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Frustrated Organic Solids Display Unexpected Gas Sorption

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The search for new materials that have unique properties, such as gas storage and/or separation, is attracting significant attention due to the impending petroleum shortage.[1] Given this fact, physical adsorption of gases on carbon nanotubes (CNTs),[2a] zeolites,[2b−d] activated carbons,[2c] pillared clays,[2c,d] porous metal−organic or covalent organic frameworks (MOFs or COFs, respectively),[2e−i] and "nonporous" organic solids (calixarenes, for example) is currently an active area of research.[2j−p] Of these materials, those with large surface areas, such as MOFs, CNTs, and activated carbons, have attracted much interest, although limited success has been achieved in storing and separating various gases under ambient conditions. Furthermore, in order to activate these materials for gas storage, the guests or solvent molecules housed by the respective molecular frameworks must be completely removed from the host lattice to afford a porous network with maximized sorptive capability. Notably, these "activation" procedures do not (to our knowledge) involve any kind of solid−solid phase transformations.

Solid−solid phase transformations are rather common, and much of the contemporary polymorphism research into pharmaceuticals and other organic materials typically relates to such phase transitions. The term "frustrated" is frequently used with regard to magnetism.[3] Thus organic solids cannot be frustrated with respect to this definition of magnetism. However, in the process of going from a solvated to desolvated form of the "bowl-shaped" host molecule *p*-*tert*-butylcalix[5]arene (TBC5, **1**, Figure 1a),[4] we have discovered a new type of material which we believe involves a frustration of the solvate lattice as it moves toward the thermodynamically stable desolvated state.[5] The frustration arises from a reduction in the solvent content within the structure during the desolvation process and results in the formation of a porous material that rapidly sorbs gases under ambient conditions. Here we present two crystal structures of TBC5 (a toluene solvate and a sublimed/desolvated form) that are both nonporous and that represent two inactive phases that are effectively "dead" with respect to gas sorption. We also show that a porous intermediate phase with partial solvent content, formed through a controlled desolvation process, unexpectedly and rapidly sorbs many gases to varied extents.

Recrystallization of pure TBC5 from toluene results in the formation of large single crystals that are suitable for X-ray diffraction studies.[5] Structural solution reveals that the asymmetric unit is comprised of two independent molecules of TBC5 (Figure 1b, types I and II for clarity), two *endo*-cavity toluene molecules (one in each host), and two disordered *exo*-cavity toluene molecules.[5] Symmetry expansion around the cavity of each TBC5 shows the calixarenes to form two distinctly different structural motifs: two type I TBC5s form a near dimeric capsule arrangement, while two type II TBC5s form a partially overlapped dimer (Figure 1b). In both motifs, the *endo*-cavity toluene molecules interact with the aromatic rings of the hosts through a total of five crystallographically unique CH$\cdots\pi$ interactions, the CH$\cdots$aryl centroid distances for which all lie in the range of 2.571−2.893 Å.[5] Sublimation of pure TBC5 results in the formation of single crystals that are suitable for X-ray diffraction studies.[5] The structural solution shows that the asymmetric unit is comprised of one-half of a TBC5 molecule, and symmetry expansion shows the molecules to pack in a "self-including" manner to form infinite chains (Figure 1c).

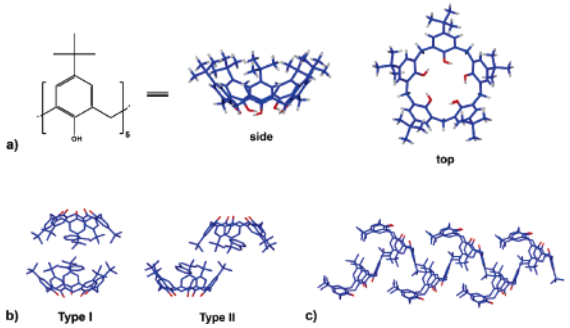

Figure 1. (a) The structure and "bowl-shape" of *p*-*tert*-butylcalix[5]arene. (b) The two types of TBC5 found in the toluene solvate and their respective "near dimeric capsule" and "partially overlapped dimer" arrangements observed upon symmetry expansion. The toluene guest molecules are shown in the centers of the TBC5 hosts. Note that the type I and II arrangements of TBC5 are shown in orientations irrespective to one another within the actual crystal structure; these views are solely for visualization of the behavior of each independent calixarene from the asymmetric unit. (c) The "self-including" chain found in the sublimed form of TBC5. Hydrogen atoms have been omitted, and disordered *tert*-butyl groups of TBC5 molecules (in both structures) are only shown in one position for clarity in (b) and (c). Atom color code: carbon = blue, oxygen = red, hydrogen = gray.

It should be noted that sublimation of TBC5 is troublesome and that much of the starting material is lost due to degradation at high temperature (350 °C under vacuum). Although this is the case, the sublimed form can easily be isolated in bulk by heating a toluene solvate sample to 160 °C overnight, with sample purity/conversion being confirmed by X-ray powder diffraction studies (XRPD).[5] Examination of both the toluene solvate and sublimed TBC5 structures through space filling representation quickly reveals that both are completely nonporous, as shown in Figure 2.[5] Furthermore, when both the solvated and desolvated forms were studied for sorptive capability, both were dead for sorption of O_2, N_2, CH_4, CO_2, and acetylene (Figure 2, left- and right-hand columns).[5]

Careful heating of the TBC5 toluene solvate at 120 °C for 8 h resulted in the formation of material with a partial solvent content (confirmed by NMR spectroscopy) that is consistent with a toluene:TBC5 ratio of 1:23 (compared to 2:1 for the pure solvate form).[5] Unfortunately, this technique afforded opaque material devoid of single crystallinity, thereby precluding the use of single-crystal X-ray diffraction for structural identification purposes. Despite this, XRPD afforded a pattern which has some peaks that are inconsistent with either the toluene solvate or desolvated forms (Figure 2).[5] Gas sorption studies with this material showed remarkably rapid sorptive capability toward CH_4, CO_2, and acetylene, although it is not highly active for H_2 sorption.[5] In comparison with *p*-*tert*-butylcalix[4]arene,

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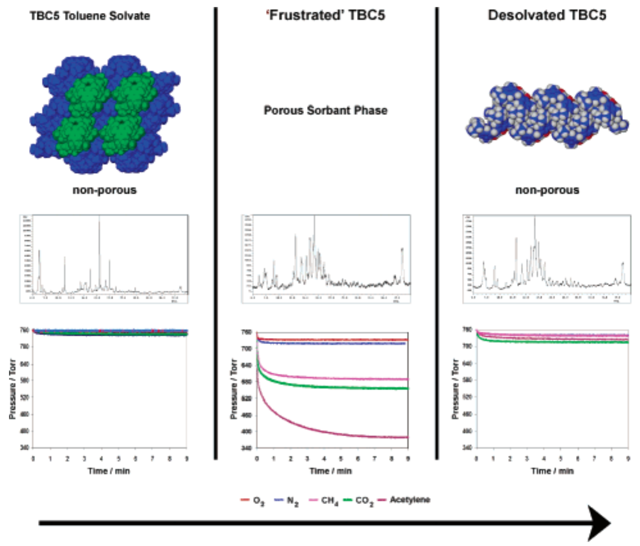

Figure 2. Diagram showing the transition from the nonporous (and inactive) TBC5 toluene solvate, through a porous and rapidly sorbant phase, to the desolvated/sublimed form of TBC5, which is also effectively inactive for sorptive purposes. X-ray powder diffraction patterns are shown for each form, as are the gas sorption curves for O_2, N_2, CH_4, CO_2, and acetylene. The nonporous nature of the toluene solvate is stressed by space filling representation relative to Figure 1b; type I and II TBC5 molecules are shown in green and blue, respectively, for clarity. Similar depiction of the desolvated form also demonstrates complete nonporosity.[5]

a “seemingly nonporous” material, acetylene sorption with this active form of TBC5 is ∼75% as efficient.[2p] However, the rate of acetylene sorption is 25 times faster than that of TBC4. This relationship is also generally true when comparing methane and carbon dioxide sorption between the two calixarenes; that is, the amount of gas sorbed is consistently less for this form of TBC5, but the rate of sorption is far greater. Notably, the powder patterns of the frustrated and desolvated phases have some similarities (Figure 2). This suggests that the frustrated phase may be partially composed of the desolvated form while also containing a proportion of active material.

Solid-state ^{13}C NMR spectroscopy performed on samples subjected to 1 atm pressure of CH_4, CO_2, or acetylene gave further proof of the porous nature of the intermediate phase.[5] Methane and carbon dioxide were not retained by the material when removed from the corresponding atmospheres, and their respective spectra resembled that of purely frustrated TBC5. Acetylene *was* retained by frustrated TBC5 and gave a characteristic signal at ∼71 ppm, which is close to that of the gas adsorbed in a porous zeolite framework.[5,6] These cases are markedly different to those concerning the sorption of these gases in seemingly nonporous TBC4, the studies for which show dramatically different guest shifts in the solid-state NMR spectra. In particular, the lack of gas retention (CH_4 and CO_2) and the chemical shift of the sorbed acetylene signal all suggest that the frustrated TBC5 phase *is* porous.

Further heating of the active frustrated phase at 160 °C results in conversion to the desolvated form (identifiable by XRPD) with a concomitant halt in sorption for the gases studied here. This phase conversion suggests that perhaps residual toluene molecules hold the extended structure in a frustrated arrangement that is incapable of full collapse into the self-including chains of the desolvated form.

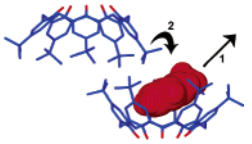

Figure 3. A proposed method for collapse of the “frustrated” organic solid: (1) final evaporation of the last remaining toluene molecules, possibly retained due to strong intermolecular CH···π interactions,[5] results in an opening for structural collapse; (2) the TBC5 molecules can collapse into the fully evacuated cavities, possibly forming a cascade process from which the desolvated “self-including” chains result.

Removal of these residual (and strongly bound[5]) solvent molecules may facilitate such a collapse, which in turn may be followed by a cascade process that results in a complete structural rearrangement to the desolvated form (Figure 3).

Clearly the active frustrated region for TBC5 represents an entire range of partial desolvates that need to be isolated, identified, and studied for gas sorption properties. The fact that the XRPD of one active phase (reported here) contains peaks for the desolvated form suggests that perhaps only a percentage of the material studied is indeed active for sorption. If this is the case, and the percentage is small, it is plausible that greatly enhanced gas sorption may be found for a pure sample of the active form.

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Supporting Information Available: Materials and experimental methods, solid-state ^{13}C NMR spectra, crystal data, full structural descriptions for the crystal structures of TBC5·toluene and sublimed TBC5, description of CH···π interactions, and additional views of the nonporous nature of both crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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