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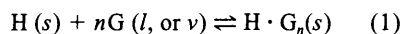
Guest Transport in a Nonporous Organic Solid via Dynamic van der Waals Cooperativity

Jerry L. Atwood,* Leonard J. Barbour,* Agoston Jerga, Brandi L. Schottel

A well-known organic host compound undergoes single-crystal-to-single-crystal phase transitions upon guest uptake and release. Despite a lack of porosity of the material, guest transport through the solid occurs readily until a thermodynamically stable structure is achieved. In order to actively facilitate this dynamic process, the host molecules undergo significant positional and/or orientational rearrangement. This transformation of the host lattice is triggered by weak van der Waals interactions between the molecular components. In order for the material to maintain its macroscopic integrity, extensive cooperativity must exist between the molecules throughout the crystal, such that rearrangement can occur in a well-orchestrated fashion. We demonstrate here that even weak dispersive forces can exert a profound influence over solid-state dynamics.

The assembly of organic molecular crystals is primarily controlled by a variety of intermolecular interactions which, in unison, immobilize the building blocks to form stable arrays (1–6). When these materials are heated beyond their melting or sublimation points, the cohesive forces are overcome, resulting in increased mobility and disorganization of the molecules. The molecules of a solid can also be mobilized by processes such as dissolution and solid-solid phase changes. The latter can occur as a result of physical stimuli (e.g., temperature, pressure, or radiation) or gain or loss of ancillary molecular components. Whereas inclusion of either a liquid or gaseous guest by a solid matrix is a well-known phenomenon, the mechanisms of such processes are poorly understood. This is particularly true for the organic solid state, where transport of the guest through the solid, and subsequent complexation, usually involves concomitant reorganization of the host lattice (7). In all but a few documented cases, guest-induced

lattice rearrangement results in severe fracturing of single crystals into polycrystalline material (8). When fracturing does not occur, structural analysis of the successive solid phases can provide valuable insight into the dynamic processes that prevail. For instance, unambiguous single-crystal-to-single-crystal transformations preclude a mechanism that entails either complete or localized dissolution of one phase with subsequent growth of another (9–11). There have been several reports of monocrystalline host-guest (H-G) inclusion or decomposition reactions of the general type

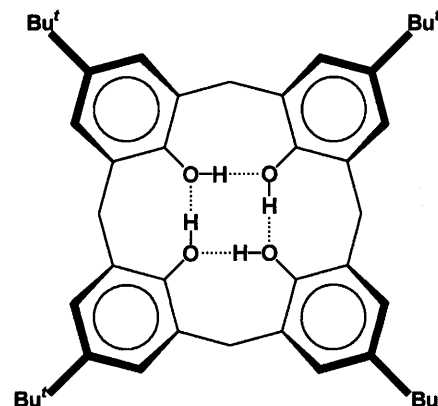


where it can be shown that the host lattice is porous (9, 12–16). In these instances, it is presumed that the structural integrity of the channels is maintained during the transition, and a plausible mechanism thus simply involves diffusion of a highly mobile guest through these channels until a thermodynamically stable host-guest structure is achieved. This implies, therefore, that the design of an organic system for guest uptake should focus primarily on porosity of the host lattice.

We report the structure of a purely organic

solid that does not contain channels, but nevertheless facilitates the diffusion of guest species through its lattice. Furthermore, guest uptake involves a single-crystal-to-single-crystal phase transformation with considerable displacement of the host molecules in two dimensions to give a nonporous inclusion complex. Our results imply that the organic solid state is often much more dynamic than generally believed and that the usually immobile molecules can be reorganized in an orderly fashion by weak dispersive forces.

Crystals of *p*-Bu^t-calix[4]arene (Scheme 1) were prepared by sublimation of **1** at 280°C under reduced pressure. Single-crystal x-ray analysis of the resulting unsolvated form, **1a**, reveals that the calixarene molecules arrange themselves into the well-known bilayer packing motif (17). Pairs of offset, facing calixarene molecules can be loosely described as dimers that form skewed capsules, each with an estimated free volume of 235 Å³. As a result of these relatively large lattice voids, **1a** has a rather low packing efficiency (PE) of 0.59. It should be noted that a polymorphic form of **1**, grown from a tetradecane solution, has recently been published (18). The latter structure, **1b**, consists of a well-packed (PE = 0.67) arrangement of calixarene dimers, where each of the two facing molecules inserts one of its Bu^t groups deep into its neighbor's cavity. Purely organic solid-state frameworks rarely contain substantial lattice voids such as those observed in **1a**. Indeed, the



Scheme 1.

Department of Chemistry, University of Missouri-Columbia, Columbia, MO 65211, USA.

*To whom correspondence should be addressed. E-mail: atwoodj@missouri.edu (J.L.A.); barbourl@missouri.edu (L.J.B.)

molecular arrangement in **1b** demonstrates that **1** is capable of packing quite efficiently in its pure form. The marked disparity in packing efficiency between **1a** and **1b** therefore suggests that **1a** should readily undergo guest inclusion reactions in order to gain further thermodynamic stability.

A single crystal (Fig. 1A) of **1a** was soaked in vinyl bromide at -5°C for 15 min. X-ray diffraction analysis of the still intact crystal (Fig. 1B) confirmed that a single-crystal-to-single-crystal phase transformation had occurred, resulting in a 1:1 H-G complex, **1c**, of **1** and vinyl bromide. Careful inspection of **1a** and **1c** shows that neither structure is porous. Nevertheless, transport of vinyl bromide through the lattice is readily facilitated as a homogeneous process, as evidenced by the unambiguous single-crystal-to-single-crystal transformation that takes place over a period of only 15 min. The significance of such a transformation is that, by virtue of eliminating the possibility of localized dissolution and regrowth (9, 10), a rational mechanism can be postulated with regard to the dynamic guest-induced process by simply comparing the three-dimensional structures of phases **1a** and **1c** (Fig.

2). It should be noted, however, that any such proposed mechanism should still be regarded as being highly speculative.

Phase **1a** crystallizes in the monoclinic system (space group $P112_1/n$) (19) and the calixarene molecules are stacked in an up-down fashion as **abcd** layers along the crystallographic c axis (Fig. 2A). Bilayers **ab** and **cd** each comprise closely-packed calixarene molecules with a stacking interval of 13.12 Å. Both surfaces of each bilayer are lined with Bu' groups, which form bulky protrusions separated by small crevices. Adjacent bilayers are only slightly interdigitated: three Bu' groups of each calixarene nestle into the crevices of an adjacent bilayer surface, whereas the remaining Bu' group is positioned in a gap between several neighboring molecules. Owing to a less constricted environment, the latter is disordered over two positions.

Upon incorporation of vinyl bromide into the calixarene lattice, the bilayer packing motif of **1a** is maintained in the resulting phase **1c** (Fig. 2). Although the relative positions of the calixarene molecules within each bilayer remain essentially unchanged, adjacent bilayers are translated along approximately the $[210]$ direction by 5.9 Å with respect to one another after guest inclusion (Fig. 3). Furthermore, the calixarene molecules of adjacent bilayers maintain their relative orientations within the crystal. The lateral translation of the bilayers results in an overall increase in the crystallographic point-group symmetry from $2/m$ in **1a** to $4/m$ in **1c** as **1**, originally stacked as **ab/cd** bilayers, reorganizes to form **ab/ab** bilayers. Consequently, the c unit cell axis of **1c** (Fig. 2B) is approximately half that of **1a** (Fig. 2A). In **1c**, each host molecule is associated with one molecule of vinyl bromide, and the overall PE is 0.64. The vinyl bromide inserts its $=\text{CH}_2$ moiety deeply into the calixarene cavity, whereas the bromine atom is positioned between the four Bu'

groups. As observed in **1a**, the Bu' groups lining the surfaces of the bilayers nestle into the crevices of adjacent bilayers. Indeed, the spacing of the bilayers in **1a** and **1c** differ by only 0.01 Å, indicating that, upon guest uptake, the bulk crystal expands by just 0.08% along the $[001]$ direction. Comparison of the unit cell dimensions shows that the crystal volume increases by 2.6%. Although the ~ 6 Å shift in the bilayers relative to one another is a large displacement on the molecular scale, this movement of the molecules is not compounded throughout the crystal, i.e., the bilayers can conceivably shift in opposing directions parallel to the (110) plane. These net translations imply that, on the macroscopic scale, the crystal experiences little physical stress during the phase transition process, thus offering a plausible explanation for the retention of its single-crystal character.

In order to gain insight into the mechanism of the phase transition, we conducted a series of vinyl bromide treatment experiments using a crystal of approximate dimensions 0.4 mm by 0.4 mm by 0.2 mm. After exposure to vinyl bromide for 5 min, the crystal retained the guest-free monoclinic structure **1a**. However, a further 5-min exposure resulted in a single crystal containing both phases **1a** and **1c** (20). Therefore, after a total of 10 min of exposure to vinyl bromide, the crystal is trapped in an intermediate stage in the single-crystal-to-single-crystal transformation. Upon exposure to the atmosphere at ambient temperature for 18 hours and with no additional vinyl bromide present, this intermediate crystal completely transformed into the tetragonal phase **1c**. Structure analysis after this 18-hour period shows 60% occupancy of vinyl bromide in the guest pockets. Thus, in the absence of vinyl bromide from the surface of the crystal, the phase transformation continues until the tetragonal structure **1c** is formed. This is

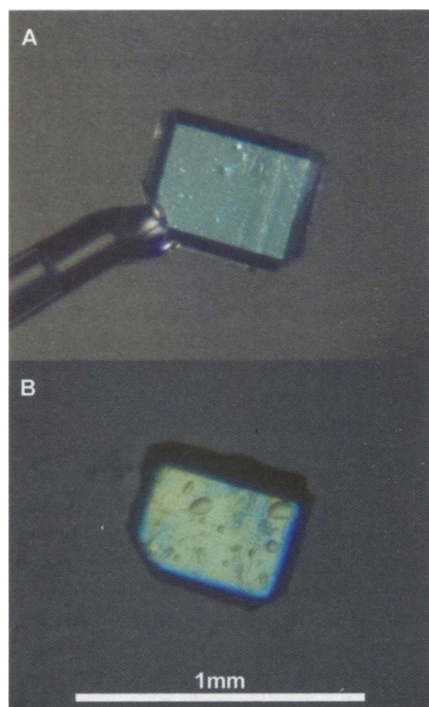


Fig. 1. Guest-induced single-crystal-to-single-crystal phase transformation. After collection of x-ray intensity data at -100°C over a period of 8 hours, a crystal of **1a** (A) was soaked in liquid vinyl bromide at -5°C for 15 min. Infusion of vinyl bromide into the lattice leaves the crystal intact (B), allowing measurement of a second set of intensity data and, thus, determination of the vinyl bromide inclusion complex structure, **1c**. It should be noted that the solubility of **1** in vinyl bromide is very low. The crystal is viewed perpendicular to the planes of the calixarene bilayers. It can be seen that, although the edges of the crystal show some deterioration in (B), the bulk of the material and the planar face have remained largely intact.

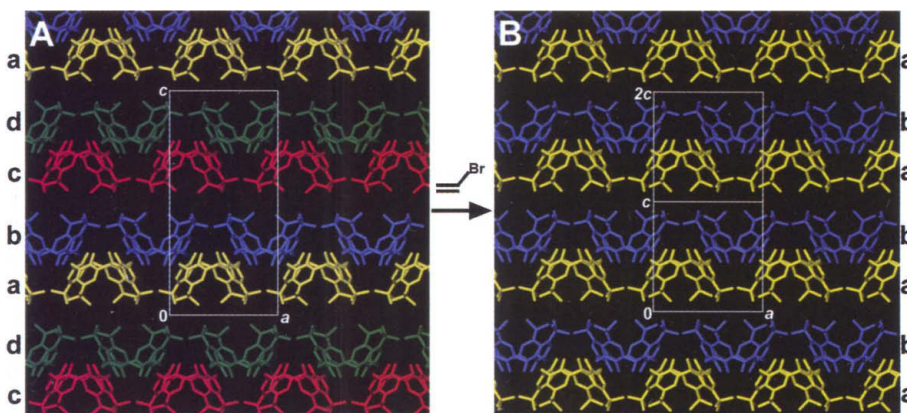


Fig. 2. Differences in packing between **1a** and **1c**; views are shown along the $[010]$ direction. (A) The calixarene molecules pack as repeating layers of type **abcd**. Two distinct bilayers, **ab** and **cd**, can be distinguished. (B) Upon inclusion of vinyl bromide by **1a** to yield **1c**, bilayers **ab** and **cd** have apparently shifted relative to one another. As a consequence of this shift, the space group symmetry of the host lattice is increased from $P112_1/n$ [pseudo-tetragonal, but monoclinic, $a = 12.675(5)$ Å, $b = 12.608(5)$ Å, $c = 25.687(10)$ Å, $\gamma = 90.273(8)^{\circ}$] to $P4/n$ [tetragonal, $a = b = 12.801(3)$ Å, $c = 12.853(6)$ Å], with the calixarene molecules now packing as repeating layers of type **abab**. [Numbers in parentheses indicate the SD of the last digit(s).] The c unit cell axis of **1c** is approximately half that of **1a**.

consistent with the postulate that once the phase transformation has been initiated, the host lattice seeks out the thermodynamically stable commensurate structure, **1c**.

A survey of the Cambridge Crystallographic Database reveals that the host lattice of **1c** is isomorphous with that of the previously reported 1:1 adduct of **1** with toluene, **1d** ($P4/n$, $a = b = 12.604$ Å, $c = 13.871$ Å). All attempts to infuse toluene into **1a** in the manner described above resulted in dissolution of the crystal. When crystals of **1d** were subjected to thermogravimetric analysis, two separate weight-loss events were observed with onset temperatures of 115° and 160°C, respectively, each accounting for half of the total amount of toluene guest. In a subsequent experiment, after heating a crystal of **1d** at 115°C for 25 min, it was found to still be suitable for single-crystal x-ray diffraction analysis. As inferred from the thermal studies, the resulting structure proved to be that of the 2:1 H-G adduct of **1** with toluene, **1e** ($P4/nnc$, $a = b = 12.911$ Å, $c = 25.061$ Å). Detailed comparison of the host lattices of **1d** and **1e** (Fig. 4) reveals that, with respect to the transition from **1a** to **1c**, an even more dramatic shift of the bilayers occurs during the single-crystal-to-single-crystal transformation, when half of the toluene is removed from the 1:1 solvate **1d**. Not only do adjacent **ab/ab** bilayers in **1d** slide along one another by ~9 Å to once again yield a motif of type **ab/cd** in **1e**, but the calixarene molecules are rotated by 38° relative to those of an adjacent bilayer. It should be noted that neither **1d** nor **1e** is porous.

We have shown in detail that *p*-Bu^t-calix[4]arene undergoes several different, but

related, phase transitions upon guest uptake and release. Furthermore, these transitions occur without destruction of the single-crystal character of the lattice on a macroscopic scale (21). Having thus eliminated the possibility of dissolution and regrowth, it is tempting to draw on the unambiguous structural data in order to postulate a plausible mechanism for guest transport through the lattice, and concomitant reorganization of the host molecules. Accordingly, we have attempted to rationalize these processes by considering the initial and final structures, as well as incremental stages along the net vector representing the overall shift of neighboring bilayers with respect to one another. Using this simplistic approach, we were unable to identify any intermediate quasi-crystalline states with the required porosity to allow unconstrained guest diffusion through the crystal. We therefore conclude that the guest transport mechanism must involve a complicated but cooperative process, whereby neighboring host molecules transfer guest molecules to one another without ever forming continuous channels that traverse the structure; that is, the mechanism must involve the active passage of delocalized guest-pockets through the lattice.

Evidently, the host molecules can be immobilized to yield highly stable structures of either the pure material or, in the presence of a suitable guest, an inclusion compound. Equally evident is that the host molecules can be mobilized in response to relatively weak van der Waals interactions with small guest species such as vinyl bromide or toluene. Indeed, during a phase transition, the dynamics of the host lattice must occur as a highly synchronized process whereby neighboring host molecules at

the advancing phase boundary cooperate with one another, not only to relay the guest through the lattice, but also to maintain continuity of the material such that the crystal does not fracture. Therefore, the implication of our observations is that, in the organic solid state, relatively large molecules can demonstrate a surprising degree of mobility involving extensive cooperation between one another, much like the components of a machine.

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19. The nonconventional space group assignment of $P112_1/n$ is used to facilitate direct comparison of the monoclinic (but pseudo-tetragonal) structure of **1a** with the tetragonal structure of **1c**.
20. Intensity data were indexed to yield a tetragonal unit cell of dimensions $a = b = 12.656(4)$ Å, $c = 25.63(1)$ Å. From these data, it was possible to determine the structure of phase **1c** in the space group $P4_2/n$. Using the same set of intensity data, it was also possible to obtain the structure of phase **1a** in the space group $P112_1/n$. Therefore, both phases **1a** and **1c** coexist in the crystal and, owing to their similar unit cell parameters, give rise to overlapping diffraction patterns. Furthermore, both phases are present in sufficient proportions such that the merged diffraction record contains adequate information to allow refinement of either.
21. Several examples of single-crystal-to-single-crystal phase transformations have been reported where guest species undergo polymerization reactions within the solid lattice. See, for example, S. Takahashi et al. [*J. Am. Chem. Soc.* **124**, 10944 (2002)].

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Tables S1 to S15

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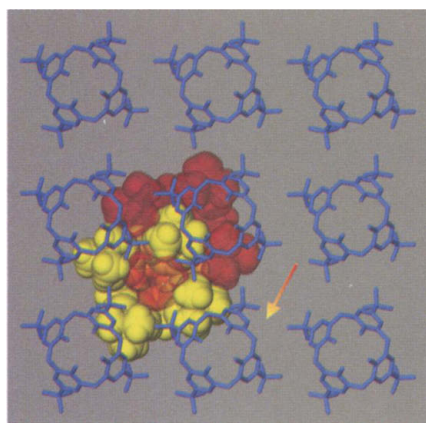


Fig. 3. Partial overlay of structures **1a** and **1c** viewed along the [001] direction. For simplicity, only the blue layer of **ab** is shown (capped-stick representation, hydrogen atoms omitted), as well as one molecule of **1** (space-filled, semi-transparent red for **1a** and yellow for **1c**) from the adjacent bilayer of each phase (Fig. 2). The vector shown represents the net shift of neighboring bilayers **ab/cd** to become **ab/ab** upon transition from **1a** to **1c**.

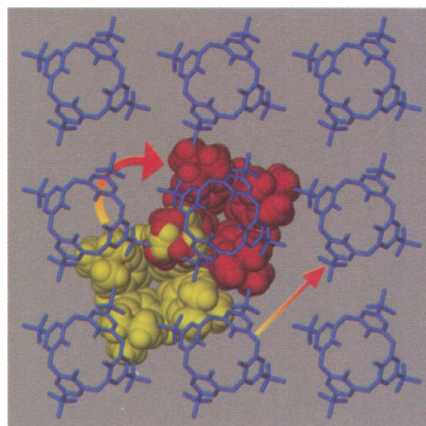


Fig. 4. Partial overlay of structures **1d** and **1e** viewed along the [001] direction. For simplicity, only the blue layer of **ab** is shown (as in Fig. 3), as well as one molecule of **1** (space-filled, yellow for **1d** and red for **1e**) from the adjacent bilayer of each phase. The vector shown (bottom right) represents the net shift by 9 Å of neighboring bilayers **ab/ab** to become **ab/cd** upon transition from **1d** to **1e**. Also indicated (curved arrow) is the rotation of molecules in the lower layer by 38° about their respective C_4 axes during the transformation.