a default value of 1.20 Å for the radius of the probe, which is an appropriate model for small guests such as water.

(11) 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*, 194−201.

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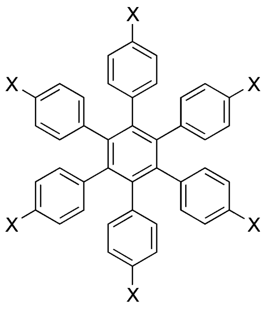
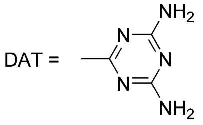
without using solvents to dissolve them,[13] and to create new types of gels, liquid crystals, films, glasses, and other materials in which particular degrees of order, porosity, and molecular diffusion must be maintained.[14]

Diverse tectons can be made conveniently by attaching appropriate hydrogen-bonding groups or other sticky sites to the periphery of cores with well-defined geometries. Many previously studied networks have been built from tectons with nominally tetrahedral cores, which tend to favor diamondoid architectures. In such structures, the volume available for including guests is often diminished or even eliminated by the interpenetration of independent networks.[15] Increasing the permeability of molecular crystals requires new types of tectons that yield networks in which interpenetration is disfavored or impossible. In addition, to ensure that the resulting networks are highly robust, each tecton must form many hydrogen bonds with its neighbors.

As part of a systematic effort to construct highly open and robust hydrogen-bonded networks, we turned our attention to tectons with complex aromatic cores related to hexaphenylbenzene. In noteworthy earlier work in crystal engineering, Kobayashi and co-workers showed that compounds **1**−**3**, which have simple hydrogen-bonding groups attached to each of the six radiating phenyl arms of hexaphenylbenzene, form open networks without interpenetration.[16−18] A summary of key features of these structures appears in Table 1. Hexakis(4-hydroxyphenyl)benzene (**1**) was shown to crystallize from two different solvent systems as inclusion compounds that both consist of hydrogen-bonded sheets.[16] In each of these two structures, the percentage of volume accessible to guests is relatively modest (42% and 48%), as is the number of hydrogen bonds in which each tecton participates (four and eight). Hexakis(4-carboxyphenyl)benzene (**2**) also crystallizes as sheets, which are held together by self-association of the carboxyl groups as cyclic hydrogen-bonded pairs.[17] This leads to a structure in which the number of hydrogen bonds per tecton increases to 12 but the percentage of accessible volume is still modest (46%). Hexakis(4-carbamoylphenyl)benzene (**3**) was found by Kobayashi and co-workers to crystallize from three solvent systems as different three-dimensional hydrogen-bonded networks.[18] Again, the percentages of volume accessible to included guests (59%, 48%, and 7%) are significantly lower than those of the most permeable molecular crystals currently known,[5,6] and the cohesive forces are modest, as measured by the number of hydrogen bonds per tecton.





1 (X = OH)
2 (X = COOH)
3 (X = CONH$_2$)
4 (X = DAT)

Table 1. Summary of Key Structural Features of the Hydrogen-Bonded Networks in Crystals of Hexaphenylbenzenes **1**−**5** and Related Compounds **6**−**8**

compound (conditions of crystallization in parentheses)	% volume accessible to guests[10,11]	number of hydrogen-bonded neighbors per tecton[a]	number of hydrogen bonds per tecton[a]	dimensionality of hydrogen-bonded network
1 (Et_2O)[16]	48	6	8	2D
1 (DMF)[16]	42	4	4	2D
2 (MeOH)[17]	46	6	12	2D
3 (DMSO)[18]	59	8	12	3D
3 (n-PrOH/H_2O)[18]	48	6	12	3D
3 (H_2O)[18]	7	10	12	3D
		10[c]	20[c]	
4 (DMSO/THF)	70	8	16	3D
4 (DMSO/toluene)	56	8	16	3D
4 (DMSO/benzene)	72	6	12	3D
4 (HCOOH/EtOH)	56	12	36	3D
5 (DMSO/MeCN)	60	6	12	3D
6 (DMSO/acetone)	55	4	8	2D
7 (DMSO/dioxane)	75	6	16	3D
7 (DMSO/MeOH)	39[b]	4	14	2D
8 (DMSO/acetone)	64	2	4	1D

[a] Hydrogen bonds involving guests are excluded. [b] This value is abnormally low in the series of compounds **4**−**8** because the network is 2-fold interpenetrated. [c] The unit cell contains two independent molecules.

Tectons **1**−**3** are structurally similar, but the resulting networks display widely different architectures for reasons that have not been delineated. Moreover, the percentages of volume accessible to guests are all less than 60%, in some cases by a large margin, and the number of hydrogen bonds per tecton does not normally exceed 12 (Table 1). Taken together, these properties do not point to tectons derived from hexaphenylbenzene as especially promising precursors for engineering highly permeable molecular crystals. However, we were encouraged to note that none of the networks formed by compounds **1**−**3** exhibits interpenetration, possibly because of the geometry of the hexaphenylbenzene core. These observations encouraged us to undertake a systematic study of derivatives of hexaphenylbenzene as sources of highly porous hydrogen-bonded networks not compromised by interpenetration.

Our initial target was tecton **4**, which incorporates six diaminotriazine groups on the periphery of the hexaphenylbenzene core. Diaminotriazines are known to self-associate reliably in the solid state by forming hydrogen-bonded motifs **I**−**III**.[5,6,19] Motif **I** is particularly favorable because it involves hydrogen bonding remote from sterically congested sites where the diaminotriazine groups are attached to the molecular core. For

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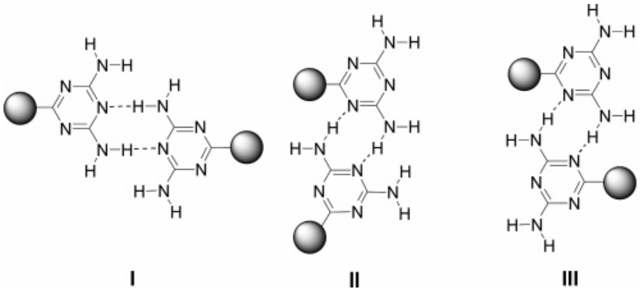
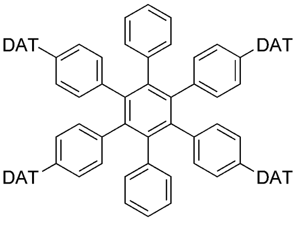


this reason, we expected tecton **4** to crystallize by associating according to motif **I**. This would lead to the formation of sheets represented by Figure 1a, in which each tecton has six hydrogen-bonded neighbors and takes part in a total of 12 hydrogen bonds. In addition, the sheets shown in Figure 1a could potentially be further connected by secondary hydrogen-bonding interactions according to motif **II** or **III**, giving a three-dimensional network and increasing the number of hydrogen bonds per tecton. In the resulting network, the sheets would be held apart and spaced by hydrogen bonding. For these reasons, we expected compound **4** to generate structures with higher percentages of volume accessible to guests, larger numbers of hydrogen bonds per tecton, and more consistent three-dimensional architectures than those produced by the simpler hexaphenylbenzenes studied by Kobayashi et al.[16−18]

In addition, we recognized that the hexaphenylbenzene core offers an attractive opportunity to modify networks rationally by changing the number and position of the hydrogen-bonding substituents. For example, removing selected hydrogen-bonding groups from the core can produce hexaphenylbenzenes such as compound **5**, and more dramatic mutations of the core itself can yield derivatives such as pentaphenylbenzene **6** and tetraphenylbenzenes **7** and **8**. We undertook these systematic alterations with the expectation that analysis of the resulting structures would deepen our understanding of how molecular crystals can be engineered.



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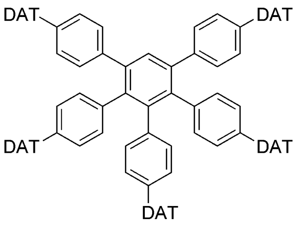

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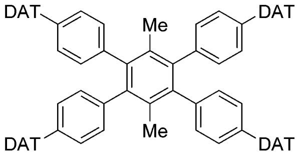

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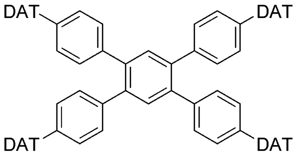

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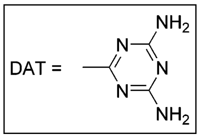

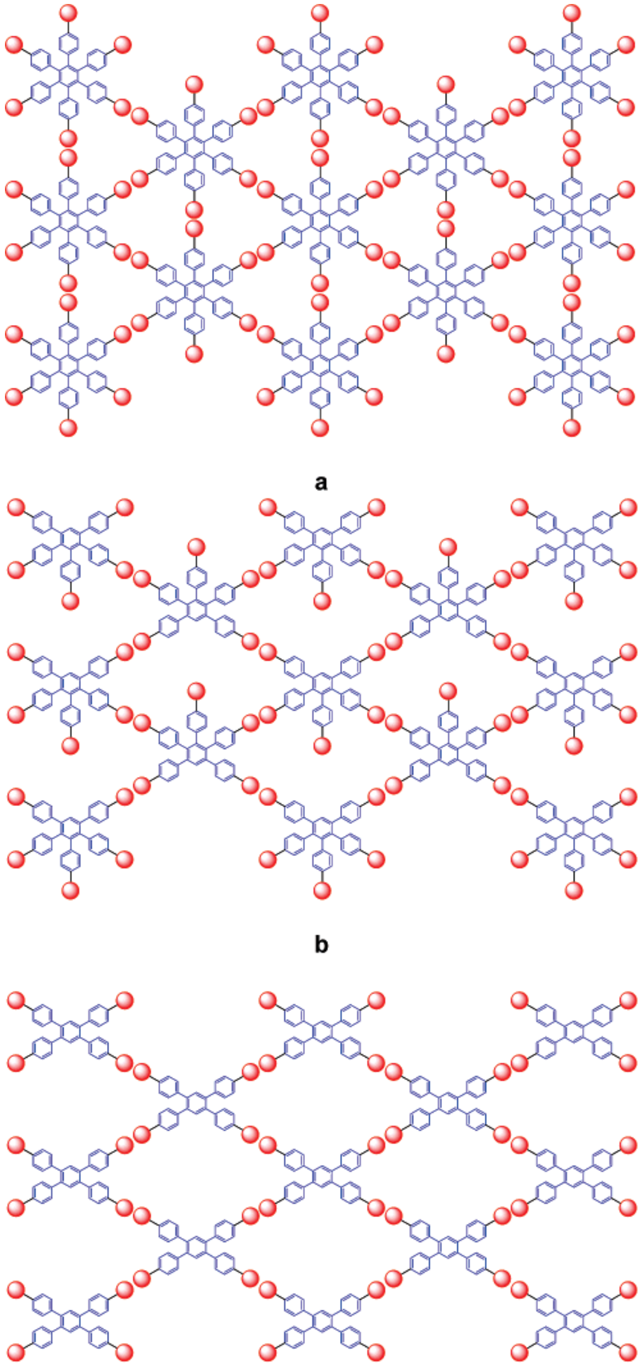

Figure 1. Schematic representations of possible networks derived from (a) a hexaphenylbenzene with six hydrogen-bonding substituents at the *para* position of each phenyl group (such as tecton **4**); (b) a pentaphenylbenzene with five hydrogen-bonding substituents (such as tecton **6**); and (c) a 1,2,4,5-tetraphenylbenzene with four hydrogen-bonding substituents (such as tecton **7**). In all images, red circles represent hydrogen-bonding substituents.

Results and Discussion

Synthesis of Tecton 4. Target **4** was prepared in four steps in an overall yield of 47% by the route outlined in Scheme 1. Hexaphenylbenzene (**9**) was synthesized in 93% yield via the Diels−Alder reaction of tetraphenylcyclopentadienone with diphenylacetylene.[20] Treatment with neat bromine then produced

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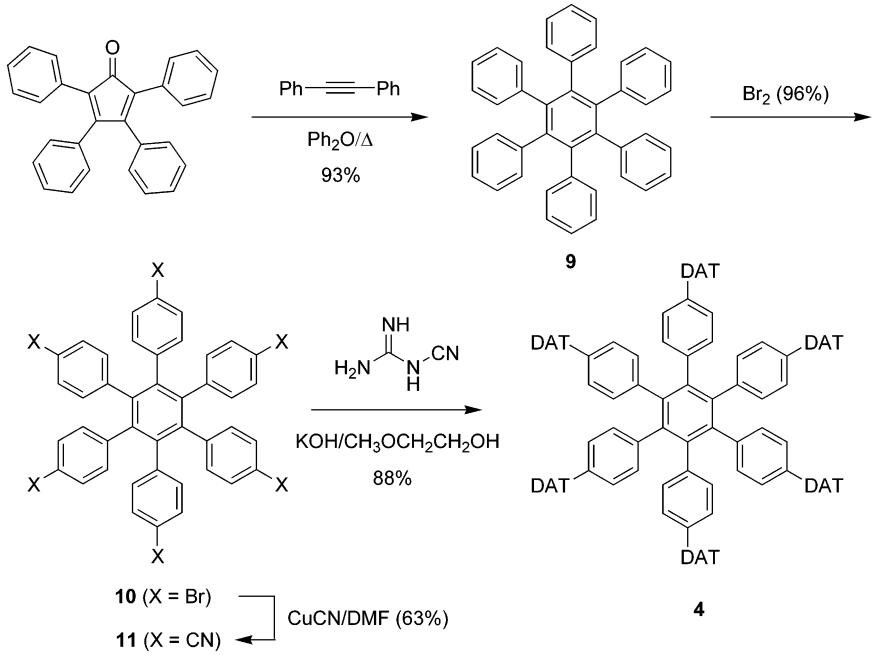
(20) Fieser, L. F. *Org. Synth.* **1966**, *46*, 44−48. Fieser, L. F. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, pp 604−608.

Scheme 1



hexakis(4-bromophenyl)benzene (**10**) in 96% yield.[21,22] Reaction of hexabromide **10** with CuCN gave hexakis(4-cyanophenyl)-benzene (**11**) in 63% yield,[23,24] and treatment of the product with dicyandiamide under basic conditions provided target **4** in 88% yield.[25]

Synthesis of Tecton 5. To synthesize derivative **5**, in which two diaminotriazine groups have been removed from opposing positions on the hexaphenylbenzene core, we took advantage of the flexibility inherent in the Diels–Alder strategy employed in Scheme 1. The reaction of 4,4′-dibromobenzil with 1,3-diphenylacetone gave dibrominated tetraphenylcyclopentadienone **12** in 85% yield (Scheme 2).[26] The Diels–Alder reaction of compound **12** with bis(4-bromophenyl)acetylene,[27] followed by loss of CO, produced tetrabrominated hexaphenylbenzene **13** in 84% yield. Treatment of compound **13** with CuCN gave the corresponding tetranitrile **14** in 60% yield, and further reaction with dicyandiamide under standard conditions provided target **5** in 83% yield.

Synthesis of Tecton 6. Pentaphenylbenzene **6** was prepared by an analogous route (Scheme 3). The reaction of tetraphenylcyclopentadienone with phenylacetylene in refluxing diphenyl ether gave pentaphenylbenzene (**15**) in 91% yield.[28] Subsequent bromination in neat bromine produced pentakis(4-bromophenyl)-benzene (**16**) in 58% yield. Treatment of compound **16** with CuCN in DMF provided pentakis(4-cyanophenyl)benzene (**17**) in 31% yield. Finally, the reaction of pentanitrile **17** with dicyandiamide under standard conditions gave compound **6** in 76% yield.

Synthesis of Tecton 7. Tetraphenylbenzene **7** was prepared from the commercially available dimer of 2,5-dimethyl-3,4-diphenylcyclopentadienone, which reacted with diphenylacetylene in hot diphenyl ether to give 1,4-dimethyl-2,3,5,6-tetraphenylbenzene (**18**) in 81% yield (Scheme 4).[29] Bromination using neat bromine produced the desired tetrabromide **19** in 81% yield. This reaction was carried out in the dark to avoid benzylic bromination. The subsequent reaction of tetrabromide **19** with CuCN in DMF provided the corresponding tetranitrile **20** in 66% yield. Finally, treatment of compound **20** with dicyandiamide under standard conditions gave target **7** in 78% yield.

Synthesis of Tecton 8. Tetraphenylbenzene **8** was most conveniently prepared by an alternative approach involving a fourfold Suzuki–Miyaura coupling of commercially available 1,2,4,5-tetrabromobenzene with 4-cyanophenylboronic acid[30] to give 1,2,4,5-tetrakis(4-cyanophenyl)benzene (**21**) in 82% yield (Scheme 5). Subsequent treatment of tetranitrile **21** with dicyandiamide under standard conditions gave target **8** in 83% yield.

Structures of Crystals of Tecton 4. Hexaphenylbenzene **4** showed low solubility in most organic solvents but could be crystallized by allowing vapors of suitable cosolvents to diffuse into solutions in DMSO or formic acid. Crystals suitable for study by X-ray diffraction were obtained from DMSO/THF, DMSO/toluene, DMSO/benzene, and formic acid/methanol. Their structures were solved to allow comparison of the resulting hydrogen-bonded networks.

Structure of Crystals of Tecton 4 Grown from DMSO/THF. The crystals were found to belong to the triclinic space

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(21) Rathore, R.; Burns, C. L.; Guzei, I. A. *J. Org. Chem.* **2004**, *69*, 1524–1530. Rathore, R.; Burns, C. L. *Org. Synth.* **2004**, *82*, 30–33.

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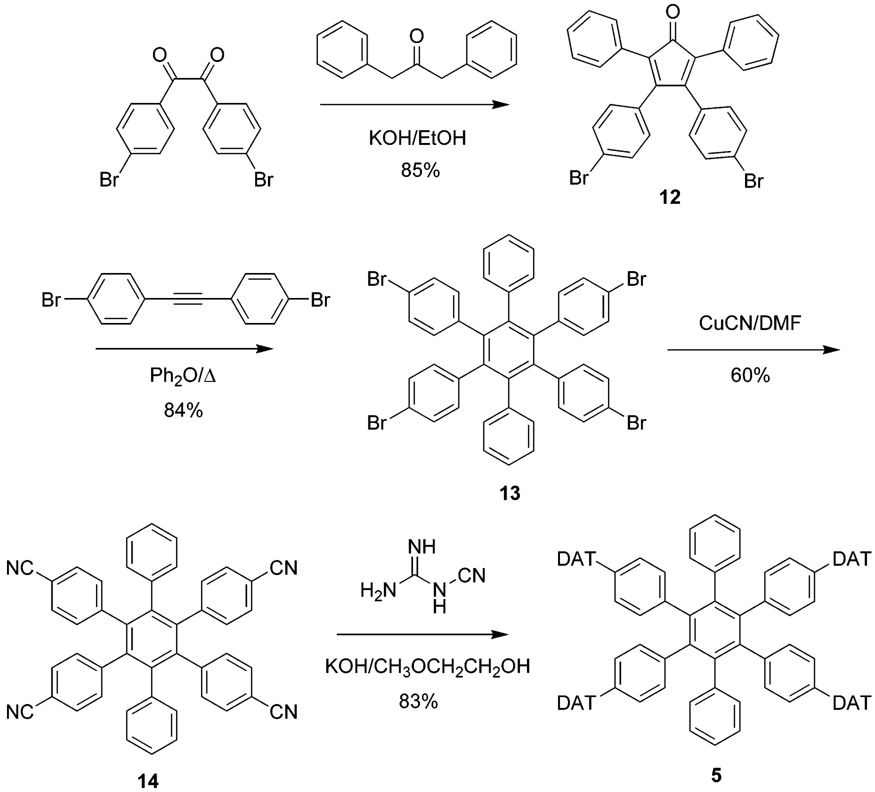
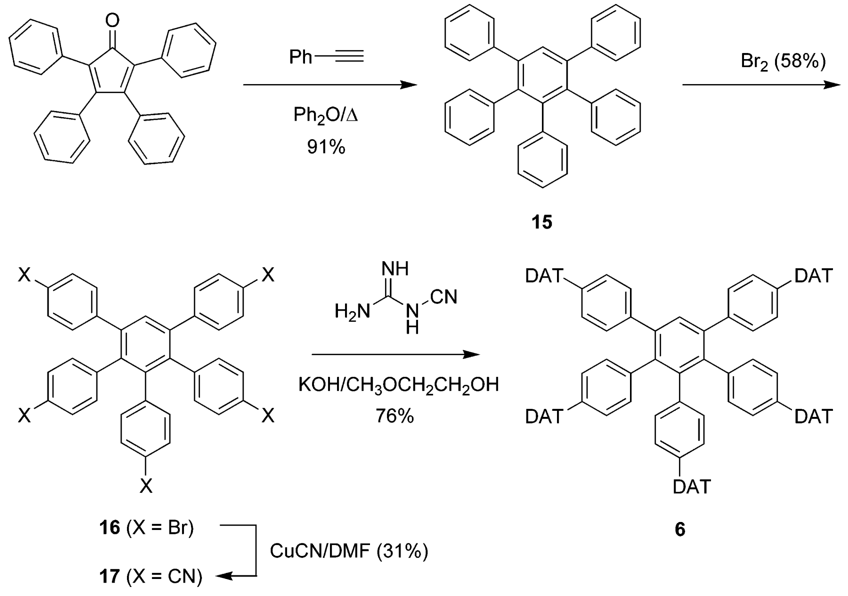
Scheme 2



Scheme 3



group $P\bar{1}$ and to have the approximate composition **4**·9DMSO·7THF·xH$_2$O.[31] As anticipated (Figure 1a), the six diaminotriazine groups of each tecton form hydrogen bonds according to motif **I** with six neighbors, thereby defining parallel sheets held together by 12 hydrogen bonds per tecton (Figure 2a). The hexaphenylbenzene core of compound **4** adopts a characteristic chiral propeller-shaped conformation with approximate 6-fold symmetry, as observed in many other derivatives of hexaphenylbenzene.[23,32] The angles between the average plane of the central aromatic ring and those of the six aryl substituents lie in the range 62.3(2)°−68.4(2)° (Table 2). The sheets consist of equal numbers of the two enantiomers.

A subtle but important element in the design of hexaphenylbenzene **4**, modified tectons **5**−**8**, and related compounds is the strong tendency of 2-phenyl-1,3,5-triazines to adopt conformations in which the phenyl and triazine rings are nearly coplanar. In 2,4,6-triphenyl-1,3,5-triazine, for example, the planes of the three phenyl substituents are tilted by an average of only 8.5° with respect to the plane of the triazine core.[33]

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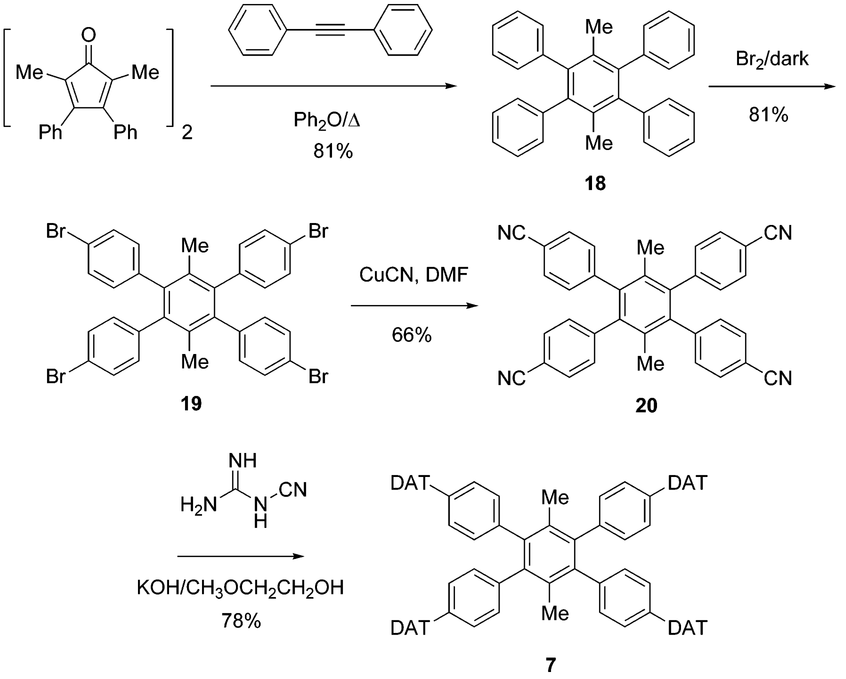
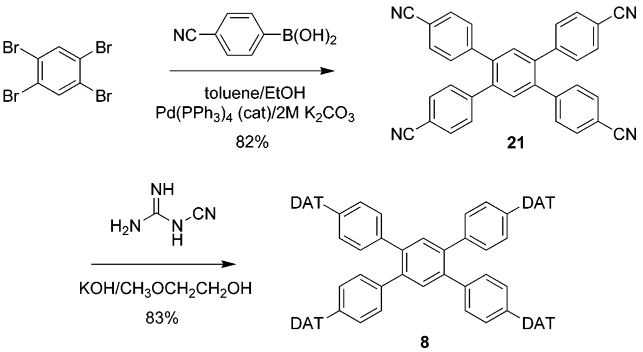
(31) The composition was estimated by X-ray diffraction and by ^{1}H NMR spectroscopy of dissolved samples. The amount of any H$_2$O included could not be determined accurately.

(32) Gagnon, E.; Maly, K. E.; Maris, T.; Wuest, J. D. *Acta Crystallogr.* **2007**, *C63*, o4−o6.

Scheme 4



Scheme 5



Similar conformational preferences have been noted in many other simple phenyltriazines.[34] Data compiled in the Cambridge Structural Database (Version 5.27) demonstrate that torsional angles in 2-phenyl-1,3,5-triazines (Figure 3a) tend to be significantly smaller than those observed for biphenyls (Figure 3b), and those found in 2-phenylpyrimidines are similarly small.[35] In crystals of tecton **4** grown from DMSO/THF, the average deviation from coplanarity is 12.9(3)°. This ensures that the diaminotriazine groups are oriented in a way that extends the propeller shape of the hexaphenylbenzene core and directs hydrogen-bonding sites out of the plane defined by each tecton and its six principal neighbors.

As a result, each tecton can form another four hydrogen bonds of type **III** to two additional neighbors in adjacent sheets (Figure 2b). This links the sheets into a three-dimensional network, and each tecton participates in a total of 16 intertectonic hydrogen bonds involving eight neighbors (Table 1). As expected, no interpenetration of independent networks is observed; instead, a single open network is favored, and 70% of the volume of the crystal is accessible to guests, which are partly disordered.[10,11] The guests occupy interconnected channels that in principle give new guests access to the interior of the crystal. The largest channels are triangular and aligned with the *b*-axis, and smaller channels run along the *a*-axis (Figure 4).

Examination of the overall structure confirms that multiple key features result predictably from design. In particular, compound **4** crystallizes as a non-interpenetrated three-dimensional hydrogen-bonded network built from sheets in which each tecton interacts as planned with six neighbors. In this design, the natural tendency of hexaphenylbenzenes and other disc-shaped molecules to form layered structures is strongly reinforced by intrasheet hydrogen bonding. As planned, the six diaminotriazine groups of compound **4** are nearly coplanar with the phenyl arms of the hexaphenylbenzene core, thereby extending its propeller conformation predictably. This ensures the formation of additional intersheet hydrogen bonds, although we acknowledge that the precise mode of stacking of the sheets and the nature of the resulting channels could not have been foreseen with confidence. As measured by the volume accessible to guests and the number of hydrogen bonds per tecton, the network formed by compound **4** is significantly more open and robust than those built from simpler analogues **1**−**3**, placing it among the most impressive molecular networks observed so far.

Structure of Crystals of Tecton 4 Grown from DMSO/Toluene. Our assertion that key features of the structure resulted from rational design was tested rigorously by searching for pseudopolymorphs formed under other conditions. Crystals grown by allowing vapors of toluene to diffuse into a solution of tecton **4** in DMSO also proved to belong to the triclinic space group $P\bar{1}$. Their composition was determined by crystallography to be **4**·6DMSO·H_2O. Again, each tecton interacts with six neighbors according to hydrogen-bonding motif **I** to define sheets.[35] The hexaphenylbenzene core is characteristically

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(33) Damiani, A.; Giglio, E.; Ripamonti, A. *Acta Crystallogr.* **1965**, *19*, 161−168.

(34) Ishi-i, T.; Kuwahara, R.; Takata, A.; Jeong, Y.; Sakurai, K.; Mataka, S. *Chem.*−*Eur. J.* **2006**, *12*, 763−776. Janczak, J.; Kubiak, R. *J. Mol. Struct.* **2005**, *751*, 74−84. Díaz-Ortiz, Á.; Elguero, J.; Foces-Foces, C.; de la Hoz, A.; Moreno, A.; Mateo, M. d. C.; Sánchez-Migallón, A.; Valiente, G. *New J. Chem.* **2004**, *28*, 952−958.

(35) See the Supporting Information for details.

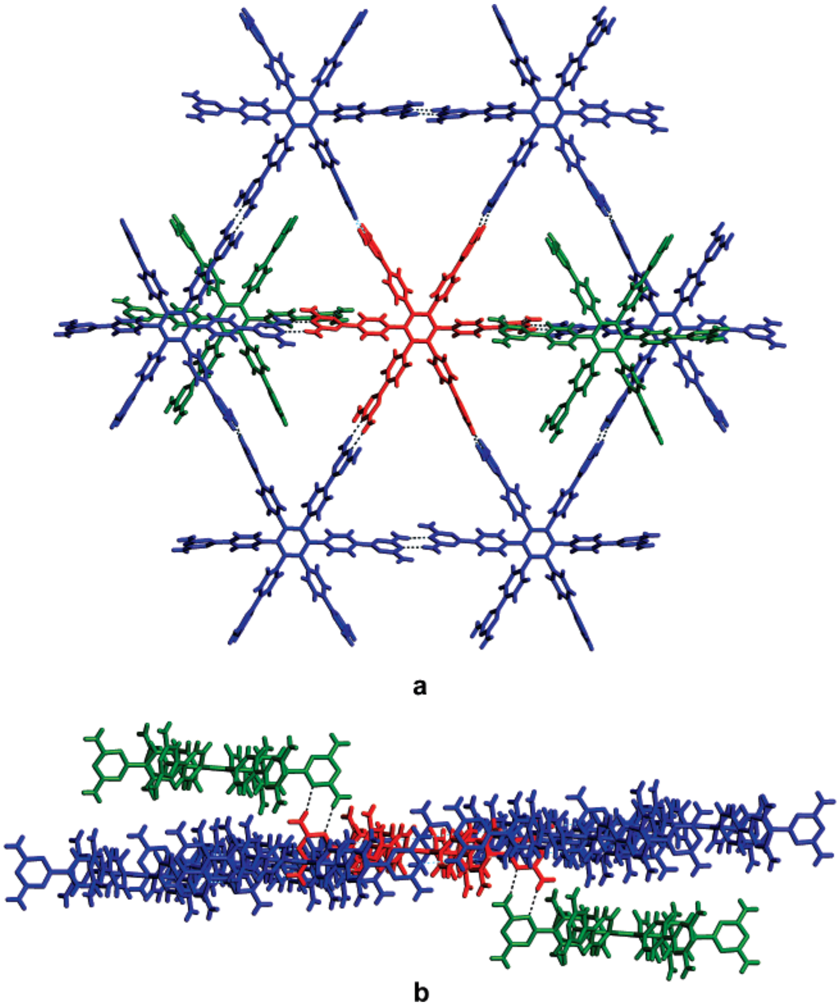

Figure 2. (a) View of the structure of crystals of tecton **4** grown from DMSO/THF, showing a central molecule (red) and its eight hydrogen-bonded neighbors (blue and green). Six of the neighbors (blue) lie approximately in the plane of the central molecule and interact according to motif **I**, and the other two (green) lie above and below the plane and form hydrogen bonds of type **III** with the central molecule (red). (b) Side view showing the two neighbors in green above and below the plane. In both views, guests are omitted for clarity, and hydrogen bonds are represented by broken lines.

Table 2. Conformations Adopted by the Arylbenzene Cores in Crystals of Hexaphenylbenzenes **4**−**5** and Related Compounds **6**−**8**

compound (conditions of crystallization in parentheses)	angles (deg) between the average planes of the aryl substituents and central ring of the arylbenzene core
4 (DMSO/THF)	67.0(2), 63.3(2), 68.4(2), 67.7(2), 62.3(2), 66.2(2)
4 (DMSO/toluene)	66.4(3), 74.1(2), 89.8(2)
4 (DMSO/benzene)	66.08(11)
4 (HCOOH/EtOH)	88.88(15)
5 (DMSO/MeCN)	59.88(9), 80.48(9), 85.63(9) (2x), 88.59(10) (2x)
6 (DMSO/acetone)	41.9(2) (2x), 56.09(19), 62.4(2) (2x)
7 (DMSO/dioxane)	84.50(12)
7 (DMSO/MeOH)	67(1), 72(1), 80(1), 81(1)
8 (DMSO/acetone)	40.06(16) (2x), 65.17(16) (2x)

nonplanar (Table 2), allowing four additional hydrogen bonds to link each tecton to two neighbors located in adjacent sheets.[35] The resulting network is three-dimensional and held together by a total of 16 hydrogen bonds per tecton (Table 1), like that found in crystals grown from DMSO/THF. The only significant architectural difference between the two networks is in the precise way the sheets are connected.[35] Packing of the sheets appears to be somewhat more efficient in crystals grown from DMSO/toluene, leading to a smaller percentage of volume accessible to guests (56%).[10,11] The guests occupy large parallel triangular channels that run along the *a*-axis and are similar to those observed in crystals grown from DMSO/THF (Figure 4a), but they are not interconnected by other significant channels. Despite these minor differences, the structures of crystals grown from DMSO/THF and DMSO/toluene show close overall similarity, supporting the conclusion that the observed networks are the result of logical design.

Structure of Crystals of Tecton 4 Grown from DMSO/Benzene. A further test of this conclusion was carried out by analyzing crystals grown by the diffusion of vapors of benzene into a solution of tecton **4** in DMSO. The resulting crystals were found to belong to the trigonal space group $R\bar{3}$ and to have the approximate composition **4**•12DMSO•12benzene•xH$_2$O.[31] The network formed is similar to the two already described, although some new features appear. Again, each tecton interacts directly with six neighbors by hydrogen bonding according to motif **I**. However, the neighbors lie alternately above and below the plane defined by the central tecton, giving rise to an irregular sheet in which the neighbors cannot interact directly but instead are bridged by hydrogen bonds to intervening molecules of DMSO (Figure 5). In this way, each molecule of hexaphenylbenzene **4** participates in 12 hydrogen bonds with neighboring

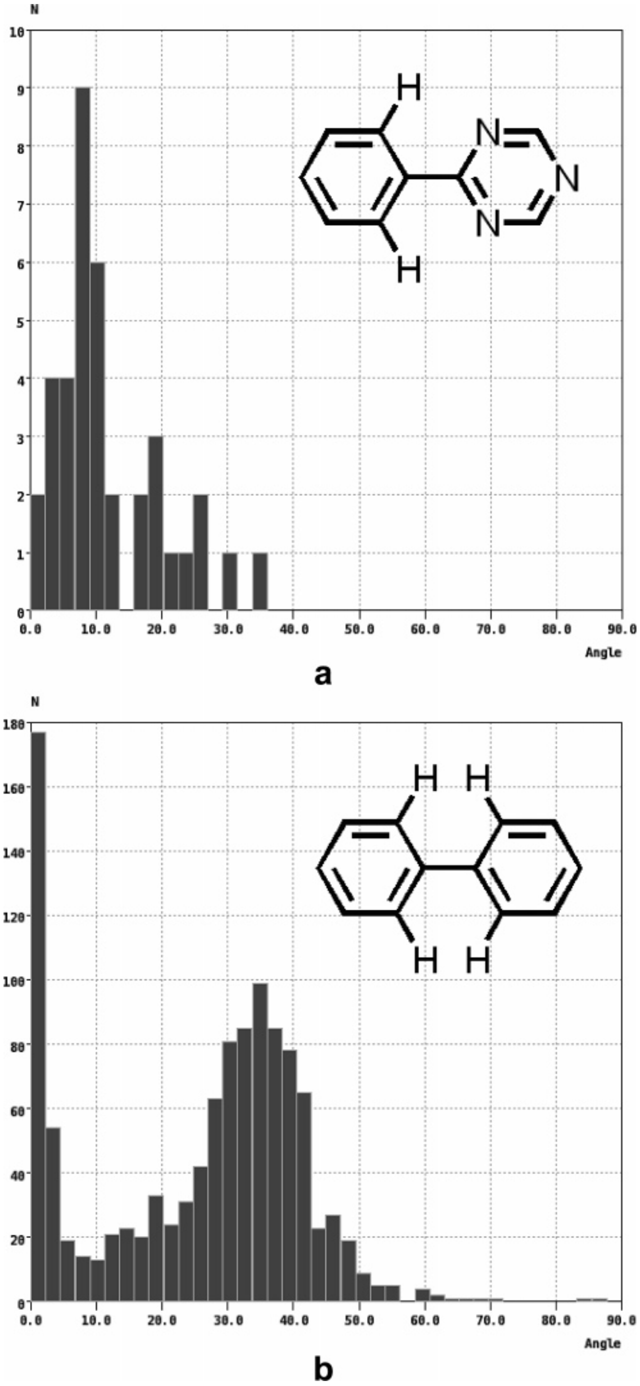

Figure 3. Histograms showing the frequency of torsional angles between the average planes of the aromatic rings in 2-phenyl-1,3,5-triazines and biphenyls, as observed in crystal structures compiled in the Cambridge Structural Database (Version 5.27). Structures containing metals or with atoms other than hydrogen at the indicated positions were not included in the analysis to avoid torsional effects arising from coordination or from ortho substitution. In addition, phenyltriazines in which the atoms of nitrogen were protonated or otherwise substituted were removed individually from the set of data.

tectons and 12 more with included molecules of DMSO (Table 1). The resulting network is highly open, and 72% of the volume is accessible to guests, which occupy interconnected channels.[10,11] The largest channels are triangular and aligned with the *c*-axis (Figure 6), and smaller channels lie in other directions. The included DMSO is hydrogen-bonded to tecton **4** and

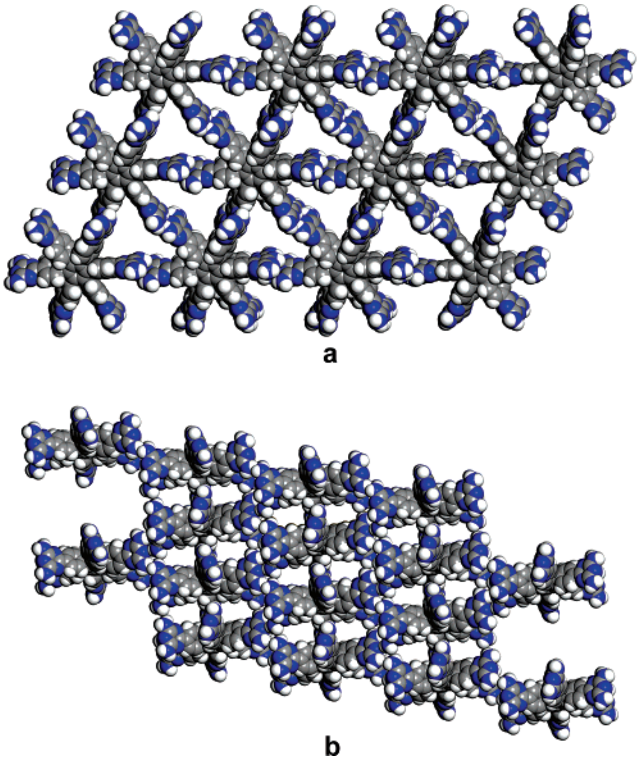

Figure 4. Views of the structure of crystals of tecton **4** grown from DMSO/THF, showing (a) large triangular channels along the *b*-axis and (b) smaller channels along the *a*-axis. Both views show a 3 × 2 × 3 array of unit cells. Guests are omitted for clarity, and atoms are represented by spheres of van der Waals radii to show the cross sections of the channels. Atoms of hydrogen appear in white; carbon in gray; and nitrogen in blue.

ordered, whereas included benzene and the phenyl arms of the hexaphenylbenzene core are statistically disordered (Table 2).

Structure of Crystals of Tecton 4 Grown from Formic Acid/Methanol. The marked tendency of hexaphenylbenzene **4** to form three-dimensional networks built from sheets in which each tecton interacts with six neighbors by forming 12 hydrogen bonds according to motif **I** was further tested by growing crystals under distinctly different conditions. Vapors of methanol were allowed to diffuse into a solution of compound **4** in formic acid, and the resulting crystals were found to belong to the trigonal space group $R\bar{3}$. Included solvent proved to be disordered, and the composition could not be determined accurately by crystallography. Again, each tecton interacts with six neighbors in the expected way, leading to the formation of sheets closely similar to those observed in crystals grown from DMSO/THF and DMSO/toluene.[35] In each tecton, the six phenyl arms of the hexaphenylbenzene core are virtually perpendicular to the central benzene ring (Table 2). This conformation allows each tecton to engage in a total of 24 additional hydrogen bonds of type **III** with six other neighbors, of which three are in each of the two adjacent sheets.[35] The resulting network is three-dimensional, each tecton participates in a total of 36 hydrogen bonds, and 56% of the volume is accessible to guests (Table 1).[10,11] In this structure, adjacent sheets are offset in a way that prevents the formation of conspicuous channels perpendicular to the plane of the characteristic sheets (Figure 7).

Together, the structures of the four pseudopolymorphs described above provide strong evidence that tecton **4** has been successfully engineered to favor crystals with the following specific features: (1) Each structure is built from a heptameric

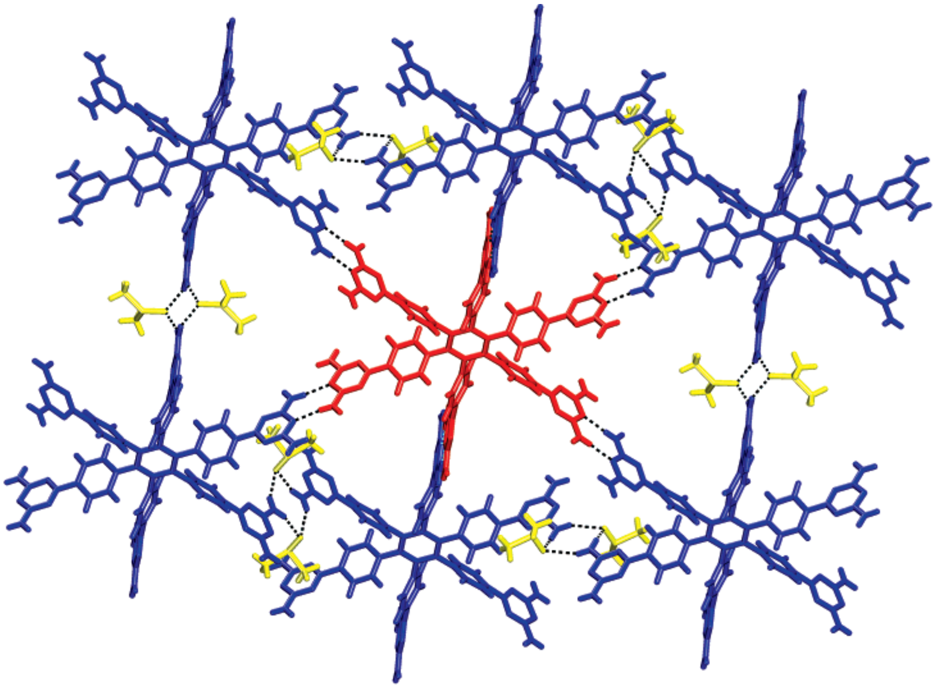

Figure 5. View of the structure of crystals of tecton **4** grown from DMSO/benzene, showing a central molecule (red) and its six hydrogen-bonded neighbors (blue). The six neighbors (blue) lie alternately above and below the plane of the central molecule (red), and they are bridged by hydrogen bonds to molecules of DMSO (yellow). Guests are omitted for clarity, and hydrogen bonds are represented by broken lines.

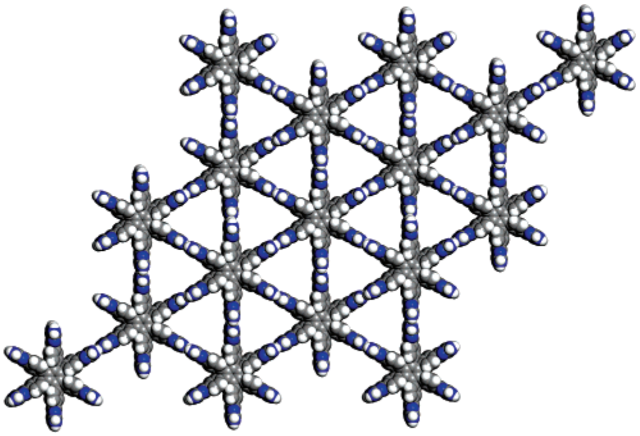

Figure 6. View of the structure of crystals of tecton **4** grown from DMSO/benzene, showing a 2 × 2 × 2 array of unit cells along the *c*-axis. Guests are omitted for clarity, and atoms are represented by spheres of van der Waals radii to show the cross sections of the channels. Atoms of hydrogen appear in white; carbon in gray; and nitrogen in blue.

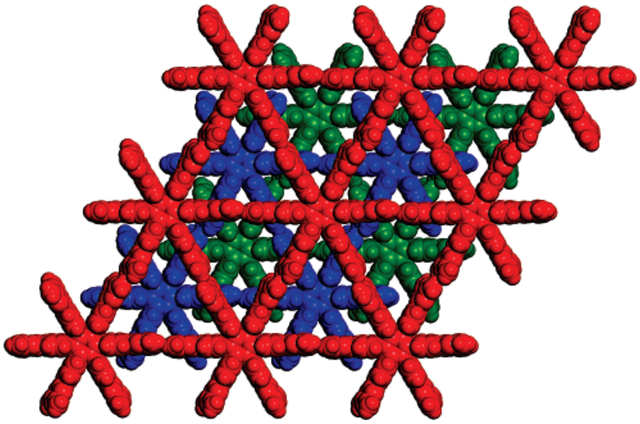

Figure 7. Representation of the structure of crystals of tecton **4** grown from formic acid/methanol, showing a 2 × 2 × 2 array of unit cells viewed along the *c*-axis. Three successive offset sheets are colored in red, blue, and green. Guests are omitted for clarity, and atoms are represented by spheres of van der Waals radii to confirm the absence of channels perpendicular to the sheets.

unit in which a central tecton forms hydrogen bonds of type **I** with six neighbors; (2) further association of these heptameric units leads to the formation of sheets; (3) the characteristic nonplanar conformations adopted by the hexaphenylbenzene core, in conjunction with the tendency of the triazine rings to lie close to the planes of the phenyl arms to which they are grafted, promote hydrogen bonding between sheets, thereby leading to the formation of three-dimensional networks held together by up to 36 hydrogen bonds per tecton; (4) no interpenetration of independent networks is observed; and (5) spaces between and within the sheets allow the inclusion of guests, and the percentage of accessible volume (56%−72%) consistently approaches the highest values so far observed in molecular networks. Although the networks produced by tecton **4** under different conditions of crystallization are not strictly identical, their close similarity supports a key principle of molecular tectonics: molecules with well-defined geometries and multiple sites of strong directional interactions do not tend to crystallize in widely divergent polymorphic forms.[7]

Hydrogen-Bonded Networks Formed by Mutated Tectons 5−8. Having demonstrated an important degree of control in constructing networks from hexaphenylbenzene **4**, we then put our understanding to a further test by probing the effect of selected structural modifications. Analogues **5**−**8** were synthesized and crystallized to reveal how removal of specific diaminotriazine groups or phenyl groups from the hexaphenylbenzene core would change how crystallization occurs.

Structure of Crystals of Tecton 6 Grown from DMSO/Acetone. In tecton **6**, one of the phenyl arms of the hexaphenylbenzene core has been excised, thereby producing a pentaphenylbenzene with five attached diaminotriazine groups.

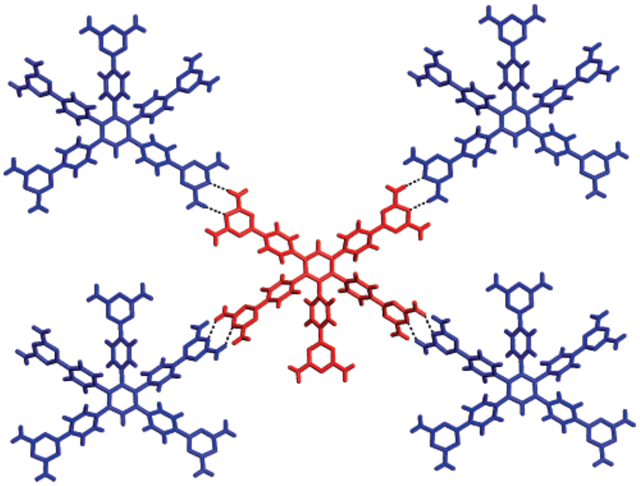

Figure 8. View of the structure of crystals of tecton **6** grown from DMSO/acetone, showing a central molecule (in red) and its four coplanar neighbors (blue), which are linked to the central molecule by hydrogen bonds of type **I**. Guests are omitted for clarity, and hydrogen bonds are represented by broken lines.

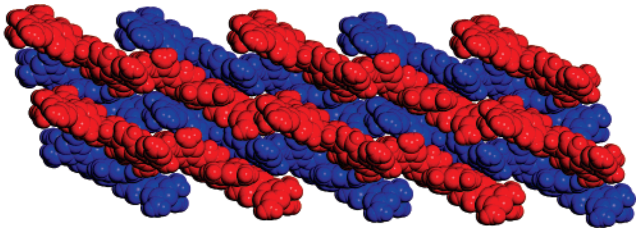

Figure 9. View of the structure of crystals of tecton **6** grown from DMSO/acetone, showing a 2 × 2 × 2 array of unit cells viewed along the *b*-axis with successive sheets colored in red and blue. Guests are omitted for clarity, and atoms are represented by spheres of van der Waals radii.

Crystals grown by diffusion of vapors of acetone into a solution of tecton **6** in DMSO proved to belong to the monoclinic space group *C*2/*c* and to have the approximate composition **6**·8DMSO·xH$_2$O.[31] In the resulting structure, each tecton uses four of its five diaminotriazine groups to form a total of eight hydrogen bonds of type **I** with four neighbors (Figure 8). The fifth group does not form hydrogen bonds with neighboring tectons and interacts instead with included molecules of DMSO. The resulting pentameric motif generates the hydrogen-bonded sheets represented by Figure 1b and shown from the side in Figure 9. Removal of one of the arms of the hexaphenylbenzene core allows the remaining phenyl spacers to adopt orientations closer to the plane of the central benzene ring (Table 2). This flattening of the molecular structure prevents tectons in one sheet from engaging in direct hydrogen bonding with tectons in adjacent sheets. Instead, the sheets are linked into an offset three-dimensional network by hydrogen bonds involving bridging molecules of DMSO. No interpenetration is observed, and 55% of the volume of the crystal is accessible to guests (Table 1).[10,11] Guests occupy distinct channels that lie along the *c*-axis and incorporate the unpaired diaminotriazine groups. The accessible volume is slightly lower than that observed in structures of tecton **4**, even though removal of a significant part of the molecule might have been expected to increase porosity. This is presumably because the flattened pentaphenylbenzene core permits closer packing of the sheets. Despite this important change, however, mutated tecton **6** continues to resemble hexaphenylbenzene **4** in key ways. Specifically, a sheet structure maintained by multiple hydrogen bonds of type **I** is retained, and the resulting network is noninterpenetrated and highly porous.

Structure of Crystals of Tecton 5 Grown from DMSO/Acetonitrile. The behavior of pentaphenylbenzene **6** helped clarify the importance of the conformation of the core and suggested that analysis of derivatives of tecton **4** with an intact hexaphenylbenzene core but less than six diaminotriazine groups would be informative. Crystals of tetrasubstituted hexaphenylbenzene **5** were grown by allowing vapors of acetonitrile to diffuse into a solution in DMSO. The crystals were found to belong to the monoclinic space group *C*2/*c* and to have the composition **5**·8DMSO·6CH$_3$CN. The observed structure is closely consistent with the pattern established by hexasubstituted analogue **4**. In particular, tecton **5** engages in a total of eight hydrogen bonds of type **I** with four neighbors, and the resulting pentameric unit defines a sheet (Figure 10a). The hexaphenylbenzene core of each tecton adopts a characteristic nonplanar conformation (Table 2), which permits the formation of four additional hydrogen bonds to two other tectons in adjacent sheets (Figure 10b). The resulting network is noninterpenetrated and highly open, with 60% of the volume of the crystal accessible to guests (Table 1).[10,11] Again, the guests occupy channels that run perpendicular to the plane of the sheets (Figure 11), and the unsubstituted phenyl groups face one another across the channels, as represented schematically by Figure 1c. The closely parallel behavior of hexaphenylbenzenes **4** and **5** provides a compelling example of successful crystal engineering and underscores the importance of maintaining a consistent molecular shape.

Structure of Crystals of Tecton 7 Grown from DMSO/Dioxane. In tetraphenylbenzene **7**, the two unsubstituted phenyl groups of hexaphenylbenzene **5** have been replaced by methyl groups. The new substituents were chosen to be (1) large enough to force tecton **7** to adopt a conformation similar to that of tecton **5**, with the remaining four phenyl groups held well out of the plane of the central aromatic ring, but (2) small enough to yield crystals in which the volume accessible to guests is increased significantly. Crystals were obtained by allowing dioxane to diffuse slowly into a solution of compound **7** in DMSO. The crystals proved to belong to the monoclinic space group *C*2/*m*, to have the approximate composition **7**·10DMSO·xH$_2$O[31] and to adopt a structure in close agreement with expectations. In particular, tecton **7** forms eight hydrogen bonds of type **I** with four neighbors to define a sheet (Figure 12a). As planned, the methyl groups enforce a conformation in which the central aromatic ring forms large dihedral angles with the four remaining phenyl arms (Table 2). Moreover, the established preference for nearly coplanar alignment of the triazines then allows the formation of four additional hydrogen bonds of type **III** to two tectons in adjacent sheets (Figure 12b). The resulting network is noninterpenetrated and defines large channels (Figures 13−15).[36] The most impressive are aligned with the *c*-axis and measure approximately 9.6 × 15 Å^2, and 75% of the volume of the crystals is accessible to guests (Table 1).[10,11] The porosity equals the current record for crystals built from small molecules.[5,6] By yielding a network with an architecture closely similar to that of model **5**, and by increasing the volume

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(36) Representations of channels were generated by the Cavities option in the program ATOMS Version 5.1 (Shape Software, 521 Hidden Valley Road, Kingsport, Tennessee 37663 U.S.A.; www.shapesoftware.com).

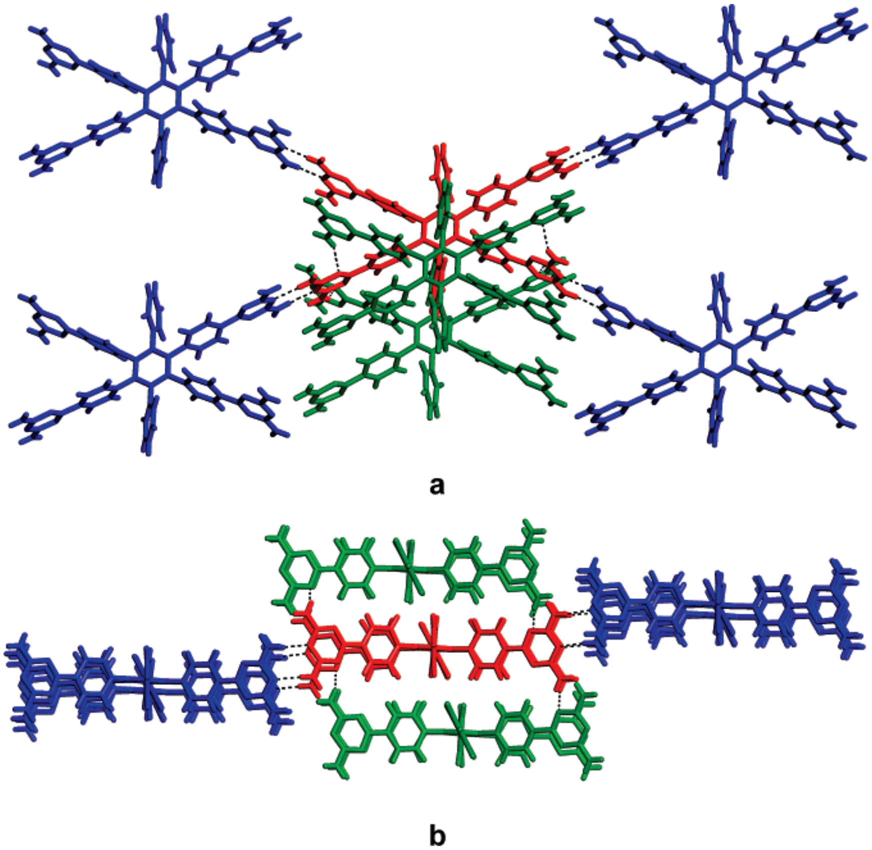

Figure 10. (a) View of the structure of crystals of tecton **5** grown from DMSO/acetonitrile, showing a central molecule (red) and its six hydrogen-bonded neighbors (blue and green). Four of the neighbors (blue) lie approximately in the plane of the central molecule and form hydrogen bonds to it via motif **I**. The remaining two neighbors (green) lie above and below the sheet. (b) Side view of the central molecule (red) and its six hydrogen-bonded neighbors (blue and green). In both views, guests are omitted for clarity, and hydrogen bonds are represented by broken lines.

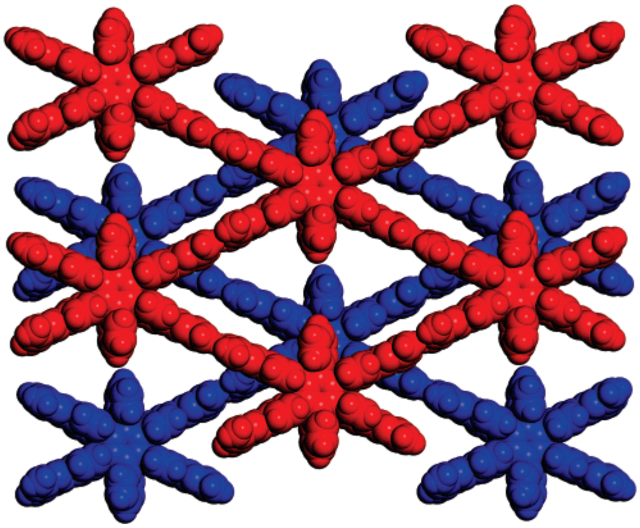

Figure 11. Representation of the structure of crystals of tecton **5** grown from DMSO/acetonitrile, showing two successive offset hydrogen-bonded sheets in red and blue. The image shows a 1 × 2 × 2 array of unit cells viewed along the *c*-axis, with guests omitted for clarity and atoms represented by spheres of van der Waals radii to reveal the cross sections of channels.

accessible to guests from 60% to 75%, tecton **7** behaved according to plan, demonstrating how new structures with predictable features can be engineered by following the guidelines of molecular tectonics.

Structure of Crystals of Tecton 7 Grown from DMSO/Methanol. To test the reliability of these guidelines, we searched for pseudopolymorphs formed under other conditions. Crystals grown by slow diffusion of methanol into a solution of compound **7** in DMSO were found to belong to the monoclinic space group $P2_1/c$ and to have the composition **7**·8DMSO·4H_2O. In the resulting structure, one of the diaminotriazine groups is disordered over two positions, which complicates analysis of the hydrogen bonding. Each tecton forms hydrogen bonds with four neighbors, thereby generating a sheet (Figure 16). Unlike all previously analyzed structures, in which the characteristic sheets are maintained by hydrogen bonds of type **I**, those generated when tecton **7** is crystallized from DMSO/methanol are held together by hydrogen bonds of types **II** and **III**. Moreover, adjacent sheets do not appear to form hydrogen bonds with each other, despite the nonplanar conformation of tecton **7** (Table 2). In addition, the network is 2-fold interpenetrated (Figure 17), and only 39% of the volume is accessible to guests (Table 1). Together, the observations of significantly lower porosity, interpenetration, and deviations from established patterns of hydrogen bonding show that significant alterations of the hexaphenylbenzene core of tectons **4** and **5** can have subtle and unexpected effects. In the particular case of tecton **7**, key conformational features of the aromatic core are successfully maintained, but the smaller methyl groups appear to allow neighboring molecules to approach more closely.

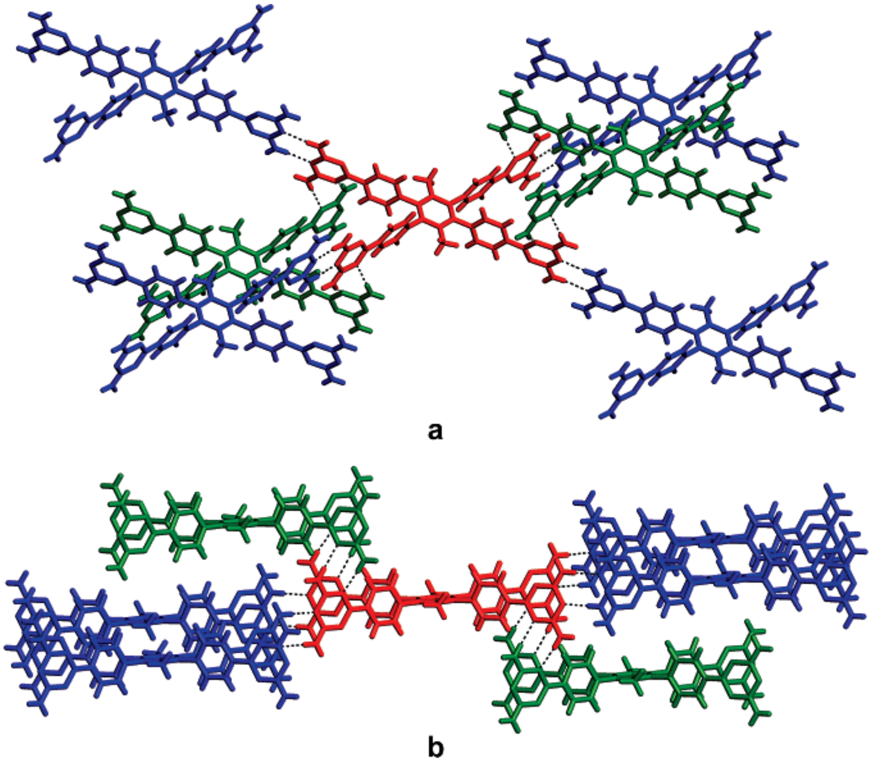

Figure 12. (a) View of the structure of crystals of tecton **7** grown from DMSO/dioxane, showing a central molecule (red) and its six hydrogen-bonded neighbors (blue and green). Four of the neighbors (blue) interact according to motif **I** and lie approximately in the plane of the central molecule, and the other two (green) form hydrogen bonds of type **III** and lie above and below the plane. (b) Side view showing the two neighbors in green above and below the plane. In both views, guests are omitted for clarity, and hydrogen bonds are represented by broken lines.

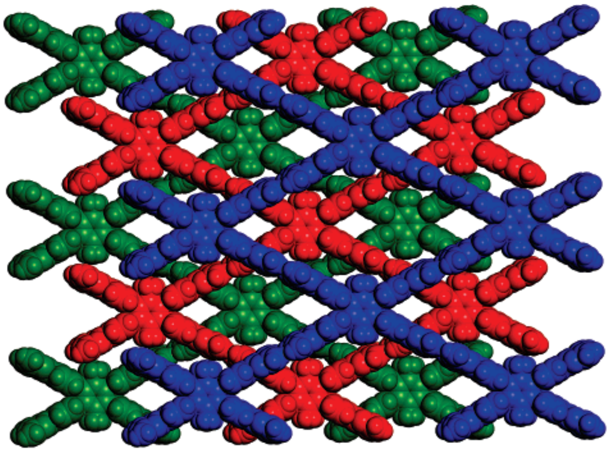

Figure 13. Representation of the structure of crystals of tecton **7** grown from DMSO/dioxane, showing three successive offset sheets colored in red, blue, and green. Guests are omitted for clarity, and atoms are represented by spheres of van der Waals radii.

Structure of Crystals of Tecton 8 Grown from DMSO/ Acetone. Further confirmation of the importance of an intact hexaphenylbenzene core was obtained by studying the behavior of tecton **8**, which is derived from 1,2,4,5-tetraphenylbenzene. Crystals grown by diffusion of vapors of acetone into a solution of compound **8** in DMSO were found to belong to the monoclinic space group $P2_1/c$ and to have the composition **8**·12DMSO. As expected, tecton **8** adopts a flattened conformation (Table 2) and generates a hydrogen-bonded network that is very different from those derived from analogous hexaphenylbenzenes. Only two diaminotriazine groups in each tecton interact with those of neighbors, thereby producing chains that extend along the *b*-axis and are held together by hydrogen bonds of type **I** (Figure 18a). The remaining diaminotriazine groups engage in hydrogen bonding with included molecules of DMSO, which form bridges to neighboring tectons (Figure 18b). The

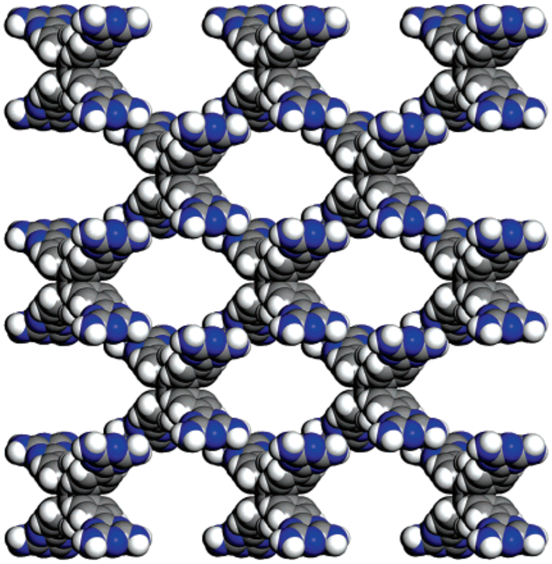

Figure 14. View of the structure of crystals of tecton **7** grown from DMSO/dioxane, showing a 2 × 2 × 2 array of unit cells along the *c*-axis. Guests are omitted for clarity, and atoms are represented by spheres of van der Waals radii to show the cross sections of the channels. Atoms of hydrogen appear in white; carbon in gray; and nitrogen in blue.

Figure 15. Representation of channels along the *c*-axis in the network resulting from crystallization of tecton **7** from DMSO/dioxane. The image shows a 2 × 2 ×2 array of unit cells. The outsides of the channels appear in dark gray, and light 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 network.[36]

resulting network is open, and 64% of the volume is accessible to guests (Table 1).

Conclusions

Our study of hydrogen-bonded networks derived from hexaphenylbenzene and related compounds, together with earlier work reported by Kobayashi et al.,[16−18] has yielded a deeper understanding of how to create molecular crystals by design. By examining the behavior of a single compound under multiple conditions of crystallization, and by analyzing the effects of a series of systematic structural modifications, we have tested molecular tectonics as a strategy for engineering crystals with predetermined properties, and we have clearly delineated its current strengths and limitations.

Our results underscore the importance of the geometry of the hexaphenylbenzene core, which reliably adopts nonplanar conformations and has a disclike shape that inherently favors parallel molecular packing and the formation of layered structures. In tectons **4** and **5**, this tendency has been powerfully reinforced by grafting diaminotriazine groups to the periphery of the hexaphenylbenzene core, thereby ensuring the formation of multiple hydrogen bonds in the molecular plane. Simultaneously, the characteristic nonplanar conformation of the core, along with the preference for nearly coplanar alignment of phenyl-substituted triazines, ensures that additional hydrogen bonds are formed between the sheets, creating three-dimensional networks. Our results show that when a consistent molecular shape is maintained, the results of crystallization have a high degree of predictability. Under all conditions examined, hexaphenylbenzene **4** crystallizes as planned to give noninterpenetrated three-dimensional networks built from sheets in which each tecton forms hydrogen bonds of type **I** with six neighbors. In addition, the behavior of analogues **5** and **7**, which have conformationally similar cores but only four diaminotriazine groups, is closely parallel. In these structures, the number of hydrogen bonds per tecton and the percentage of volume accessible to guests consistently exceed those reported for the simpler derivatives studied earlier by Kobayashi et al., and they reach the highest values so far observed in molecular networks. Together, these results provide an impressive demonstration of the ability of molecular tectonics to control crystallization, and they suggest that new tectons with more complex nonplanar aromatic cores and multiple sites of hydrogen bonding can be designed to produce networks with even higher degrees of porosity and robustness.

Our results also demonstrate that major structural alterations of the hexaphenylbenzene core can change the architecture of the resulting network significantly. In particular, analogues with flatter pentaphenylbenzene and tetraphenylbenzene cores yield crystals with different features. It is important to note that we have not been able to compare the structures of crystals of tectons **4**−**8** grown under identical conditions. However, our thorough investigation of the pseudopolymorphs of compound **4** has established that key structural features are maintained in all crystals examined. Moreover, the networks generated by tectons **4**−**8** have many shared properties despite significant differences in the conditions of crystallization. For these reasons, we believe that our work defines the current state of the art in crystal engineering and illustrates primarily the systematic effect of modifying the molecular components of crystals, not the conditions of crystallization.

Experimental Section

All reagents and solvents were purchased from commercial sources and used without further purification unless otherwise indicated. Hexakis(4-cyanophenyl)benzene (**11**) was prepared from hexakis(4-bromophenyl)benzene (**10**)[21,22] as described previously.[23] Anhydrous and oxygen-free solvents (DMF and toluene) were obtained by passage through columns packed with activated alumina and supported copper catalyst (Glass Contour, Irvine, CA). NMR spectra were recorded using a Bruker AV400 spectrometer, and high-resolution mass spectra were obtained using an Agilent LC-MSD TOF spectrometer. Elemental analyses were performed at the Université de Montréal.

Hexakis[4-(2,4-diamino-1,3,5-triazin-6-yl)phenyl]benzene (4). Hexakis(4-cyanophenyl)benzene (**11**) (315 mg, 0.460 mmol)[23,24] was combined with dicyandiamide (474 mg, 5.64 mmol) and KOH (75 mg, 1.34 mmol) in 2-methoxyethanol (10 mL), and the mixture was heated at reflux for 15 h. The resulting mixture was then cooled to 25 °C, and volatiles were removed by evaporation in vacuo. The residue was suspended in water, and the solid fraction was separated by filtration and then washed with hot water, ethanol, and methanol. The product was dried to give hexakis[4-(2,4-diamino-1,3,5-triazin-6-yl)phenyl]benzene (**4**; 467 mg, 0.393 mmol, 85%) as a colorless solid. A sample was further purified for analysis by recrystallization from formic acid/ethyl acetate: mp > 300 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.62 (s, 24H), 6.96 (d, 12H, $^3J = 8$ Hz), 7.67 (d, 12H, $^3J = 8$ Hz); ^{13}C NMR (100 MHz, DCOOD) δ 127.3, 127.6, 132.4, 139.6, 146.0, 160.7, 163.4; HRMS (ESI) calcd for $C_{60}H_{48}N_{30} + H$ *m*/*e* 1189.47510, found 1189.47404. Anal. Calcd for $C_{60}H_{48}N_{30}$ + HCOOH: C, 59.31; H, 4.08; N, 34.02. Found: C, 59.79; H, 4.11; N, 33.83.

3,4-Bis(4-bromophenyl)-2,5-diphenyl-2,4-cyclopentadien-1-one (12).[26] A solution of KOH (0.29 g, 5.2 mmol) in ethanol (5 mL) was added to a mixture of 4,4′-dibromobenzil (3.68 g, 10.0 mmol) and 1,3-diphenylacetone (2.10 g, 10.0 mmol) in ethanol (20 mL). The resulting mixture was heated at reflux for 1 h. The mixture was then cooled to 0 °C, and the resulting precipitate was collected by filtration and dried to give 3,4-bis(4-bromophenyl)-2,5-diphenyl-2,4-cyclopentadien-1-one (**12**; 4.61 g, 8.50 mmol, 85%) as a dark purple solid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.80 (d, 4H, $^3J = 8.4$ Hz), 7.1−7.3 (m, 10H), 7.35 (d, 4H, $^3J = 8.4$ Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 123.6, 126.3, 128.3, 128.7, 130.5, 130.6, 131.4, 131.9, 132.1, 153.0, 200.0.

1,2,4,5-Tetrakis(4-bromophenyl)-3,6-diphenylbenzene (13). A mixture of 3,4-bis(4-bromophenyl)-2,5-diphenyl-2,4-cyclopentadien-

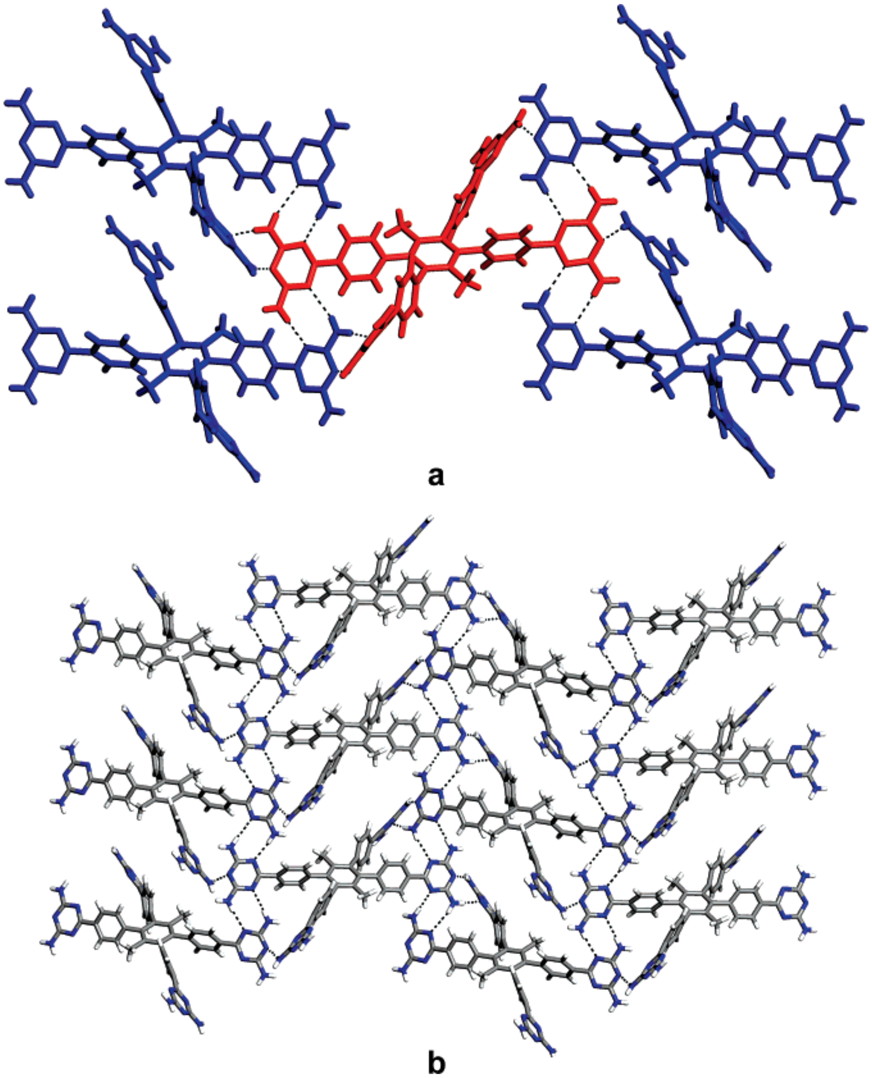

Figure 16. (a) View of the structure of crystals of tecton **7** grown from DMSO/methanol, showing a central molecule (red) and its four hydrogen-bonded neighbors (blue). (b) View of the resulting hydrogen-bonded sheet, with atoms of hydrogen appearing in white; carbon in gray; and nitrogen in blue. In both views, guests are omitted for clarity, and hydrogen bonds are represented by broken lines.

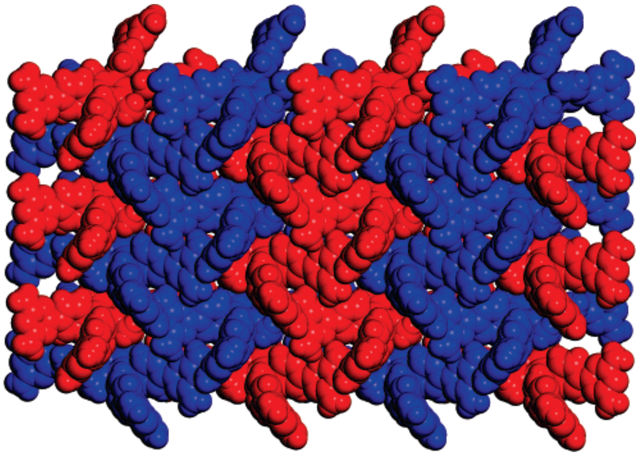

Figure 17. Representation of the structure of crystals of tecton **7** grown from DMSO/methanol, showing the 2-fold interpenetration of hydrogen-bonded sheets (red and blue). Guests are omitted for clarity, and atoms are represented by spheres of van der Waals radii.

1-one (**12**; 2.16 g, 3.98 mmol) and bis(4-bromophenyl)acetylene (1.34 g, 3.99 mmol)[27] in diphenyl ether (5 mL) was heated at reflux under N_2 for 48 h. The resulting mixture was cooled to 25 °C and then diluted with ethanol. The precipitate was collected by filtration, washed with ethanol and hexane, and dried to give 1,2,4,5-tetrakis(4-bromophenyl)-3,6-diphenylbenzene (**13**; 2.83 g, 3.33 mmol, 84%) as a nearly colorless solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.67 (d, 8H, $^3J = 8.4$ Hz), 6.78 (m, 4H), 6.94 (m, 6H), 7.04 (d, 8H, $^3J = 8.4$ Hz). Anal. Calcd for $C_{42}H_{26}Br_4$: C, 59.33; H, 3.08. Found: C, 59.11; H, 2.75.

1,2,4,5-Tetrakis(4-cyanophenyl)-3,6-diphenylbenzene (14). 1,2,4,5-Tetrakis(4-bromophenyl)-3,6-diphenylbenzene (**13**; 1.70 g, 2.00 mmol) was combined with CuCN (1.08 g, 12.1 mmol) in dry DMF (10 mL). The mixture was heated at reflux under N_2 for 21 h. The resulting mixture was then cooled to 25 °C and diluted with water. The precipitate was collected by filtration, washed with a mixture of water and ethylenediamine, and extracted with CH_2Cl_2. The extracts were washed several times with a mixture of water and ethylenediamine, 1 M aqueous HCl, and brine. The organic phase was then dried ($MgSO_4$) and filtered, and volatiles were removed by evaporation under reduced pressure. The crude residue was purified by passage through a short column of silica gel (100% CH_2Cl_2) to yield 1,2,4,5-tetrakis(4-cyanophenyl)-3,6-diphenylbenzene (**14**; 780 mg, 1.23 mmol, 61%) as a nearly colorless solid: mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 (m, 4H), 6.90 (d, 8H, $^3J = 8.2$ Hz), 6.94 (m, 6H), 7.21 (d, 8H, $^3J = 8.2$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.7, 118.8, 127.3, 128.0, 131.1, 131.5, 132.0, 138.4, 139.8, 140.9, 144.6; HRMS (ESI)

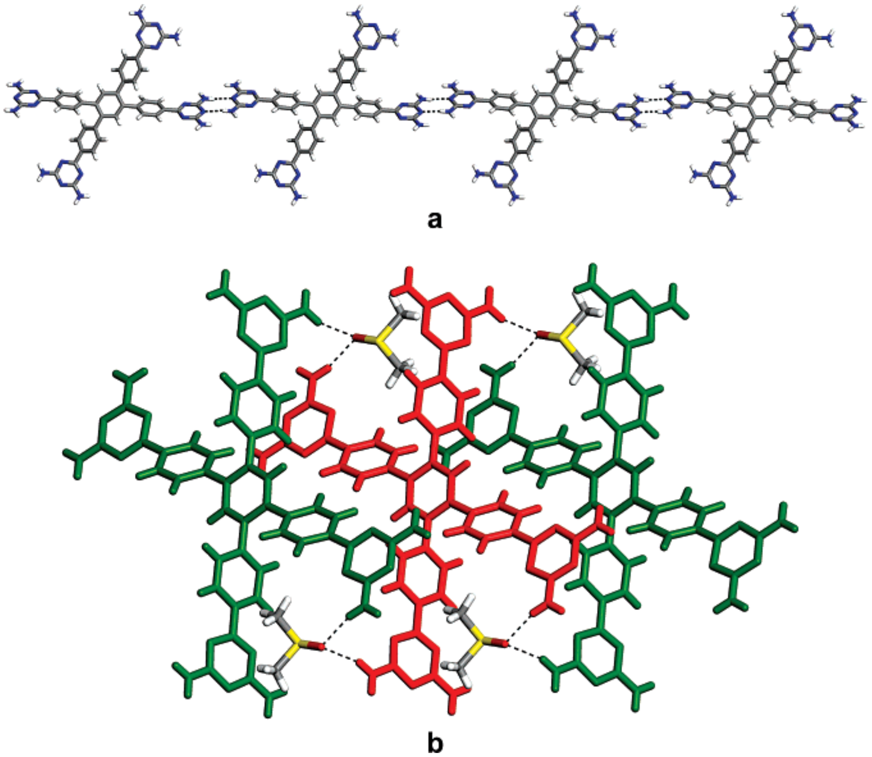

Figure 18. (a) View of the structure of crystals of tecton **8** grown from DMSO/acetone, showing how molecules are linked into chains by hydrogen bonds of motif **I**. Atoms of hydrogen appear in white; carbon in gray; and nitrogen in blue. (b) Additional view of the structure showing how hydrogen bonds involving bridging molecules of DMSO link each tecton (red) to two additional neighbors in adjacent chains (green).

calcd for $C_{46}H_{26}N_4 + H$ *m*/*e* 635.2230, found 635.2232. Anal. Calcd for $C_{46}H_{26}N_4$: C, 87.04; H, 4.13; N, 8.83. Found: C, 86.93; H, 3.77; N, 8.88.

1,2,4,5-Tetrakis[4-(2,4-diamino-1,3,5-triazin-6-yl)phenyl]-3,6-diphenylbenzene (5). 1,2,4,5-Tetrakis(4-cyanophenyl)-3,6-diphenylbenzene (**14**; 160 mg, 0.252 mmol) and dicyandiamide (106 mg, 1.26 mmol) were added to a solution of KOH (55 mg, 0.98 mmol) in 2-methoxyethanol (5 mL), and the mixture was heated at reflux for 12 h. The resulting mixture was cooled to 25 °C and diluted with water. The precipitate was collected by filtration, washed with hot water and ethanol, and dried to give 1,2,4,5-tetrakis[4-(2,4-diamino-1,3,5-triazin-6-yl)phenyl]-3,6-diphenylbenzene (**5**; 204 mg, 0.210 mmol, 83%) as a colorless solid: mp > 300 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.61 (br s, 16H), 6.8−6.9 (m, 10H), 6.95 (d, 8H, $^3J = 8.4$ Hz), 7.67 (d, 8H, $^3J = 8.4$ Hz); ^{13}C NMR (100 MHz, DCOOD) 126.7, 126.7, 127.2, 127.5, 131.3, 132.5, 138.8, 139.6, 140.4, 147.1, 160.8, 163.4; HRMS (ESI) calcd for $C_{54}H_{42}N_{20} + H$ *m*/*e* 971.3974, found 971.4007.

Pentaphenylbenzene (15).[28] Tetraphenylcyclopentadienone (3.84 g, 9.99 mmol) and phenylacetylene (1.1 mL, 10 mmol) were combined in diphenyl ether (10 mL), and the mixture was heated at reflux under N_2 for 30 min. During this time, the mixture became light orange. The mixture was cooled to 25 °C and diluted with ethanol (150 mL). The resulting precipitate was collected by filtration, washed with ethanol and hexane, and dried to give pentaphenylbenzene (**15**; 4.16 g, 9.07 mmol, 91%) as a colorless solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (m, 2H), 6.90 (m, 7H), 6.96 (m, 6H), 7.19 (m, 10 H), 7.63 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.8, 126.0, 126.7, 127.1, 127.4, 128.0, 130.4, 131.8, 131.9, 132.0, 139.7, 140.4, 140.8, 141.2, 142.1, 142.2.

Pentakis(4-bromophenyl)benzene (16). Pentaphenylbenzene (1.73 g, 3.77 mmol) was spread in a thin layer at the bottom of a beaker and covered with neat bromine (6.5 mL, 130 mmol). The mixture was allowed to stand overnight at 25 °C. The crude product was washed with ethanol and hexane, dried, recrystallized from xylenes, and dried again to give pure pentakis(4-bromophenyl)benzene (**16**; 1.88 g, 2.20 mmol, 58%) as a colorless solid: mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59 (d, 2H, $^3J = 8.4$ Hz), 6.65 (d, 4H, $^3J = 8.4$ Hz), 6.95 (d, 4H, $^3J = 8.4$ Hz), 7.07 (d, 2H, $^3J = 8.4$ Hz), 7.13 (d, 4H, $^3J = 8.3$ Hz), 7.32 (d, 4H, $^3J = 8.4$ Hz), 7.45 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.8, 121.0, 121.6, 129.3, 130.9, 131.1, 131.5, 131.7, 133.1, 133.2, 138.4, 138.7, 138.7, 140.1, 140.5, 141.0. Anal. Calcd for $C_{36}H_{21}Br_5$: C, 50.69; H, 2.48. Found: C, 51.29; H, 2.39.

Pentakis(4-cyanophenyl)benzene (17). Pentakis(4-bromophenyl)-benzene (**16**; 1.34 g, 1.57 mmol) and CuCN (1.05 g, 11.7 mmol) were combined in dry DMF (10 mL), and the mixture was heated at reflux under N_2 for 18 h. The resulting mixture was then cooled to 25 °C and poured into water. The precipitate was collected by filtration and washed with water and then with water/ethylenediamine (3:1 v/v). The solid residue was suspended in CH_2Cl_2 and washed repeatedly with water/ethylenediamine until the aqueous washings were colorless. The organic phase was then washed with 1 M aqueous HCl and brine, dried over $MgSO_4$, and filtered. Removal of volatiles by evaporation under reduced pressure left a residue that was purified by flash chromatography (100% CH_2Cl_2) to give pentakis(4-cyanophenyl)benzene (**17**; 0.280 g, 0.480 mmol, 31%) as a colorless solid: mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (d, 2H, $^3J = 8.2$ Hz), 6.91 (d, 4H, $^3J = 8.2$ Hz), 7.20 (d, 4H, $^3J = 8.3$ Hz), 7.27 (d, 2H, $^3J = 8.2$ Hz), 7.32 (d, 4H, $^3J = 8.2$ Hz), 7.52 (d, 4H, $^3J = 8.3$ Hz), 7.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.6, 111.8, 112.1, 118.3, 118.3, 118.6, 130.7, 131.8, 131.9, 132.0, 132.1, 132.2, 132.5, 138.7, 140.5, 140.8, 143.1, 143.4, 144.6; HRMS (ESI) calcd for $C_{41}H_{21}N_5 + Na$ *m*/*e* 606.16892, found 606.16852. Anal. Calcd for $C_{41}H_{21}N_5 + 0.25\ CH_2Cl_2$: C, 81.91; H, 3.58; N, 11.58. Found: C, 82.03; H, 3.59; N, 11.63.

Pentakis[4-(2,4-diamino-1,3,5-triazin-6-yl)phenyl]benzene (6). Pentakis(4-cyanophenyl)benzene (**17**; 255 mg, 0.437 mmol), dicyandiamide (370 mg, 4.40 mmol), and KOH (123 mg, 2.19 mmol) were combined in 2-methoxyethanol (5 mL), and the mixture was heated at reflux for 19 h. The resulting mixture was cooled to 25 °C and poured into water. The precipitate was collected by filtration, washed with hot water and methanol, and then dried to give pentakis[4-(2,4-diamino-1,3,5-triazin-6-yl)phenyl]benzene (**6**; 335 mg, 0.334 mmol, 76%) as a colorless solid: mp > 300 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.6−6.8 (br m, 20H), 6.93 (d, 2H, $^3J = 8.4$ Hz), 6.97 (d, 4H, $^3J = 8.2$ Hz), 7.27 (d, 4H, $^3J = 8.2$ Hz), 7.69 (s, 1H), 7.70 (d, 2H, $^3J = 8.4$ Hz), 7.75 (d, 4H, $^3J = 8.2$ Hz), 8.02 (d, 4H, $^3J = 8.2$ Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 127.0, 127.3, 128.0, 130.4, 131.9, 132.0, 132.0, 135.4, 135.7, 136.2, 139.5, 141.0, 141.8, 142.8, 143.2, 144.2, 168.1, 168.2, 168.2, 170.7, 170.9, 170.9; HRMS (ESI) calcd for $C_{51}H_{41}N_{25}$ + H m/e 1004.40495, found 1004.40531.

1,4-Dimethyl-2,3,5,6-tetraphenylbenzene (18).[29] A stirred mixture of the dimer of 2,5-dimethyl-3,4-diphenylcyclopentadienone (2.00 g, 3.84 mmol) and diphenylacetylene (2.05 g, 11.5 mmol) in diphenyl ether (5 mL) was heated at reflux for 2 h. During this time, the mixture turned deep red and then faded to orange. Slow cooling yielded crystals after 24 h, which were collected by filtration and washed with hexane. The product was further purified by recrystallization from xylenes, giving 1,4-dimethyl-2,3,5,6-tetraphenylbenzene (**18**; 2.54 g, 6.19 mmol, 81%) as a colorless solid: mp > 300 °C (lit.[29] 363−365 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.80 (s, 6H), 7.05 (m, 12H), 7.13 (m, 8H).

1,4-Dimethyl-2,3,5,6-tetrakis(4-bromophenyl)benzene (19). 1,4-Dimethyl-2,3,5,6-tetraphenylbenzene (3.50 g, 8.52 mmol) was powdered and covered with neat bromine (35 mL). The mixture was kept at 25 °C in the dark for 24 h and was then added to stirred ethanol (125 mL) precooled to −78 °C. The resulting solid was separated by filtration and washed with cold ethanol (25 mL) and then with small portions of 5% (w/v) aqueous $Na_2S_2O_3$ (total of 75 mL). Recrystallization from xylenes afforded 1,4-dimethyl-2,3,5,6-tetrakis(4-bromophenyl)benzene (**19**; 5.00 g, 6.89 mmol, 81%) as a colorless solid. An analytically pure sample was obtained by further recrystallization from toluene: mp > 300 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.72 (s, 6H), 6.88 (d, 8H, $^3J = 8.2$ Hz), 7.31 (d, 8H, $^3J = 8.2$ Hz). Anal. Calcd for $C_{32}H_{22}Br_4$: C, 52.93; H, 3.05. Found: C, 52.57; H, 2.72.

1,4-Dimethyl-2,3,5,6-tetrakis(4-cyanophenyl)benzene (20). A mixture of 1,4-dimethyl-2,3,5,6-tetrakis(4-bromophenyl)benzene (0.500 g, 0.689 mmol) and CuCN (0.617 g, 6.89 mmol) in dry DMF (40 mL) was heated at reflux under N_2 for 42 h. The mixture was cooled to 25 °C, water (80 mL) was added, and the resulting precipitate was collected by filtration. The solid was then washed with a 30% aqueous solution of ethylenediamine until the washings were colorless. The solid was treated with CH_2Cl_2, and the suspension was washed with 30% aqueous ethylenediamine, then with water, and finally with brine. The organic phase was dried over anhydrous $MgSO_4$ and filtered, and volatiles were then removed by evaporation under reduced pressure. Flash chromatography on silica gel (100% CH_2Cl_2) afforded 1,4-dimethyl-2,3,5,6-tetrakis(4-cyanophenyl)benzene (**20**; 0.231 g, 0.452 mmol, 66%) as a colorless solid: mp > 300 °C; ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 1.72 (s, 6H), 7.15 (d, 8H, $^3J = 8.4$ Hz), 7.50 (d, 8H, $^3J = 8.4$ Hz); ^{13}C NMR (100 MHz, CD$_2$Cl$_2$) δ 19.5, 111.3, 119.1, 131.3, 131.7, 132.4, 140.3, 145.7; HRMS (ESI) calcd for $C_{36}H_{22}N_4$ + H m/e 511.19172, found 511.19221.

1,2,4,5-Tetrakis[4-(2,4-diamino-1,3,5-triazin-6-yl)phenyl]-3,6-dimethylbenzene (7). 1,4-Dimethyl-2,3,5,6-tetrakis(4-cyanophenyl)benzene (0.200 g, 0.392 mmol), dicyandiamide (0.527 g, 6.27 mmol), and powdered KOH (0.056 g, 1.0 mmol) were suspended in 2-methoxyethanol (5 mL). The reaction mixture was heated at reflux for 24 h, cooled to 25 °C, and treated with water (5 mL). The resulting precipitate was separated by filtration and washed successively with boiling water, methanol, and dichloromethane to give 1,2,4,5-tetrakis[4-(2,4-diamino-1,3,5-triazin-6-yl)phenyl]-3,6-dimethylbenzene (**7**; 0.260 g, 0.307 mmol, 78%) as a colorless solid. Further purification could be achieved by (1) dissolving the compound (40 mg) in DMSO (20 mL) with the assistance of slight heating and sonication, (2) filtering the resulting mixture through a 0.45 μm PTFE filter, (3) adding a supernatant layer of anhydrous ethanol (120 mL) on top of the filtered solution, and (4) keeping the mixture undisturbed in a closed vessel overnight until small crystals appeared: mp > 300 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.79 (s, 6H), 6.68 (br s, 16H), 7.17 (d, 8H, $^3J = 8.3$ Hz), 8.00 (d, 8H, $^3J = 8.3$ Hz); HRMS (ESI) calcd for $C_{44}H_{38}N_{20}$ + H m/e 847.3661, found 847.3663.

1,2,4,5-Tetrakis(4-cyanophenyl)benzene (21). A mixture of 1,2,4,5-tetrabromobenzene (0.394 g, 1.00 mmol) and 4-cyanophenylboronic acid (0.882 g, 6.00 mmol) in toluene (80 mL), ethanol (40 mL), and aqueous K_2CO_3 (40 mL, 2 M) was degassed by allowing N_2 to bubble through it. Pd(PPh$_3$)$_4$ (115 mg, 0.100 mmol) was then added, and the mixture was degassed again. The mixture was heated at 90 °C for 24 h under N_2 and was then exposed to air for 1 h to oxidize the catalyst. The resulting mixture was partitioned between toluene (100 mL) and aqueous NaOH (50 mL, 1 M). The organic phase was separated and treated with acetone cyanohydrin (3 mL) and triethylamine (3 mL). As the mixture was stirred for 1 h, it turned from black to yellow. The mixture was filtered through silica gel, using CHCl$_3$ to help elute the product. Volatiles were then removed from the filtrate by evaporation under reduced pressure. Recrystallization of the residue from dioxane, followed by repeated dissolution of the product in CHCl$_3$ and evaporation to eliminate dioxane, yielded 1,2,4,5-tetrakis(4-cyanophenyl)benzene (**21**; 0.396 g, 0.821 mmol, 82%) as a colorless solid: mp > 300 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.44 (d, 8H, $^3J = 8.2$ Hz), 7.63 (s, 2H), 7.80 (d, 8H, $^3J = 8.2$ Hz); ^{13}C NMR (100 MHz, DMSO-d_6) 111.06, 119.49, 131.61, 133.13, 133.66, 139.52, 144.98; HRMS (ESI) calcd for $C_{34}H_{18}N_4$ + H m/e 483.16042, found 483.15952.

1,2,4,5-Tetrakis[4-(2,4-diamino-1,3,5-triazin-6-yl)phenyl]benzene (8). 1,2,4,5-Tetrakis(4-cyanophenyl)benzene (0.340 g, 0.705 mmol), dicyandiamide (0.296 g, 3.52 mmol), and powdered KOH (0.198 g, 3.53 mmol) were suspended in 2-methoxyethanol (10 mL). The mixture was heated at reflux for 24 h, cooled to 25 °C, and treated with water (10 mL). The resulting suspension was filtered, and the solid was washed with boiling water and then with cold methanol. Drying in air yielded 1,2,4,5-tetrakis[4-(2,4-diamino-1,3,5-triazin-6-yl)phenyl]benzene (**8**; 0.479 g, 0.585 mmol, 83%) as a colorless solid. Further purification was achieved by dissolving the product in hot DMSO, filtering, and reprecipitating the solid by adding four volumes of ethyl acetate. The product was collected by filtration and freed of DMSO by trituration with ethyl acetate: mp > 300 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.75 (br s, 16H), 7.32 (d, 8H, $^3J = 8.3$ Hz), 7.65 (s, 2H), 8.10 (d, 8H, $^3J = 8.3$ Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 127.4, 129.4, 132.1, 135.6, 139.0, 142.6, 167.3, 169.8; HRMS (ESI) calcd for $C_{42}H_{34}N_{20}$ + H m/e 819.3348, found 819.3346.

X-ray Crystallographic Studies. Data were collected using (1) a Bruker AXS SMART 4K/Platform diffractometer or (2) a Bruker Microstar diffractometer with Cu Kα radiation at 100, 200, or 240 K. Structures were solved by direct methods using SHELXS-97 and refined using SHELXL-97.[37] All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were placed in ideal positions and defined as riding atoms.

Structure of Crystals of Hexakis[4-(2,4-diamino-1,3,5-triazin-6-yl)phenyl]benzene (4) Grown from DMSO/THF. Crystals were found to belong to the triclinic space group $P\bar{1}$ with $a = 17.770(2)$ Å, $b = 21.235(3)$ Å, $c = 21.691(2)$ Å, $\alpha = 98.400(6)°$, $\beta = 110.518(5)°$, $\gamma = 103.475(6)°$, $V = 7217.9(14)$ Å^3, $D_{\text{calcd}} = 1.128$ g/cm^3, and $Z = 2$. Full-matrix least-squares refinements on F^2 led to final residuals $R_f = 0.1160$, $R_w = 0.2902$, and GOF = 1.096 for 23 987 reflections with $I > 2\sigma(I)$.

Structure of Crystals of Hexakis[4-(2,4-diamino-1,3,5-triazin-6-yl)phenyl]benzene (4) Grown from DMSO/Toluene. Crystals were found to belong to the triclinic space group $P\bar{1}$ with $a = 8.4178(11)$ Å, $b = 16.424(2)$ Å, $c = 20.251(3)$ Å, $\alpha = 105.291(5)°$, $\beta = 97.289(6)°$, $\gamma = 93.544(6)°$, $V = 2665.7(6)$ Å^3, $D_{\text{calcd}} = 1.347$ g/cm^3, and $Z = 2$. Full-matrix least-squares refinements on F^2 led to final residuals $R_f = 0.0792$, $R_w = 0.1865$, and GOF = 1.045 for 5999 reflections with $I > 2\sigma(I)$.

Structure of Crystals of Hexakis[4-(2,4-diamino-1,3,5-triazin-6-yl)phenyl]benzene (4) Grown from DMSO/Benzene. Crystals were found to belong to the trigonal space group $R\bar{3}$ with $a = b = 38.6740$-

(9) Å, $c = 10.010(3)$ Å, $V = 12966(4)$ Å^3, $D_{calcd} = 1.177$ g/cm^3, and $Z = 3$. Full-matrix least-squares refinements on F^2 led to final residuals $R_f = 0.0587$, $R_w = 0.1369$, and GOF = 1.028 for 5226 reflections with $I > 2\sigma(I)$.

Structure of Crystals of Hexakis[4-(2,4-diamino-1,3,5-triazin-6-yl)phenyl]benzene (4) Grown from Formic Acid/Methanol. Crystals were found to belong to the trigonal space group $R\bar{3}$ with $a = b = 22.8070(9)$ Å, $c = 17.2915(16)$ Å, $V = 7789.3(8)$ Å^3, $D_{calcd} = 0.761$ g/cm^3, and $Z = 3$. Full-matrix least-squares refinements on F^2 led to final residuals $R_f = 0.0614$, $R_w = 0.1513$, and GOF = 1.048 for 1912 reflections with $I > 2\sigma(I)$.

Structure of Crystals of 1,2,4,5-Tetrakis[4-(2,4-diamino-1,3,5-triazin-6-yl)phenyl]-3,6-diphenylbenzene (5) Grown from DMSO/Acetonitrile. Crystals were found to belong to the monoclinic space group $C2/c$ with $a = 40.3960(13)$ Å, $b = 20.6327(7)$ Å, $c = 12.0265(4)$ Å, $\beta = 99.926(2)°$, $V = 9873.8(6)$ Å^3, $D_{calcd} = 1.239$ g/cm^3, and $Z = 4$. Full-matrix least-squares refinements on F^2 led to final residuals $R_f = 0.0622$, $R_w = 0.1476$, and GOF = 1.003 for 6853 reflections with $I > 2\sigma(I)$.

Structure of Crystals of Pentakis[4-(2,4-diamino-1,3,5-triazin-6-yl)phenyl]benzene (6) Grown from DMSO/Acetone. Crystals were found to belong to the monoclinic space group $C2/c$ with $a = 31.282(15)$ Å, $b = 24.617(3)$ Å, $c = 11.704(9)$ Å, $\beta = 108.302(4)°$, $V = 8557(8)$ Å^3, $D_{calcd} = 1.265$ g/cm^3, and $Z = 4$. Full-matrix least-squares refinements on F^2 led to final residuals $R_f = 0.0890$, $R_w = 0.1426$, and GOF = 1.00 for 8129 reflections with $I > 2\sigma(I)$.

Structure of Crystals of 1,2,4,5-Tetrakis[4-(2,4-diamino-1,3,5-triazin-6-yl)phenyl]-3,6-dimethylbenzene (7) Grown from DMSO/Dioxane. Crystals were found to belong to the monoclinic space group $C2/m$ with $a = 20.4638(8)$ Å, $b = 21.4603(8)$ Å, $c = 15.8607(6)$ Å, $\beta = 104.885(2)°$, $V = 6307.2(4)$ Å^3, $D_{calcd} = 0.940$ g/cm^3, and $Z = 2$. Full-matrix least-squares refinements on F^2 led to final residuals $R_f = 0.0730$, $R_w = 0.1611$, and GOF = 1.181 for 1988 reflections with $I > 2\sigma(I)$.

Structure of Crystals of 1,2,4,5-Tetrakis[4-(2,4-diamino-1,3,5-triazin-6-yl)phenyl]-3,6-dimethylbenzene (7) Grown from DMSO/Methanol. Crystals were found to belong to the monoclinic space group $P2_1/c$ with $a = 34.706(2)$ Å, $b = 14.9704(9)$ Å, $c = 12.064(7)$ Å, $\beta = 91.318(2)°$, $V = 6246.8(7)$ Å^3, $D_{calcd} = 1.271$ g/cm^3, and $Z = 4$. Full-matrix least-squares refinements on F^2 led to final residuals $R_f = 0.0794$, $R_w = 0.1704$, and GOF = 1.115 for 8635 reflections with $I > 2\sigma(I)$.

Structure of Crystals of 1,2,4,5-Tetrakis[4-(2,4-diamino-1,3,5-triazin-6-yl)phenyl]benzene (8) Grown from DMSO/Acetone. Crystals were found to belong to the monoclinic space group $P2_1/c$ with $a = 8.9750(3)$ Å, $b = 22.7525(6)$ Å, $c = 21.9316(8)$ Å, $\beta = 101.4980(10)°$, $V = 4388.6(2)$ Å^3, $D_{calcd} = 1.329$ g/cm^3, and $Z = 2$. Full-matrix least-squares refinements on F^2 led to final residuals $R_f = 0.0651$, $R_w = 0.1491$, and GOF = 1.085 for 7838 reflections with $I > 2\sigma(I)$.

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Supporting Information Available: Additional crystallographic details, including ORTEP drawings and tables of structural data for compounds **4**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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