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A Theoretical Study of Cohesion, Structural Deformation, Inclusion, and Dynamics in Porous Hydrogen-Bonded Molecular Networks

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Abstract: Molecules with multiple sites of hydrogen bonding attached to suitable cores tend to crystallize as open networks. The resulting crystals can have the following unusual properties: They can include significant amounts of guest molecules; the guests are typically located in channels and can be exchanged without loss of crystallinity; and the geometry of the networks can change in response to new guests. We have found that DFT calculations can provide accurate simulations of the unusual structure and properties of such materials, represented by crystals of prototypic tetrapyridinone **1**. These calculations have yielded three key insights that cannot be obtained directly from experiments. (1) The hypothetical porous network obtained by removing guests from crystals of compound **1** is highly flexible, and its deformations are inherently anisotropic, leading to lengthening or shortening of the channels along the *c* axis and no significant changes along the *a* and *b* axes. (2) Quantitative analysis of the total cohesive energy has revealed that hydrogen bonding within the network makes a dominant contribution, along with interactions of guests with the network. (3) Differences in the overall stability of crystals of compound **1** as the guests are varied do not arise primarily from significant changes in the cohesive energy of the network itself; instead, differences in guest−guest interactions play a key role, resulting from the nature of the guests and constraints imposed by the surrounding network. These insights, together with the results of ab initio molecular dynamics, help explain how hydrogen-bonded networks can be robust yet permit molecular movement that underlies the exchange of guests and adaptive porosity. These insights promise to be of general value to scientists studying ordered molecular materials in which strong directional interactions are prominent.

Introduction

Crystal engineering seeks to predict and control the structure and properties of crystalline materials, and it has become an intensely active area of science.[1] Part of the interest springs from a desire to learn more about the basic phenomenon of crystallization, which is commonplace but poorly understood. In addition, researchers are drawn to crystal engineering by the opportunity to create useful new materials by design. A further attraction is the intrinsic appeal of exploring a field in which fundamental problems remain unsolved. As expressed by Maddox in a celebrated declaration published in *Nature* almost 20 years ago,[2] "One of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition." Despite significant intervening progress in the field of crystal engineering, this statement still holds true today.

As summarized in a recent review by Dunitz,[3] one of the most effective strategies in the current arsenal of crystal engineers is based on "...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 has indeed become one of the tenets of crystal engineering." Successful use of this approach requires a set of sticky functional groups that engage in strong, reliable, and directional intermolecular interactions, thereby ensuring that neighboring molecules are positioned with a high degree of predictability. Molecules that have proven to be especially suitable for engineering crystals with predetermined structures and properties can be constructed by orienting multiple sticky sites around the periphery of selected cores. Such compounds

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(1) (a) Braga, D. *Chem. Commun.* **2003**, 2751. (b) Hollingsworth, M. D. *Science* **2002**, *295*, 2410. (c) Braga, D., Grepioni, F., Orpen, A. G., Eds. *Crystal Engineering: From Molecules and Crystals to Materials*; Kluwer: Dordrecht, The Netherlands, 1999. (d) Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*: Elsevier: Amsterdam, The Netherlands, 1989.

(2) Maddox, J. *Nature* **1988**, *335*, 201.

(3) Dunitz, J. D. *Chem. Commun.* **2003**, 545.

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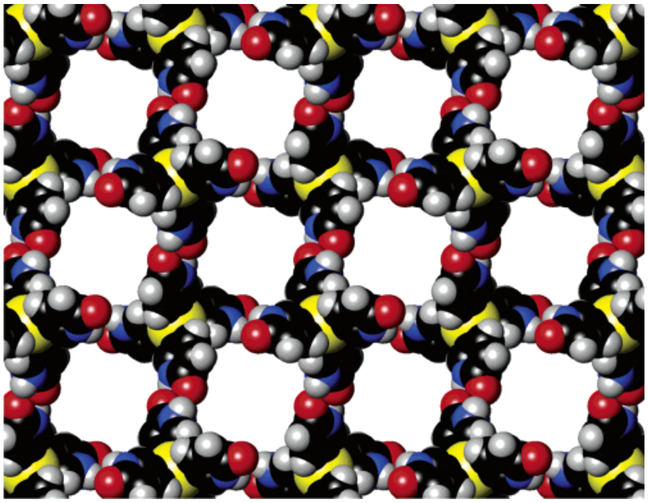


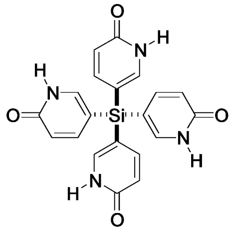
Figure 1. View along the *c* axis showing the cross sections of adjacent parallel channels in crystals of tecton $\mathbf{1}\cdot 4\ CH_3CH_2COOH$, with guests removed for clarity and with atoms represented by spheres of van der Waals radii. Carbon is shown in black, hydrogen is in gray, nitrogen is in blue, oxygen is in red, and silicon is in yellow.

have been given the name tectons, which is derived from the Greek word for builder.[4,5] Tectons are designed to interact strongly with their neighbors in specific and directional ways, leading to the formation of ordered networks by a process of programmed self-assembly. These features endow materials constructed from tectons with properties not normally observed in materials composed of conventional molecules.

In networks built from tectons, cohesion is ensured, in part, by directional noncovalent interactions such as hydrogen bonds[6] or by stronger forces such as coordination to metals.[7] Normal molecules usually form crystals that are considered close-packed, with no included guests and only small intermolecular voids.[8] In contrast, tectons cannot typically yield crystals in which packing and directional interactions are optimized simultaneously. The directional forces normally predominate, leading to the construction of open networks with significant capacities for inclusion. Accessible volume in these networks is then filled by a combination of independent interpenetrating networks[9] and included guests.

The resulting materials incorporate open networks that are molecular analogues of the porous inorganic frameworks of zeolites. Although porous tectonic networks are built from molecules joined only by noncovalent interactions, they can be remarkably robust. Included guests can often be exchanged in single crystals without loss of crystallinity. In favorable cases, guests can even be fully or partly removed to create porous materials that retain crystallinity. If the tectons themselves have an element of flexibility or if their intermolecular interactions can accommodate deformations, then the ordered networks can undergo significant changes of shape and show adaptive porosity, all without loss of crystallinity.

A prototypic hydrogen-bonded molecular network that can undergo exchanges of guests and show adaptive porosity can be constructed by crystallizing tecton **1**.[10,11] In compound **1**, four pyridinone groups are attached to a nominally tetrahedral



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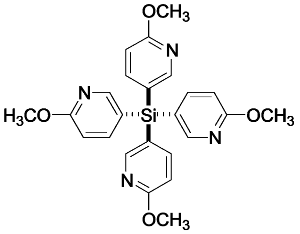

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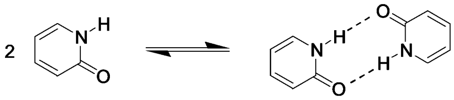

(1)

Si core. The reliable tendency of pyridinones to self-associate according to eq 1, coupled with the nominally tetrahedral geometry of the core, predisposes tecton **1** to crystallize as a diamondoid network. The resulting network is open enough to permit 2-fold interpenetration. Despite this interpenetration, about 60% of the volume of crystals of tetrapyridinone **1** remains accessible to guests, as measured by standard methods.[12] In crystals of close structural analogue **2**, which lacks the critical ability to form strong directional intermolecular interactions, none of the volume is accessible to guests.[13] Such large differences are typical and provide strong justification for treating tectons as a distinct class of molecules.

Crystals of tecton **1** grown from carboxylic acids typically belong to the tetragonal space group $P4_2/n$, and included solvent occupies prominent parallel channels aligned with the *c* axis (Figure 1). When the identity of the guests is changed, either by recrystallizing tecton **1** from a new acid or by exposing single crystals to a new guest, the overall architecture remains the same, but the value of the crystallographic *c* parameter varies in response to the dimensions of the guest. When the guest increases in size from acrylic acid to isovaleric acid, *c* lengthens from 7.360(2) to 9.584(2) Å, a change of more than 30%. In contrast, the values of the *a* and *b* parameters remain nearly constant. The ability of single crystals of tecton **1** to include significant quantities of guests, allow their exchange without loss of crystallinity, and undergo large dynamic deformations in adapting to new guests underscores the potential of molecular tectonics as a strategy for producing materials with properties not previously observed.

This potential now makes it important to develop a deeper understanding of the unusual behavior of porous hydrogen-bonded molecular networks. Unfortunately, some of the most intriguing questions about these materials cannot be answered

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(4) Simard, M.; Su, D.; Wuest, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 4696.

(5) Wuest, J. D. *Chem. Commun.* **2005**, 5830.

(6) (a) Burrows, A. D. *Struct. Bonding* **2004**, *108*, 55. (b) Steiner, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 48. (c) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (d) Prins, L. J.; Reinhoudt, D. N.; Timmerman, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2382.

(7) (a) Ockwig, N. W.; Delgado-Friedrichs, O.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2005**, *38*, 176. (b) Kitagawa, S.; Kitaura, R.; Noro, S.-i. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334.

(8) (a) Bernstein, J. In *Organic Solid State Chemistry*; Desiraju, G. R., Ed.; Elsevier: Amsterdam, The Netherlands, 1987; pp 471−518. (b) Kitaigorodskii, A. I. *Molecular Crystals and Molecules*; Academic Press: New York, 1973.

(9) (a) Batten, S. R. *CrystEngComm* **2001**, 76. (b) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460.

(10) Wang, X.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1994**, *116*, 12119.

(11) Saied, O.; Maris, T.; Wuest, J. D. *J. Am. Chem. Soc.* **2003**, *125*, 14956.

(12) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*: Utrecht University: Utrecht, The Netherlands, 2001.

(13) Saied, O.; Maris, T.; Simard, M.; Wuest, J. D. *Acta Crystallogr., Sect. E* **2005**, *61*, O4136.

at present by experimental studies. To help provide new insight, we have therefore undertaken a detailed theoretical analysis of crystals built from prototypic tecton **1**. Previous theoretical work in crystal engineering has typically focused on predicting structures.[14] The well-established difficulty of this objective has tended to limit theoretical studies to investigations of simple small molecules, often with little flexibility, nearly planar structures, first-row atoms, and few functional groups able to engage in hydrogen bonding or in other strong directional intermolecular interactions. In contrast, the present work examines crystals of a complex, three-dimensional molecule that forms porous networks in which hydrogen bonding and the inclusion of guests are prominent features. Furthermore, the objective of our study is not merely to predict structures but also to reveal how the collective properties of crystals are related to the nature of the individual molecular components and their local intermolecular interactions.[15] Developing a clear understanding of how individual molecules determine the properties of materials built from them is among the greatest challenges in science today. Our theoretical analysis has probed three subjects of particular importance: (1) cohesive forces, deformations, and adaptive porosity observed in hydrogen-bonded molecular crystals, as exemplified by tecton **1**; (2) thermodynamic aspects of the exchange of guests in these crystals; and (3) dynamics of the crystals, focusing on movement of individual tectons and guests. The results of these calculations have provided key insights likely to be of general value to scientists studying a wide range of ordered molecular materials.

Results and Discussion

Crystals of tecton **1** are held together by subtle bonding forces and contain molecules of significant complexity. As a result, the theoretical methods used to calculate their structure must be accurate yet able to handle unit cells containing more than 200 atoms. Until recently, similar requirements have thwarted the use of ab initio calculations of total energy in supramolecular chemistry.[16] However, density functional theory (DFT), associated with the techniques of plane-wave basis sets and pseudopotentials, has now reached a level permitting analyses of complex systems such as molecular crystals. DFT offers accurate treatment of covalent and electrostatic interactions, and its ability to describe hydrogen bonds is good.[17] Although it reproduces weak attractive van der Waals interactions less well, this limitation is mitigated in analyses of structures in which hydrogen bonding plays a dominant role.

Complete removal of guests from crystals of tecton **1** without changing the position of the tectons would yield a hypothetical porous, doubly interpenetrated diamondoid network. Such structures are of significant practical importance because they are purely molecular analogues of zeolites and related ordered microporous materials. Unfortunately, all attempts to experimentally produce an empty structure by heating crystals of tecton **1** or by placing them under vacuum have failed. Loss of guests occurs, as expected, but it triggers extensive reorganization of the tectons. The resulting solid is crystalline, but its structure is compact.[18] Because the original material loses approximately 60% of its contents when guests are removed, the network of hydrogen bonds initially present in crystals of tecton **1** is presumably no longer able to resist forces favoring closer packing of the remaining molecules. The hypothetical empty diamondoid structure constructed from tecton **1** is experimentally inaccessible; therefore, theoretical methods offer the only way to examine its properties. Such simulations are a crucial starting point for understanding structural deformations that occur in permeable molecular crystals during loss or exchange of guests.

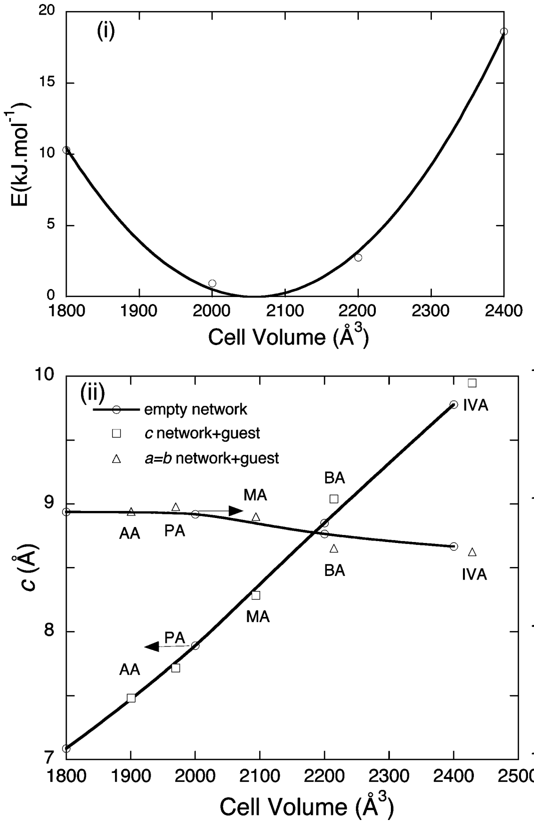

Figure 2. (i) Calculated relative energy of the hypothetical empty network constructed from tecton **1**, given as a function of the imposed unit cell volume. The energy is normalized to one unit cell (two molecules of tecton **1**), and a parabola is used to fit the data. (ii) Traces corresponding to calculated values (open circles) of the unit cell parameters *c* (left axis) and $a = b$ (right axis) as a function of imposed cell volume for the hypothetical empty network. The graphic simultaneously shows the *c* parameters (squares) and $a = b$ parameters (triangles) calculated for the structures of the five inclusion compounds **1**·4 HOOCR containing isovaleric acid (IVA), butyric acid (BA), methacrylic acid (MA), propionic acid (PA), and acrylic acid (AA). The symbols have been placed at the optimal unit cell volume calculated for each structure.

To assess the inherent ability of the hypothetical empty network to undergo deformations, we fixed the volume of the unit cell at various values, and then we calculated the crystal energy and structural parameters. The results, which are summarized graphically in Figure 2i, clearly demonstrate the extremely high flexibility of the hypothetical empty network. The optimal volume of the unit cell is calculated to be $\sim$2060 Å^3

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(14) For recent references, see: (a) Gavezzotti, A. *Struct. Chem.* **2005**, *16*, 177. (b) Day, G. M.; *et al. Acta Crystallogr., Sect. B* **2005**, *61*, 511.

(15) For other theoretical studies of the properties of molecular crystals using ab initio methods, see: (a) Kearley, G. J.; Johnson, M. R.; Tomkinson, J. *J. Chem. Phys.* **2006**, *124*, 044514. (b) Brand, H. V. *J. Phys. Chem. B* **2005**, *109*, 13668. (c) Li, T.; Feng, S. *J. Phys. Chem. A* **2005**, *109*, 7258. (d) Ju, X.-H.; Xiao, H.-M.; Chen, L.-T. *Int. J. Quantum Chem.* **2005**, *102*, 224. (e) Tóbik, J.; Dal Corso, A.; Scandolo, S.; Tosatti, E. *Surf. Sci.* **2004**, *566*−*568*, 644.

(16) (a) Henry, M.; Hosseini, M. W. *New J. Chem.* **2004**, *28*, 897. (b) Chin, D. N.; Palmore, G. T. R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1999**, *121*, 2115.

(17) Poulet, G.; Sautet, P.; Tuel, A. *J. Phys. Chem. B* **2002**, *106*, 8599.

(18) Trolliet, C.; Maris, T.; Saied, O.; Sautet, P.; Wuest, J. D. Unpublished results.

but changes in volume of ±10% are associated with increases in energy of only about 5 kJ mol^{-1} per unit cell, which is remarkably small. Diamondoid networks generated from tetrahedral subunits would normally be expected to undergo isotropic deformations upon imposed changes in unit cell volume. However, Figure 2ii reveals that (1) the change in the volume of the unit cell is caused primarily by a variation in the *c* parameter and (2) the *a* and *b* parameters remain essentially constant. Compression or expansion is related to the *c* parameter almost linearly, and the crystal responds in a unidimensional way to the imposed changes in volume. This allows the channels containing guests to lengthen or shorten along *c*, without significantly changing their diameter. The calculated anisotropic deformation along *c*, despite the initial isotropic geometry of the individual tectons, is well in line with our experimental observations, which show similar changes of cell parameters when guests are exchanged.

Because the calculations involve a guest-free network, the preference for anisotropic deformation cannot be attributed to the identity of the guests, their packing, their interaction with the network, or other factors related to the guests; rather, it must reflect an intrinsic preference of the hydrogen-bonded tectonic network itself. Expansion or contraction of the crystal does not involve symmetric deformations of nominally tetrahedral tecton **1**, which must be energetically costly; instead, expansion of the crystal along the *c* axis is associated with an asymmetric C_{2v} deformation of the tecton. This deformation is facilitated by the presence of a second-row atom (Si) at the core and by the ability of the pyridinone groups to undergo small additional deformations. In principle, a C_{2v} distortion of tecton **1** should cause not only a deformation along *c* but also inverse changes in the *a* and *b* parameters. Hence, it should not result in a significant change of the volume. This is not the case because subtle rotations of tecton **1** around the *c* axis and minor changes in hydrogen bonding roughly counteract the expected deformations along *a* and *b*. The ability of our DFT calculations to reproduce these subtle effects is noteworthy for two reasons. (1) It made us confident that other aspects of the structure, discussed later in this paper, have also been simulated faithfully, and (2) it alerts other researchers studying complex ordered molecular materials to the potential of modern DFT methods for rationalizing or predicting unusual properties.

The hypothetical empty double-diamond network built from tecton **1** was then filled with five different carboxylic acids to create materials with the composition **1**·4 HOOCR, and the new structures were optimized. The five acids selected were among those previously studied experimentally, isovaleric acid (IVA, R = $CH_2CH(CH_3)_2$), butyric acid (BA, R = $CH_2CH_2CH_3$), methacrylic acid (MA, R = $C(CH_3){=}CH_2$), propionic acid (PA, R = CH_2CH_3), and acrylic acid (AA, R = $CH{=}CH_2$). Calculated unit cell parameters, along with selected bond angles and distances, are reported in Table 1 for the series of relaxed structures, and structural data previously obtained by single-crystal X-ray diffraction are also provided for comparison. The experimentally observed trend in the evolution of the cell parameters, in which a large variation in *c* accompanies minor changes in *a* and *b* as the guests are changed, is reproduced well by theory. When the values of the computed parameters are plotted as a function of optimal unit cell volume on the graph shown in Figure 2ii, the data coincide almost perfectly with the model traces calculated for the hypothetical empty network. This coincidence shows that the need to provide a sufficient unit cell volume is the key factor determining how the hypothetical empty network adapts to guests and that other factors such as the precise shape of the guest or the specific nature of its interaction with the network are less important.

Table 1. Calculated Unit Cell and Geometric Parameters for Crystals of the Inclusion Compounds **1**·4 HOOCR for Five Different Guests[a]

HOOCR	IVA[b]	BA[b]	MA[b]	PA[b]	AA[b]
c (Å)	9.94	9.04	8.28	7.71	7.48
	(9.58)	(8.80)	(7.88)	(7.66)	(7.36)
a = *b* (Å)	15.62	15.65	15.90	15.98	15.94
	(15.41)	(15.46)	(15.66)	(15.65)	(15.66)
O···Si···O (°)[c]	103.0	106.6	111.4	114.4	115.1
	(104.9)	(107.7)	(111.4)	(113.4)	(114.2)
N···O (Å)[d]	2.83	2.79	2.79	2.78	2.77
	(2.78)	(2.78)	(2.74)	(2.76)	(2.80)
V (Å^3)	2428	2214	2093	1969	1901
	(2277)	(2103)	(1933)	(1875)	(1804)

[a] Experimental values determined by X-ray crystallography at 220 K are shown in parentheses. [b] IVA = isovaleric acid (R = $CH_2CH(CH_3)_2$), BA = butyric acid (R = $CH_2CH_2CH_3$), MA = methacrylic acid (R = $C(CH_3){=}CH_2$), PA = propionic acid (R = CH_2CH_3), and AA = acrylic acid (R = $CH{=}CH_2$). [c] Angle between the oxygen atoms of two pyridinone groups and the central Si atom, which measures the C_{2v} distortion of tecton **1**. The particular O···Si···O angle bisected by the *c* axis has been chosen so that a small value is associated with a large value of *c*. [d] Intermolecular N···O distance between hydrogen-bonded pyridinone groups.

Table 2. Calculated Total Cohesive Energy E_c (kJ mol^{-1}) in Crystals of Inclusion Compounds **1**·4 HOOCR for Five Different Guests and Its Decomposition into the Individual Terms Defined in the Text[a]

guest[b]	E_c	$E_{dist}(T)$ +	$E_{int}(T)$ =	$E_c(T)$	$E(GG)$ +	$E(GT)$ =	$E_c(G)$
IVA	−378	38	−205	−167	27	−238	−211
BA	−409	42	−213	−171	5	−243	−238
MA	−404	38	−210	−172	−18	−214	−232
PA	−391	37	−208	−171	−3	−217	−220
AA	−412	41	−217	−176	−15	−221	−236

[a] All energies are normalized to one tecton **1** and four molecules of guest. [b] IVA = isovaleric acid (R = $CH_2CH(CH_3)_2$), BA = butyric acid (R = $CH_2CH_2CH_3$), MA = methacrylic acid (R = $C(CH_3){=}CH_2$), PA = propionic acid (R = CH_2CH_3), and AA = acrylic acid (R = $CH{=}CH_2$).

Atomic positions in the calculated structures also agree well with those determined experimentally by X-ray diffraction, with an average displacement of only 0.03 Å for atoms in the tectons themselves and of 0.18 Å for atoms in the smallest and most mobile guests. As expected, hydrogen-bonded contacts are well-described by theory. It is encouraging to note that the calculations reproduce the observed structures accurately. Theory cannot, at present, offer a general solution to the vexing problem of predicting the structures of molecular crystals, even in the simplest cases. However, our results suggest that theory may prove to be a more powerful predictive tool when applied to the subset of molecules defined by tectons, which strongly favor structures in which specific directional intermolecular forces are dominant.

Further DFT calculations have yielded valuable new information about energy and cohesion in porous hydrogen-bonded networks (Table 2). Such insights cannot easily be obtained from experiments, and they are keys to the future design of optimized networks. The cohesive energy (E_c) in crystals of composition **1**·4 HOOCR, normalized here to one tecton and four molecules of guest, is defined as the total energy minus the energy of an isolated tecton and four isolated guests, in their optimized geometry. The cohesive energy decreases significantly (34 kJ mol^{-1}, ∼10%) from the smallest guest (acrylic acid) to the largest (isovaleric acid), presumably because the bulkier guests impose constraints that prevent the networks in which they are included from enjoying optimal hydrogen bonding. However, the cohesive energy does not decrease monotonically with an increase in the volume of the unit cell. The calculated cohesive energies are in agreement with the preferred directions of exchange that have been observed experimentally.[11] In particular, isovaleric acid can easily be replaced by butyric acid and propionic acid, and both processes correspond to increases in the computed cohesive energy. ΔS for replacing a larger carboxylic acid by a smaller one is presumably positive because the alkyl chains can adopt more conformations outside the ordered network. Our calculations therefore suggest that an inherently favorable ΔS is reinforced by a favorable ΔH arising from stronger cohesion of the network.

Partitioning the total cohesive energy in crystals of tecton **1** into four distinct terms, as set out in Table 2, helps identify which elementary interactions play a dominant role. This information cannot be derived from experiments and can only be obtained by a theoretical approach. In this approach, the crystal is built stepwise, starting from isolated tecton **1** in the gas phase. The first term, $E_{\mathrm{dis}}(\mathrm{T})$, is the cost to distort tecton **1** into the geometry that it adopts in the crystal. The second term, $E_{\mathrm{int}}(\mathrm{T})$, is the stabilization associated with forming intermolecularly hydrogen-bonded pairs of pyridinone groups, which ensure the integrity of the network. The sum of these first two terms yields the cohesive energy of the tectonic network, $E_{\mathrm{c}}(\mathrm{T})$, in the geometry found in the actual crystal but without considering interactions with the guests, which remain to be added. The guests to be added are first assembled in the geometry they occupy in the crystal but without considering interactions with the surrounding tectonic network. This gives the guest−guest interaction, $E(\mathrm{GG})$. Finally, the preconstructed empty network and the preassembled guests are allowed to interact to give the remaining guest−tecton term, $E(\mathrm{GT})$. The sum of $E(\mathrm{GG})$ and $E(\mathrm{GT})$ is the overall contribution of guests to cohesion of the crystal, $E_{\mathrm{c}}(\mathrm{G})$. The sum of the cohesive contribution of the tectons, $E_{\mathrm{c}}(\mathrm{T})$, and that of the guests, $E_{\mathrm{c}}(\mathrm{G})$, then yields the total cohesive energy E_{c}.

Remarkably, the three terms associated with tectonic contributions to the total cohesive energy ($E_{\mathrm{dis}}(\mathrm{T})$, $E_{\mathrm{int}}(\mathrm{T})$, and $E_{\mathrm{c}}(\mathrm{T})$) are all nearly independent of the guests and of the degree of distortion present in the networks. This independence underlies the inherent ability of the basic network to flex and adapt to guests. The large values of $E_{\mathrm{int}}(\mathrm{T})$ denote strong tecton−tecton interactions with a main contribution from hydrogen bonding (∼50 kJ mol^{-1} per hydrogen bond), probably arising from a combination of electrostatic effects, charge transfer,[19] and resonance assistance by the π system of the pyridinone rings.[20] The calculated strength of these interactions in the solid state agrees well with values obtained in studies of the self-association of related pyridinones in the gas phase.[21] The magnitude of $E_{\mathrm{int}}(\mathrm{T})$ provides a significant driving force for assembly of the predicted diamondoid network, and it explains the robustness of the structure and the ability of single crystals to withstand the exchange of guests without loss of crystallinity.

Of all of the individual terms that contribute to the total cohesive energy (Table 2), the guest−guest interaction, $E(\mathrm{GG})$, is most sensitive to the nature of the guest. This term varies over 45 kJ mol^{-1} as the guest is changed and can be either attractive or repulsive. The next most sensitive term is the host−guest interaction, $E(\mathrm{GT})$; however, this term ranges over only 29 kJ mol^{-1} and is always attractive. The contribution from the guest−guest interaction gradually becomes more repulsive as the guest becomes larger, as seen in the series PA (−3 kJ mol^{-1}), BA (5 kJ mol^{-1}), and IVA (27 kJ mol^{-1}). In the calculation of $E(\mathrm{GG})$, guests are constrained to remain in the geometry they occupy in the tectonic network, and they cannot relax to engage in optimal hydrogen bonding or packing. $E(\mathrm{GG})$ primarily reflects diffuse interactions between the alkyl chains of neighboring guests, and the various guests form similar structures within the network. Hydrogen bonds are present between guests and the network but not between guests. The interaction between guests changes from slightly attractive for PA to repulsive for the bulkier BA and IVA. The network responds to the change of molecular size by adapting its unit cell volume, but larger guests are kept in a state of slightly compressive stress. Unsaturation in MA and AA yields stabilizing interactions resulting from polarization, which causes these two guests to behave unlike their saturated analogues.

Stabilization resulting from interactions of the tectonic network with included guests, $E(\mathrm{GT})$, makes a very important contribution to the total cohesion. The calculated value, which corresponds to more than 50 kJ mol^{-1} per molecule of guest, arises primarily from hydrogen bonding between carboxyl groups of the guest and the pyridinone groups of tecton **1**. Because guests make a major contribution to the overall stability of the crystals, exchange presumably occurs by progressive interdiffusion of new and old guests, rather than by the transient formation of networks with a substantial degree of emptiness.

We have completed this picture of cohesion, deformation, and inclusion in crystals of compound **1** by analyzing the mobility of the tectons and guests, using ab initio molecular dynamics. Our calculations suggest that the tectons undergo significant movement at 300 K. For the oxygen atoms of the pyridinone groups, the square root of the mean quadratic displacement is 0.26 Å, in good agreement with the experimental value of isotropic displacement for these atoms (0.36 Å), as determined by structure refinement in the reported X-ray crystallographic study.[10,11] Analysis of the double hydrogen bonds shared by paired pyridinone rings (eq 1) also reveals substantial movement, with an oscillation range of ∼0.2 Å for the O···H distance and ∼20° for the N−H···O angle. As a result of these molecular movements in the network, important fluctuations can occur in the cross sections of the channels in which guests are included (Figure 1). These temporary fluctuations are a characteristic feature of the crystals, and they presumably help determine the mechanism and rate of the diffusion and exchange of guests. In particular, the dynamics calculations provide important new insight by explaining how guests that appear to be somewhat too large to pass through

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[19] Fonseca Guerra, C.; Bickelhaupt, F. M.; Snijders, J. G.; Baerends, E. J. *Chem.−Eur. J.* **1999**, *5*, 3581.

[20] (a) Gilli, G.; Bertolasi, V.; Ferretti, V.; Gilli, P. *Acta Crystallogr., Sect. B* **1993**, *49*, 564. (b) Gilli, G.; Belluci, F.; Ferretti, V.; Bertolasi, V. *J. Am. Chem. Soc.* **1989**, *111*, 1023. (c) Huggins, M. L. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 147.

[21] (a) Frey, J. A.; Leutwyler, S. *Chimia* **2005**, *59*, 511. (b) Fu, A.; Li, H.; Du, D.; Zhou, Z. *J. Phys. Chem. A* **2005**, *109*, 1468. (c) Müller, A.; Losada, M.; Leutwyler, S. *J. Phys. Chem. A* **2004**, *108*, 157.

constrictions in the channels may, nevertheless, penetrate the crystals. Furthermore, the calculations advance our understanding by suggesting that zeolites and permeable molecular analogues may work in distinctly different ways. Specifically, molecular analogues can exploit temporary structural fluctuations resulting from the inherently deformable nature of the intermolecular hydrogen bonds that hold the networks together.

Because crystals of tecton **1** can undergo complete exchange of guests without loss of crystallinity, the mobility of the guests must be much higher than that of the tectons. Similar observations have been made in studies of exchange and topotactic reactions[5,22] in many other crystals in which related porous hydrogen-bonded networks are present. Although such behavior is well-established, a detailed understanding of the phenomenon cannot be obtained by experimental approaches. Theory provides valuable insight by showing that, in crystals of tecton **1**, the most dynamic structural element is the hydrogen bond between the network and the guests. At 300 K, the O−H distance in the carboxyl group of the guest oscillates with a maximum amplitude of ∼0.4 Å, and the proton of the guest shows a large square root of the quadratic displacement of ∼0.6 Å. For short intervals, the proton occupies a bridging position between oxygen atoms of the guest and a nearby tecton, but complete transfer does not occur. In these ways, calculations using ab initio molecular dynamics provide valuable information about molecular movement in crystals of tecton **1** during the short intervals that are computationally accessible (a few picoseconds). Unfortunately, these intervals are much too short to allow the actual diffusion of guests to be followed.

Conclusions

Molecules with multiple sites of hydrogen bonding attached to suitable cores tend to crystallize as open networks. The resulting crystals can include significant amounts of guests, allow guests to be exchanged without loss of crystallinity, and flex in response to new guests. We have found that DFT calculations can provide accurate simulations of the unusual structure and properties of such materials, represented by crystals of prototypic tetrapyridinone **1**. These calculations have yielded a series of key insights that cannot be obtained directly from experiments. In particular, the ability of these networks to undergo easy deformations arises from the flexibility of the individual molecules and distortions of the directional interactions that hold them together. Moreover, our calculations explain how these deformations can be anisotropic, even when the individual molecules have high symmetry. Quantitative dissection of the total cohesive energy of the crystals into individual components has revealed that hydrogen bonding within the network makes a dominant contribution, along with interactions of guests with the network. Furthermore, differences in the overall stability of crystals of compound **1** as the guests are varied do not arise primarily from significant changes in the cohesive energy of the network itself; instead, differences in guest−guest interactions play a key role, resulting from the nature of the guests and constraints imposed by the surrounding network. Our computational results, completed by analyses using ab initio molecular dynamics, help explain how hydrogen-bonded networks can be robust yet permit molecular movement that underlies the exchange of guests and adaptive porosity. These insights are new and promise to be of general value to scientists studying a wide range of molecular materials. Our results will encourage these researchers to make more extensive use of theoretical methods based on DFT to develop a full understanding of their observations and to plan new experiments.

Experimental Section

Calculations were performed with density functional theory applied to periodic systems, as implemented in the VASP code,[23] with the Perdew−Wang 91 generalized gradient approximation.[24] The one-electron wave function was developed using a plane-wave basis set, and the projector-augmented wave method[25] was used to describe atomic cores. A plane-wave cutoff of 500 eV allowed good accuracy to be attained in the optimization of unit cells, whereas in calculations with fixed cell parameters, a reduced cutoff of 400 eV could be used. Due to the large size of the cell, Brillouin zone sampling was performed on a grid with two irreducible *k* points from a 1 × 1 × 3 Monskort−Pack mesh. Fixed-volume molecular dynamics calculations were conducted using the algorithm of Nosé[26] in a simulated canonical ensemble, with a time step of 0.5 fs. They were performed on the unit cell of the crystal at 300 K for trajectories from 1 to 3 ps, allowing proper thermalization.

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Supporting Information Available: Complete reference 14b. Optimized unit cell parameters and atomic coordinates for crystals of the inclusion compounds **1**·4 HOOCR for five different guests. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Brunet, P.; Demers, E.; Maris, T.; Enright, G. D.; Wuest, J. D. *Angew. Chem., Int. Ed.* **2003**, *42*, 5303.

(23) Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *47*, 558.

(24) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

(25) Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758.

(26) Nosé, S. *Prog. Theor. Phys. Suppl.* **1991**, *103*, 1.