

Storage of Methane and Freon by Interstitial van der Waals Confinement

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A known host-guest assembly, organized only by means of relatively weak dispersive forces, exhibits hitherto unappreciated thermal stability. The hexagonal close-packed arrangement of calix[4]arene contains lattice voids that can occlude small, highly volatile molecules. This host-guest system can be exploited to retain a range of freons, as well as methane, not only well above their normal boiling points, but also at relatively high temperatures and low pressures. The usually overlooked van der Waals interactions in organic crystals can indeed be used in a highly stable supramolecular system for gas storage.

Perhaps the most basic tenet of organic solid-state chemistry is that molecules will try to organize themselves such that a compromise is reached between the optimization of both space and intermolecular interactions (1). Molecules in crystals are always tightly packed (2, 3), and molecular crystals possessing unoccupied lattice voids larger than about 25 Å³ in volume are generally considered to be rare. Furthermore, the molecules in a pure substance will usually assemble to form a framework quite different from the one it would assume when crystallized in a mixed system (4). Even the presence of small solvent molecules can markedly influence the overall structure (4). Were this not generally the case, many pure crystalline substances would necessarily contain relatively large lattice voids. Although only a handful of such exceptions are known to exist (5–7), the structure of these substances is strongly influenced by intermolecular interactions such as hydrogen bonds. We reveal an organic supramolecular framework that contains large, unoccupied lattice voids while being stabilized purely by van der Waals forces. We also show that the lattice voids of such a system can be used to entrap and retain highly volatile gases indefinitely at high temperatures even under vacuum.

The calixarenes (8) comprise an extensively studied class of macrocyclic, polyphenolic compounds that are usually strongly associated with host-guest inclusion chemistry. The simplest representative of this family of compounds is calix[4]arene, **1**, a bowl-shaped molecule with a shallow cleft. Its rigid cone conformation is stabilized by a cyclic array of hydrogen bonds between adjacent phenolic OH groups at the lower rim. To date, only nine structural reports of crystal-

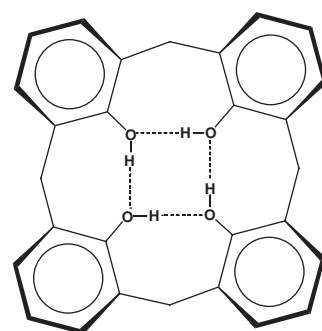
line inclusion compounds incorporating calix[4]arene have been published. During our ongoing studies of molecular cavitands and their supramolecular derivatives (9–12), we revisited **1** and discovered that its crystalline inclusion compounds exhibit unusual structural characteristics, in addition to extraordinary thermal stability.

Calix[4]arene is soluble in a variety of aromatic and aliphatic solvents, and the structure of an acetone solvate, **1a** (easily obtained by evaporation of a solution of **1** in acetone) (13), is accurately described as a 1:1 host:guest complex with each acetone guest molecule inserting one of its methyl groups into a calixarene cavity. When exposed to air, the crystalline material decomposes readily as 2/3 of the acetone is released in vapor form, with concomitant rearrangement of the host lattice and the remaining acetone guest. As expected, desolvation results in powdering of the crystals, and even mild heating (50°C) accelerates the process considerably.

Diffraction-quality single crystals of pure **1** were grown by sublimation at 300°C under reduced pressure, and the guest-free structure was elucidated. Comparison of the calculated powder x-ray diffraction (XRD) pattern of the sublimed phase with that obtained exper-

imentally for the 2/3 desolvated acetone phase confirms that the two structures are isomorphous. Pure **1** crystallizes in the hexagonal space group $P6_3/m$: Three calixarene molecules adopt a cyclic, mutually included arrangement (**2**) (Fig. 1A). The trimer thus formed is approximately spherical in shape, and the extended structure is simply a hexagonal close-packed (hcp) assembly of **2**. No intermolecular hydrogen bonds are present in the structure, and **2** appears to be held together only by the relatively weak van der Waals interactions.

An ideal hcp lattice of spherical entities contains a three-dimensional network of parallel and oblique channels (with respect to the crystallographic c axis) that link interstitial voids. One can distinguish two types of channels that run parallel to [001]. Type **a** channels are continuous and link voids that are bounded by a trigonal antiprismatic arrangement of six spheres. Type **b** channels are not



1 calix[4]arene

Scheme 1.

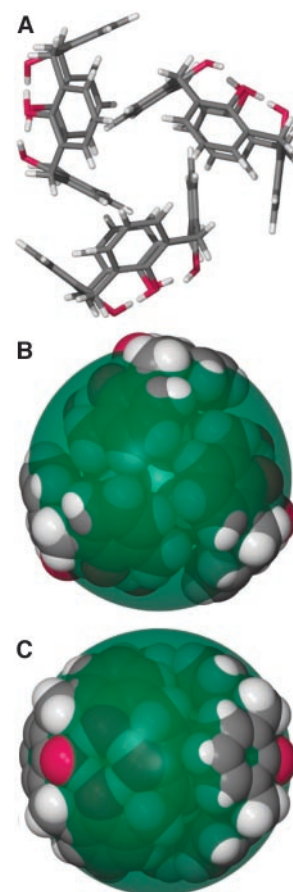


Fig. 1. Views of **2**, the cyclic, trimeric arrangement of **1**, in (A) capped-stick representation viewed along the threefold axis, (B) space-filling representation viewed along the threefold axis, and (C) space-filling representation viewed perpendicular to the threefold axis. The semitransparent green spheres (radius = 7.3 Å) shown in (B) and (C) are included to emphasize the minor deviation of **2** from true spherical geometry. Colors: gray, carbon; white, hydrogen; and red, oxygen.

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continuous and are surrounded by five spheres in a trigonal bipyramidal environment. The structure of **2** deviates from ideal spherical geometry such that minor protrusions and indentations manifest themselves (Fig. 1, B and C). These undulations result in substantial dilation of the type **b** channels to yield “solvent-accessible” voids of $\sim 153 \text{ \AA}^3$. Furthermore, constriction of the oblique and type **a** channels ensures that the bulk structure is nonporous. The hcp arrangement of pure **2**, as described above, also obtains in the dichloromethane (14), chloroform (15), and acetonitrile solvates (16). In all three cases, the guest is situated in the interstitial void and is intricately disordered as a result of its loose fit and the presence of high crystallographic site symmetry. A second acetone solvate phase, **2a**, was also reported in which the acetone molecule is similarly situated in the void (13) and is almost certainly the same phase obtained by 2/3 desolvation of the acetone phase **1a**.

To probe the cavity size, we prepared crystals of the CCl_4 solvate by slow evaporation of a solution of **1** in CCl_4 . Again we observed the now familiar hcp host framework, but in this case the more symmetrical CCl_4 solvent is not disordered and therefore is easily modeled. The guest is trapped in the interstitial lattice cavity and makes only van der Waals contact with the host. Although it is not unusual to encounter a family of host-guest systems in which the host lattice is effectively invariant (17, 18), it is extraordinary for an organic host to assume the same structure in its inclusion compounds as that of its pure phase (1); notable exceptions include β -quinol (5) and Dianin’s compound (6). This intriguing observation prompted us to investigate the thermal stability of the hcp inclusion compounds of **1** relative to that of its pure phase. Thermogravimetric analysis (TGA) of the CCl_4 solvate shows that the inclusion compound is stable up to 200°C . This temperature marks the onset (T_{on}) of guest release (the weight loss recorded be-

tween 200° and 250°C corresponds to a 1:1 complex of **2** and CCl_4), in sharp contrast to the guest release by the non-hcp structure **1a** at 50°C .

The parameter ($T_{\text{on}} - T_{\text{b}}$) has been shown to be a reliable measure of the relative thermal stability of host-guest systems, where T_{b} is the normal boiling point of the guest (19). The thermal stability of the hcp host lattice is unusually high, despite the presence of a relatively volatile guest ($T_{\text{on}} - T_{\text{b}}$ for $2 \cdot \text{CCl}_4 = 120^\circ\text{C}$, compared with -8°C for **1a**). In view of these findings, we assessed the ability of the host lattice to stabilize increasingly volatile guests that are structurally related to CCl_4 . The possibility thus presents itself of entrapping a range of highly volatile freon and halon compounds in the hcp interstitial cavity. Several such host-guest compounds were indeed prepared as single crystals, and pertinent parameters are given in Table 1. All of these crystals exhibited unusually high thermal stability as determined by TGA.

The very low solubility of **1** in condensed volatile freons such as CF_3Br , C_2F_6 , and CF_4 precludes the growth of diffraction-quality crystals with the procedure used to obtain $2 \cdot \text{CCl}_4$. However, while studying the solvates of **1**, we had noted that solvent-free hcp crystals could be precipitated by the addition of propan-2-ol to a solution of **1** in toluene. A modification of this method involving dissolution of a condensed freon or halon of interest in the toluene allowed us to easily obtain diffraction-quality single crystals within 30 min. As before, in some cases, satisfactory modeling of the guest within the hcp lattice was hampered by disorder and thermal motion. However, in all cases, microanalysis and solution ^{19}F nuclear magnetic resonance (NMR) confirmed the presence of the halo-carbon guest. Host-guest ratios were determined by means of TGA. In the case of the CF_3Br inclusion compound, the guest was simply disordered over two positions and easily modeled. Figure 2 shows CF_3Br posi-

tioned in the interstitial cavity of the hcp lattice.

Because clathration necessitates a phase transformation of the host lattice for the guest to become lodged in the lattice voids, we focused on the previously observed desolvation of the metastable, non-hcp acetone solvate **1a**. Large, single crystals of the latter were grown, crushed, and placed in a steel pressure vessel. Freon gas was introduced into the vessel, which was then sealed and heated to 50°C . After about 12 hours, the crystals were removed and subjected to XRD, NMR, TGA, and microanalysis, which together confirmed the hexagonal structure as well as the near-stoichiometric lattice inclusion of the gas. These results show that, in the presence of a suitable guest vapor, even a solid-solid phase transition of the host to the hcp lattice structure facilitates guest inclusion.

We also were able to entrap CH_4 at room temperature by exposure at 100 atm for 72 hours. The resulting powder was dissolved in d^6 -benzene and analyzed by $^1\text{H-NMR}$, which unequivocally revealed the presence of methane [$\sigma = 0.15$ parts per million (ppm)], as well as trace amounts of acetone ($\sigma = 1.52$ ppm). TGA analysis yielded a weight loss of 2.43% with $T_{\text{on}} = 150^\circ$ to 170°C , corresponding to two methane molecules per lattice void [calculated CH_4 weight loss for $2 \cdot (\text{CH}_4)_2 = 2.45\%$]. Although single crystals containing methane could be obtained from toluene/propan-2-ol under a high pressure of methane, a reasonable model incorporating methane could not be elucidated because of guest disorder.

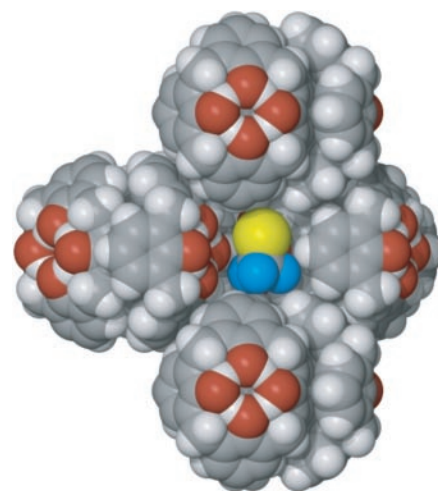


Fig. 2. Space-filling representation of $2 \cdot \text{CF}_3\text{Br}$ viewed perpendicular to the crystallographic c axis. The interstitial void of the host lattice is occupied by one molecule of CF_3Br , which is surrounded by five units of **2** (one unit has been omitted from the foreground to reveal the guest). The disorder of the guest over two different positions is not illustrated. Only van der Waals contacts occur between host and guest atoms. Colors: gray, carbon; white, hydrogen; red, oxygen; blue, fluorine; and yellow, bromine.

Table 1. Inclusion compounds of **1** with selected guest compounds, guest boiling points (b.p.), and hexagonal unit cell parameters.

No.	Complex	Guest b.p. ($^\circ\text{C}$)	a (\AA)	c (\AA)
—	2*	—	14.3443	18.6271
3	$2 \cdot \text{CCl}_4$	76.8	14.5923	18.3862
4 (15)	$2 \cdot \text{CHCl}_3$	61.2	14.6975	17.9534
5 (14)	$2 \cdot \text{CH}_2\text{Cl}_2$	39.8	14.698	17.99
6	$2 \cdot \text{CFCl}_3$	23.7	14.6369	18.2454
7	$2 \cdot \text{CF}_2\text{ClBr}$	—4	14.6432	18.2357
8	$2 \cdot \text{CF}_3\text{CH}_2\text{F}$	—15	14.6401	18.2204
9	$2 \cdot \text{CF}_3\text{Br}$	—57.7	14.4878	18.2273
10	$2 \cdot \text{C}_2\text{F}_6$	—78.2	14.6474	18.1957
11	$2 \cdot \text{CF}_4$	—127.9	14.6153	18.2847
12	$2 \cdot (\text{CH}_4)_2$	—160	14.5991	18.2832

*Pure **1** obtained by sublimation at 300°C under vacuum.

We attribute the high thermal stability of the hcp inclusion compounds [$(T_{\text{on}} - T_{\text{b}})$: $2\cdot\text{CF}_3\text{Br}$, 260°C ; $2\cdot\text{CF}_4$, 370°C ; $2\cdot\text{CH}_4$, 320°C] to the host lattice being isomorphous with its pure phase—the host lattice cannot gain much stability by releasing the guest because the initial and final lattices would be identical, even at elevated temperatures. In contrast to the zeolites, the guest cannot easily diffuse through the host lattice because the channels are nonporous.

The stabilization of volatile species in a solid matrix purely by van der Waals forces is not without precedent: An argon inclusion compound of the approximately spherical molecule tetra-*tert*-butyltetrahydrocyclohexane has been reported (20). This complex also crystallizes as a hcp array of host molecules with the argon guest situated in interstitial voids (space group $P6_3/m$, $a = 15.73\text{\AA}$, $c = 13.92\text{\AA}$). However, the complex is only stable below about -50°C . Above this temperature, the guest is released and the host lattice is destroyed. In sharp contrast, we have shown that $2\cdot\text{CF}_4$ is stable up to 240°C . To account for this extreme difference in stability between the two seemingly analogous structures, we carefully examined the host-guest packing modes. The most notable difference between the two inclusion systems is that the guest-containing voids of the argon inclusion compound are formed by periodic dilation of type **a** channels, whereas the type **b** channels are constricted. On the basis of this observation, we propose that, to stabilize highly volatile guests in a hexagonal crystal system, the guest molecules should reside within a void fashioned from a type **b** channel. An approach to designing suitable host matrices based on the principles of crystal engineering would thus involve a judicious choice of host such that its geometry would facilitate enlargement of type **b** channels and shrinking of type **a** channels.

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Conformational Dynamics in a Dipeptide After Single-Mode Vibrational Excitation

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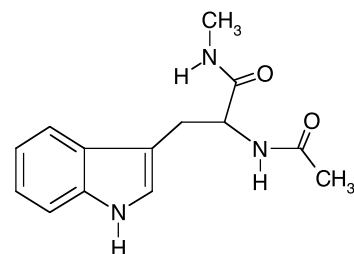
The dynamics of conformational isomerization are explored in a methyl-capped dipeptide, *N*-acetyl-tryptophan methyl amide (NATMA), using infrared-ultraviolet (IR-UV) hole-filling and IR-induced population transfer spectroscopies. IR radiation selectively excites individual NH stretch vibrational fundamentals of single conformations of the molecule in the early portions of a gas-phase expansion, and then this excited population is collisionally recoiled into its conformational minima for subsequent conformation-specific detection. Efficient isomerization is induced by the IR excitation that redistributes population between the same conformations that have population in the absence of IR excitation. The quantum yields for transfer of the population into the various conformational minima depend uniquely on which conformation is excited and on which NH stretch vibration is excited within a given conformation.

Experimental studies of the mechanisms and dynamics of conformational isomerization in flexible molecules are faced with very different tasks, depending on the size of the molecule of interest. In the simplest case, two conformational minima are separated by a single transition state involving motion along a well-defined reaction coordinate (e.g., *cis/trans* isomerization in $\text{XHC}=\text{CHY}$) (1). Large macromolecules undergo conformational change on a potential energy landscape that involves millions of conformational minima and an even greater number of pathways connecting them (2, 3). Between these two extremes lies an interesting size regime in which the conformational landscape exhibits considerable complexity, but selective excitation and detection of single conformations are still possible. Furthermore, precise amounts of energy can be placed in the molecule in well-defined initial vibrations, enabling mode-specific effects to be probed. Here we describe initial results from a laser-based, IR-UV pump-probe method that can be applied with considerable precision to

study conformational isomerization and energy flow in isolated molecules in this intermediate-size regime.

We chose for our initial study *N*-acetyl-tryptophan methyl amide (NATMA), a methyl-capped dipeptide. An exhaustive search of the conformational space of this molecule with the AMBER force field (4) reveals that it has 164 minima connected by 714 transition states (5). There are 65 conformational minima calculated to lie within 40 kJ/mol of the global minimum. The conformational minima of NATMA can be categorized into “families” of structures that share a common dipeptide backbone configuration (6).

The three lowest-energy conformers of



N-acetyl-tryptophan methyl amide, NATMA
Structure 1.

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