Inclusion Compounds

Isolation and Structure of an "Imploded" Cryptophane**

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Molecules and molecular assemblies of effectively closed-shell topologies have been the subject of much contemporary interest because of their ability to encapsulate smaller molecular substrates.[1,2] The cavity interiors have been used for a number of remarkable applications, including for enantioselective recognition,[3] for stabilizing and characterizing reactive species,[4] as microreaction chambers,[5] and to demonstrate new forms of stereoisomerism.[6] The unique properties of the so-called container molecules or capsules stem directly from their ability to bind guests constrictively.[7] That is, the nearly closed surfaces of molecular containers provide comparatively large steric barriers to the ingress and egress of guests.The resulting complexes experience a corresponding enhancement in their kinetic stabilities, thus allowing encapsulation phenomena to be studied in detail. We have initiated a program aimed at tuning the thermal stabilities of materials generally derived from container molecules, one future goal of which is the synthesis of novel microporous materials with potential uses for gas storage or small-molecule separations. Our hypothesis is that, relative to traditional clathrates and solid-state inclusion compounds, those materials constructed from container-like molecules ought to exhibit appreciable kinetic stabilities with respect to the thermal loss of encapsulated guests. This feature augurs well for gas separation or storage applications, and organic materials possessing empty voids for such purposes are emerging.[8]

Collet's elegant cryptophanes,[1] constructed by the covalent bridging of two cuplike C_3-substituted cyclotribenzylenes (CTBs), are quintessential molecular containers. They typically encapsulate guests constrictively, with constrictive binding energies (that is, the activation energies of complexation, $\Delta G_c^{\pm}$) in excess of about 40 kJ mol^{-1}.[1,9] Furthermore, they display an impressive ability to bind and discriminate between guests on the basis of size, shape, and electronic characteristics in both hydrophilic and lipophilic solvents. We report

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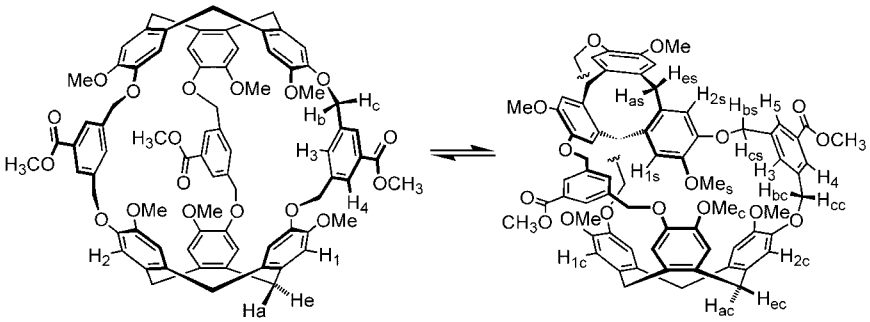
[**] This work was supported by Georgetown University and by the National Science Foundation CAREER award program (DMR-0349316). S.T.M. thanks the Metropolitan Washington section of the Achievement Rewards for College Scientists for financial support.

Supporting information for this article (experimental details, including synthetic procedures, kinetic data, and 2D NMR spectra) is available on the WWW under http://www.angewandte.org or from the author.

 DOI: 10.1002/ange.200460866

herein the synthesis of a new *exo*-ester-functionalized *m*-xylyl-bridged cryptophane[10] (±)-*anti*-**1** (Scheme 1) and the structure and thermal behavior of its crystalline inclusion compound with tetrahydrofuran (THF). Our studies reveal



anti-**1**
pseudo-D_3

imp-**1**
C_1, C_3(avg.)

Scheme 1.

that, once emptied, the cryptophane containers equilibrate between "empty" and "imploded" conformers at high temperatures in the solid state, the latter of which is a kinetically stable atropisomer that has been isolated and structurally characterized.

Cryptophane (±)-*anti*-**1** was synthesized in racemic form (10–12% yield) by the formic acid catalyzed cyclization of the appropriate bis(vanillyl alcohol) precursor according to the two-step method developed by Canceill and Collet.[11] Separation of (±)-*anti*-**1** from the lower-yielded *syn* diastereomer was readily accomplished by flash chromatography. Dissolution of crude (±)-*anti*-**1** in tetrahydrofuran results in the precipitation of crystalline racemic [(±)-*anti*-**1**⊃thf]·3 THF over a period of a few minutes. The single-crystal structure reveals, as expected, one thf molecule to be centrally located within the cryptophane molecular cavity.[12] A space-filling representation illustrates the encapsulation of this guest (Figure 1). In the solid state, the host cryptophane deviates significantly from the idealized D_3 symmetry observed in solution. Eleven of the twelve OCH_3 and OCH_2 groups are roughly in plane with the aromatic rings of the CTB cups, although differences in the C(cup)-O-C-C(xylyl) dihedral angles result in the skewed conformation depicted in Figure 1. Although some positional disorder is evident, the major orientation of the encapsulated THF molecule shows the oxygen atom to be located near the xylyl-guarded portals of the cryptophane and in close contact to the inwardly directed arene and methylenic CH moieties.

Crystalline [(±)-*anti*-**1**⊃thf]·3 THF loses THF spontaneously under ambient conditions, but guest loss does not go to completion. Thermogravimetric analysis (TGA) of freshly prepared material shows that THF loss occurs in at least two steps and also that high temperatures are required to remove all of the included solvent (Figure 2). Indeed, if [(±)-*anti*-**1**⊃thf]·3 THF is left under ambient conditions for several days, or heated at 85 °C for over ten hours, THF loss occurs only to the extent of exactly three equivalents and a 1:1 [(±)-*anti*-**1**⊃thf] material can be isolated. TGA confirms the 1:1 stoichiometry (5.2% found, 5.3% calcd) and illustrates the remarkable kinetic stability of this material. Whereas the onset temperature for THF loss from [(±)-*anti*-**1**⊃thf]·3 THF is below room temperature, the onset temperature for [(±)-*anti*-**1**⊃thf] is over 100 °C—more than 35° above the normal boiling point of THF—and we surmise that the structure of [(±)-*anti*-**1**⊃thf] consists of cryptophane container molecules essentially fully occupied with a guest. Molecular models of (±)-*anti*-**1** reveal that the *m*-xylyl bridges cannot readily fill the cryptophane cavity; thus, it seems reasonable to infer that the glassy, guest-free (±)-*anti*-**1** material possesses empty cryptophane cavities in the solid state.

The ^{1}H NMR spectrum of [(±)-*anti*-**1**⊃thf] dissolved in $CDCl_3$ is uncomplicated and illustrates the pseudo-D_3 symmetry of the cryptophane (Figure 3a). Doublet resonances centered at $\delta = 4.59$ and 3.33 ppm are characteristic of the axial and equatorial (H_a, H_e) methylenic protons at the lower rim of CTBs in the cup conformation (Scheme 1), the former being shifted significantly downfield as a result of steric crowding at the base of the cup ($H_a \cdots H_a \approx 2.0$ Å). Remarkably, complete emptying of the cryptophanes by

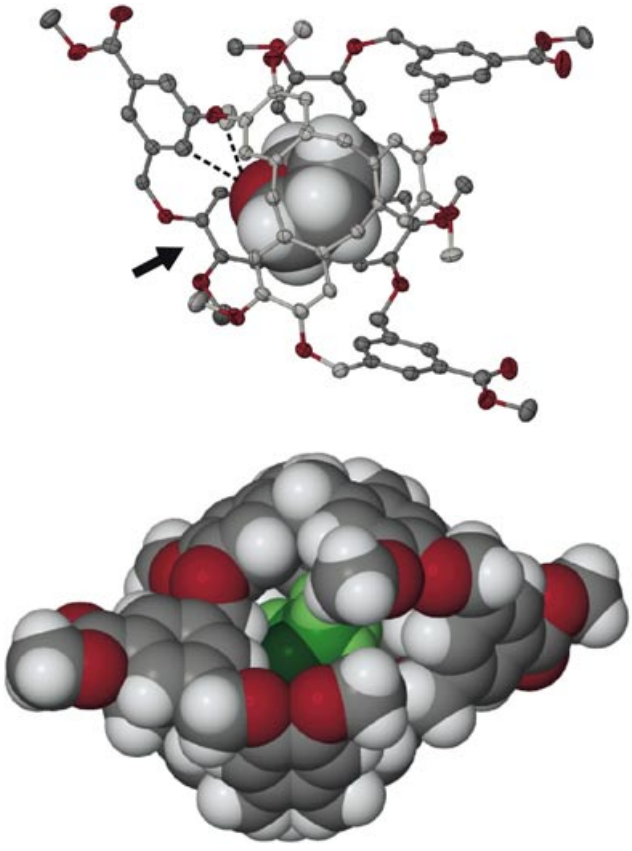


Figure 1. ORTEP (top) and space-filling (bottom) representations of the [(±)-*anti*-**1**⊃thf] complex observed in the single-crystal structure of [(±)-*anti*-**1**⊃thf]·3 THF. The arrow shows the view taken for the space-filling illustration. In the bottom image, atoms corresponding to the THF molecule are shaded green for clarity.

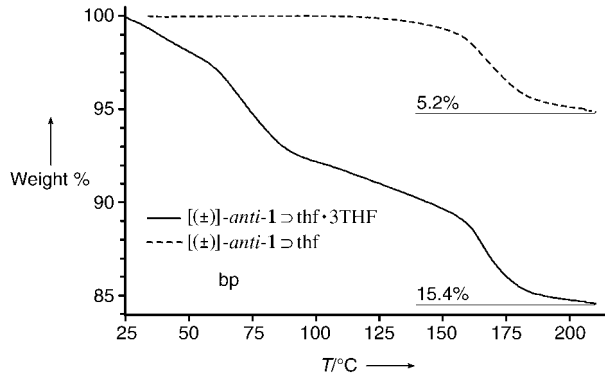


Figure 2. TGA (5 °C min^{-1}) of [(±)-*anti*-**1**⊃thf]·3THF (15.4% found, 18.4% calcd) and [*anti*-**1**⊃thf] (5.2% found, 5.3% calcd) illustrating the enhanced kinetic stability of encapsulated versus lattice-included guests.

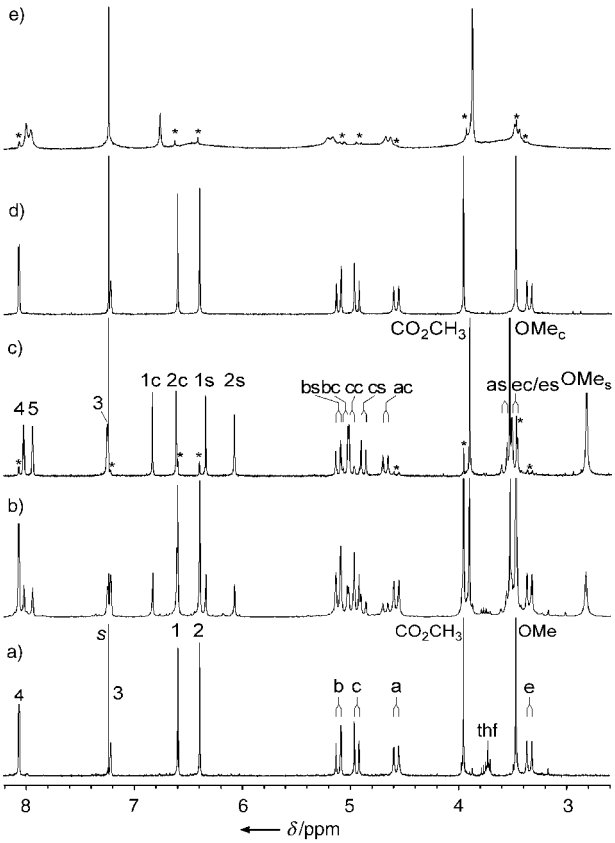


Figure 3. ^{1}H NMR spectra (300 MHz, $CDCl_3$, 298 K unless noted otherwise) of: a) [(±)-*anti*-**1**⊃thf]; b) "emptied" (±)-*anti*-**1** immediately following thermogravimetry of (±)-*anti*-**1**⊃thf] to 210 °C; c) purified (±)-*imp*-**1**; d) the same sample as in (c), but after 3 days at ambient temperature; e) the same sample as in (c), but at −55 °C. Signal assignments are according to Scheme 1 (cup = H_{-c}, saddle-twist = H_{-s}, ⋆ = trace (±)-*anti*-**1**) and are supported by 2D ROESY and COSY experiments (see Supporting Information).

thermogravimetry at 210 °C results in approximately 40% conversion of (±)-*anti*-**1** into a species with a different spectroscopic signature (Figure 3b). Separation of this species from residual (±)-*anti*-**1** has been accomplished by preparative TLC (silica gel, CH_2Cl_2/Et_2O 8:1, $R_f = 0.36$ and 0.43, respectively). The ^{1}H NMR spectrum of the purified compound taken in $CDCl_3$ at room temperature is consistent with a loss of the C_2 rotation axes and a reduction to an apparent C_3 symmetry, which symbolizes an inequivalence of the CTB moieties (Figure 3c). The ^{1}H NMR spectrum observed in Figure 3c reverts cleanly to the original spectrum of (±)-*anti*-**1** on standing of the sample in $CDCl_3$ or other solvents (Figure 3d), thus implying that the newly formed species possesses the same atomic connectivity and is merely an atropisomer of (±)-*anti*-**1**. Collet and co-workers previously observed that other cryptophanes give rise to spectral characteristics very similar to those seen in Figure 3b.[1a,13] It was proposed that the apparently C_3-symmetric species is an effectively imploded "in-out" cup-within-cup conformer wherein one of the two CTB cups is completely inverted.

Purification of the "imploded" atropisomer of (±)-*anti*-**1** (hereafter (±)-*imp*-**1**) allows for detailed ^{1}H NMR spectral characterization, with peak assignments supported by 2D COSY and ROESY experiments. Although the 1D spectrum recorded at room temperature clearly exhibits a time-averaged C_3 symmetry, two notable features are seemingly at odds with the assignment of (±)-*imp*-**1** as an "in-out" cup-within-cup structure: 1) of the two sets of H_a/H_e protons ascribed to the methylenic bridges of the orthocyclophane moieties, one set does not display the approximately 1.2 ppm chemical shift difference characteristic of a cuplike conformation ($\Delta\delta = 0.14$ ppm), and 2) of the two unique methoxy signals one is significantly broadened and shifted upfield by approximately −0.65 ppm relative to that of (±)-*anti*-**1**—this observation suggests dynamic behavior and a shielded environment for the methoxy groups.

Single crystals of (±)-*imp*-**1**·11 $CHCl_3$ were obtained by vapor diffusion of *n*-pentane into a solution of purified (±)-*imp*-**1** in $CHCl_3$ at −20 °C.[12] Although the data set is of poor quality because of the presence of 11 equivalents of partially disordered solvent, X-ray analysis confirms that (±)-*imp*-**1** is indeed an atropisomer of (±)-*anti*-**1**, but not the "in-out" cup-within-cup form. As seen in Figure 4, *imp*-**1** adopts a C_1 conformation. One of the two CTB moieties maintains the cup conformation whereas the other exists in the so-called saddle-twist conformation, whereby one of the three methylenic groups is inverted inwardly though the intrannular ring. In the crystal, the center of mass of the saddle-twisted CTB is significantly offset from that of the cup-shaped one such that one of the twisted arene rings is able to project its methoxy substituent into the cup, thereby filling the cryptophane cavity. (±)-*Imp*-**1** thus represents the first observation of the saddle-twist form of a CTB congener wherein the cup form has not been specifically destabilized by substitution.[1b]

The X-ray structure (±)-*imp*-**1** is consistent with the known conformational behavior of CTBs. The rate-determining step for cup-to-cup interconversion in CTBs is the intrannular flipping of the first methylenic group, with a barrier of $\Delta G^{\ddagger}_{298K} = 110$–115 kJ mol^{-1} for all known examples.[1] The resulting highly flexible saddle-twist form—which can revert either to the original or the inverted-cup configuration—is typically 13–16 kJ mol^{-1} higher in energy than the cup form, thus implying that the barrier to conversion from the saddle-twist form into the cup form is in the range 94–

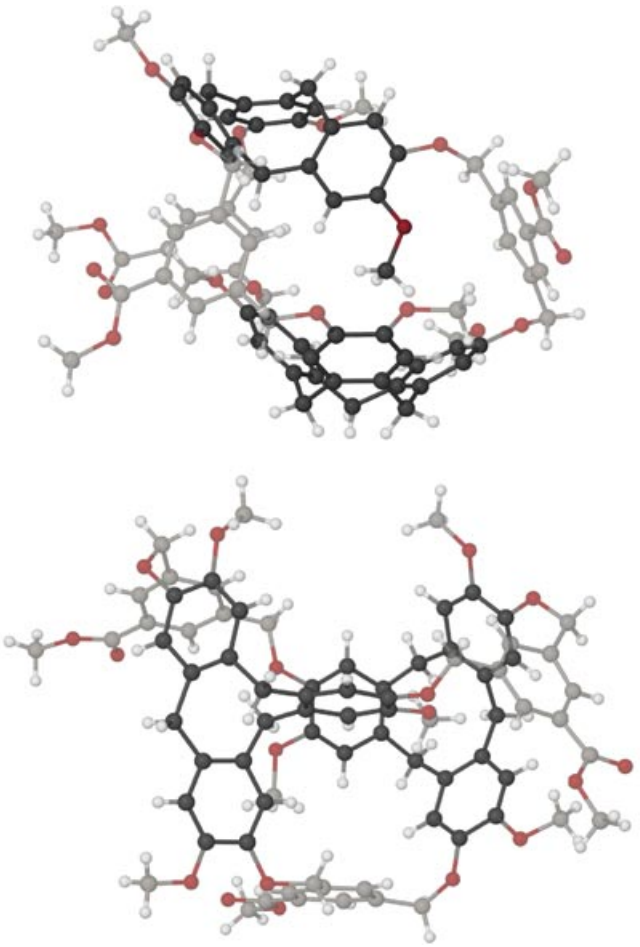


Figure 4. Two views of the imploded cryptophane *imp*-**1** as determined by the single-crystal structure of (±)-*imp*-**1**·11 $CHCl_3$. The carbon atoms of the CTB rings are shaded dark for clarity.

102 kJ mol^{-1}. These facts are consistent with rate studies which indicate that reversion of (±)-*imp*-**1** to (±)-*anti*-**1** in $CDCl_3$ follows first order kinetics with an energy barrier of $\Delta G^{\pm}_{298K} = 99(3)$ kJ mol^{-1} ($\Delta H^{\pm}_{298K} = 70(3)$ kJ mol^{-1} and $\Delta S^{\pm} = -98(5)$ J mol^{-1} K^{-1}). Moreover, the measured energy barrier is considerably lower than what would be expected for a cup-within-cup conformer. Furthermore, the saddle-twist structure of (±)-*imp*-**1** allows for rationalization of the aforementioned ^{1}H NMR spectral peculiarities and signal assignments (Figure 3c). Specifically, relative to the cup conformation, the highly flexible saddle-twist conformer relieves steric congestion between the H_{as} protons at the base of the CTB moiety, and the result is a smaller difference in chemical shift between H_{as} and H_{es}. Additionally, the known conformational flexibility of the saddle-twist form is consistent with the observed time-averaged C_3 symmetry of (±)-*imp*-**1** in the ^{1}H NMR spectrum recorded at room temperature.[1b] The C_1 conformer apparently interconverts rapidly with two equivalent C_1 forms, presumably via readily accessible saddle-twist forms wherein two of the three methylenic groups are flipped. The process is akin to a chiral propeller-like motion, such that the methoxy groups of each ring spend an equal amount of time projected into the cavity of the lower CTB cup, thus inducing an upfield shift of the signals ($\Delta\delta = -0.65$ ppm). The time-averaged upfield shift is consistent with the large induced shifts (up to −4.5 ppm) that are commonly observed for guests encapsulated within the electronic-rich cavities of other cryptophanes.[1] Cooling of the sample results in dramatic broadening of the signals as the rate of conversion between the C_1 conformers is slowed (Figure 3e). Nonetheless, even at −60 °C in $CDCl_3$, the signals corresponding to a frozen C_1 conformer are unresolved and the energy barrier for conversion between the saddle-twist forms was not determined.

In summary, we have synthesized a new *m*-xylyl-bridged cryptophane, (±)-*anti*-**1**. The thermal behavior of its crystalline inclusion compound with tetrahydrofuran illustrates that encapsulated guests are held onto more strongly than those in the lattice, presumably as a consequence of encapsulation. Complete thermal liberation of the guests results in (±)-*anti*-**1** partially undergoing a conformational "implosion" to form the isolable atropisomer (±)-*imp*-**1**, wherein one of the CTB moieties of the cryptophane exists in the saddle-twist conformation. These results have implications in the study of molecular-encapsulation phenomena and also for the design of guest-free container-molecule-based materials, the unique sorption and storage properties of which we are currently examining.

Received: June 4, 2004

Keywords: atropisomerism · cryptophanes · host–guest systems · inclusion compounds

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[12] Single crystal structure of racemic [±-*anti*-**1**]⊃thf·3THF: $C_{94}H_{104}O_{22}$, $0.48\times0.45\times0.40$ mm, monoclinic, space group $P2_1/n$, $a=20.233(2)$, $b=18.070(2)$, $c=23.638(2)$ Å, $\beta=108.474(2)°$, $V=8196.6(14)$ Å^3, $Z=4$, $\rho_{calcd}=1.285$ g cm^{-3}, $Mo_{K\alpha}$ radiation, $\lambda=0.71073$ Å, $2\theta_{max}=50°$, ω scans, 173(2) K, 52817 total reflections, 14430 unique reflections, 7507 reflections with $I>2\sigma(I)$ ($R_{int}=0.0753$); absorption correction SADABS ($T_{min}=0.9577$, $T_{max}=0.9646$, $\mu=0.09$ mm^{-1}), structure solution using SHELXS, refinement (against $|F^2|$) with SHELX-97-2, 1090 parameters, 0 restraints, H atoms placed in calculated positions and refined with a riding model, $R_1=0.0650$ ($I>2\sigma(I)$) and $wR_2=0.1785$ (all data), residual electron density max./min. = 0.55/−0.35 e^- Å^{-3}, GOF = 0.966. Single-crystal structure of racemic *imp*-**1**·11 $CHCl_3$: $C_{89}H_{83}O_{36}Cl_{33}$, $0.56\times0.32\times0.12$ mm, triclinic, space group $P\bar{1}$, $a=14.094(5)$, $b=16.361(5)$, $c=26.247(8)$ Å, $\alpha=103.372(5)$, $\beta=101.191(5)$, $\gamma=104.318(5)°$, $V=5499(3)$ Å^3, $Z=2$, $\rho_{calcd}=1.577$ g cm^{-3}, $Mo_{K\alpha}$ radiation, $\lambda=0.71073$ Å, $2\theta_{max}=45°$, ω scans, 183(2) K, 31876 total reflections, 14293 unique reflections, 7834 reflections with $I>2\sigma(I)$ ($R_{int}=0.0835$); absorption correction SADABS ($T_{min}=0.6403$, $T_{max}=0.9024$, $\mu=0.874$ mm^{-1}), structure solution with SHELXS, refinement (against $|F^2|$) using SHELX-97-2, 1419 parameters, 0 restraints, H atoms placed in calculated positions on ordered moieties and refined with a riding model, $R_1=0.1309$ ($I>2\sigma(I)$) and $wR_2=0.3400$ (all data), residual electron density max./min. = 0.76/−0.93 e^- Å^{-3}, GOF = 1.060. The relatively high values of the merging and final R factors are directly attributed to the presence of a large number of highly disordered solvent molecules and unavoidable partial decomposition of the sample on transfer to the low-temperature stream. Disordered chloroform molecules are modeled as partial occupancy carbon and chlorine atoms. The stoichiometry of the crystal was estimated by using the SQUEEZE subroutine of the program PLATON,[14] which estimates the solvent-accessible volume of 2738 Å^3 (50% of the unit cell) to be occupied by 1239 electrons (calcd 10.7 equivalents $CHCl_3$). The program X-Seed[15] was used as a graphical interface to SHELX and for the generation of figures. CCDC-239970 and 240116 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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