

## Shell Closures of Tetrabenzyl Chloride Cavitands with Tetrabenzylthiol Cavitands Provide Carceplexes in which One or Two Guest Molecules are Incarcerated

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Carceplexes form with high structural recognition of their incarcerated guests (2MeOH, MeCN, 2MeCN, EtOH, Me<sub>2</sub>NCHO, MeCOEt, or Et<sub>2</sub>CO); the physical properties of these complexes depend on the structures of both host and guest.

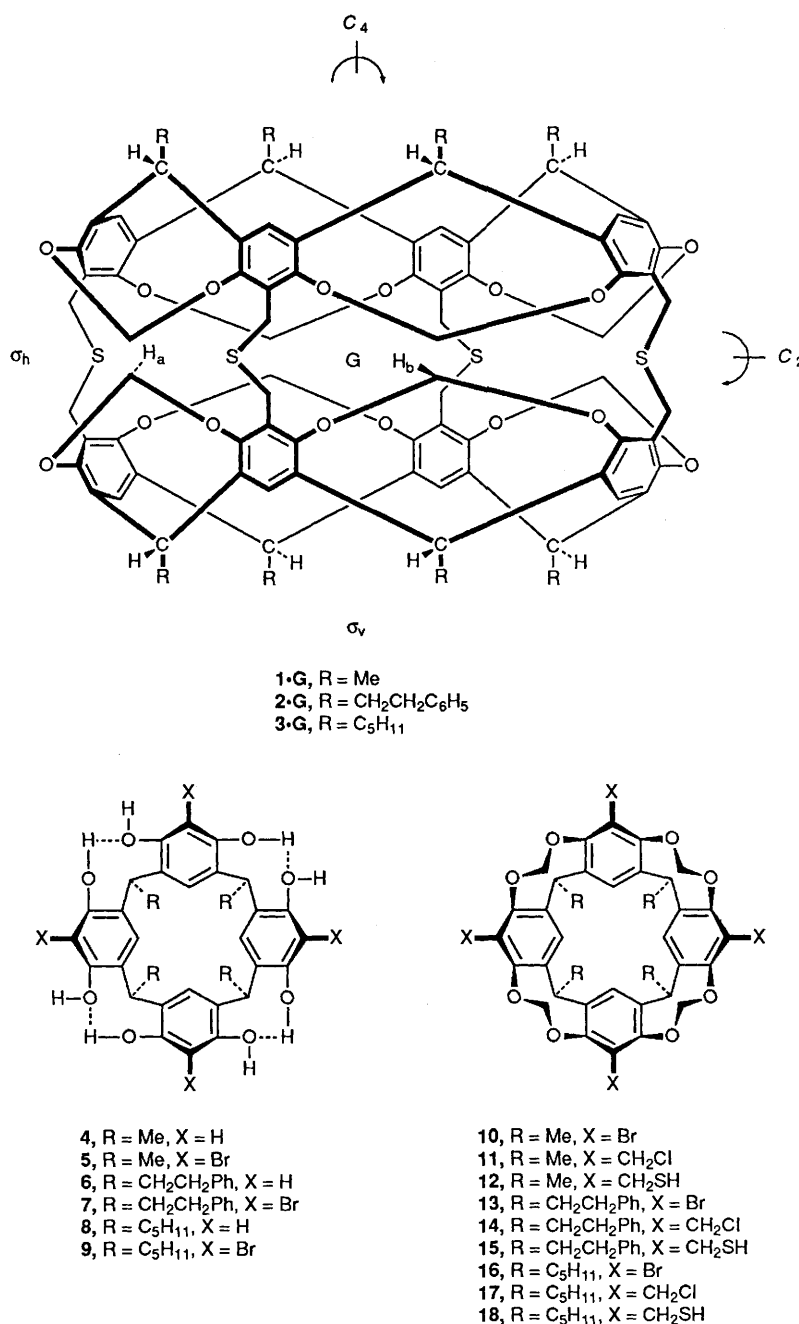
Previously, we reported the first carceplexes **1**·**G** as insoluble solids with enforced hollow interiors containing solvent, Cs<sup>+</sup> and/or argon.<sup>1</sup> Later, a new family of soluble carceplexes was prepared that is identical to **2**·**G** except that four OCH<sub>2</sub>O groups linked the 'northern' and 'southern' hemispheres in place of the four CH<sub>2</sub>SCH<sub>2</sub> groups of **2**.

Here we report the syntheses and characterization of seven carceplexes of structures **2**·**G** or **3**·**G**. The syntheses of which closely follow reported procedures for **4** → **5** → **10** → **11** → **12** → **1**·**G**,<sup>1</sup> and for **6** → **7** → **13**.<sup>2</sup> The reaction sequences, **13** → **14** → **15** and **8**<sup>3</sup> → **9** → **16** → **17** → **18** went in 40 and 12% overall yields, respectively.† The crucial shell closures were run at moderately high dilution with alkali-metal carbonates as base in solvents we wished to incarcerate (20–32% yields). Each carceplex (except **2**·2MeCN) was purified by chromatography, and gave elemental analyses (C, H, O, S and N when present) individually within 0.3% of theory, and which collectively varied from 99.75 to 100.24%. An attempted run

in C<sub>6</sub>H<sub>6</sub> gave no **3**·C<sub>6</sub>H<sub>6</sub>. The runs leading to **2**·2MeOH, **2**·MeCN, or **3**·EtOH made in 1:1 (v) MeOH–C<sub>6</sub>H<sub>6</sub>, 1:1 (v), MeCN–C<sub>6</sub>H<sub>6</sub>, or 1:1 (v) EtOH–C<sub>6</sub>H<sub>6</sub>, respectively, gave no carceplex containing C<sub>6</sub>H<sub>6</sub>, although molecular models (Corey–Pauling–Koltun) of **2**·C<sub>6</sub>H<sub>6</sub> or **3**·C<sub>6</sub>H<sub>6</sub> are easily assembled. The absence of such products is interpreted as being an artifact of the S<sub>N</sub>2 transition states requiring stabilization by polar solvents in the medium. The run made in MeCN–C<sub>6</sub>H<sub>6</sub> led to a 1.2:1.0 mixture of **2**·2MeCN to **2**·MeCN (<sup>1</sup>H NMR) which was converted to **2**·MeCN by heating (110 °C for 72 h in MeC<sub>6</sub>H<sub>5</sub>, <sup>1</sup>H NMR). The DCI MS spectra (Me<sub>3</sub>C<sup>+</sup> bombardment)<sup>4</sup> of each carceplex (except **2**·2CH<sub>3</sub>CN) gave the parent as the most abundant ion in both the positive and negative modes except for **2**·MeCN, which provided in the negative mode a substantial M<sup>+</sup> signal, which was not the base peak.

The 500 MHz <sup>1</sup>H NMR spectra of the seven carceplexes in CDCl<sub>3</sub> at 25 °C provided interesting structural information. Proton counting of host and guest confirmed the absence of empty host, and corroborated host–guest ratios derived from elemental analyses and mass spectra. In molecular models, **2** and **3** have a long polar C<sub>4</sub> axis and four shorter equatorial C<sub>2</sub>

† These new compounds gave C and H elemental analyses within 0.30% of theory, mass spectra with strong M + H<sup>+</sup> peaks and the expected <sup>1</sup>H NMR spectra.



axes, four  $\sigma_v$  and one  $\sigma_h$  mirror planes (overall  $D_{4h}$  symmetry). The chemical shifts of the  $H_a$  and  $H_b$  carcerand signals are guest-sensitive, and their multiplicities indicate which rotations of the guest relative to the host are slow and which are fast on the  $^1\text{H}$  NMR time scale. The chemical shifts of the guest hydrogens provide information about whether their protons are located in the strongly shielding 'temperate' or weakly shielding 'torrid' zones of the global hosts.

The spectrum of 3-MeCOEt gave two kinds of  $H_a$  and  $H_b$  signals, indicating that the guests are rotating rapidly around the long polar axis of the host (coincident to the long guest axis), but not about the shorter equatorial axes. The spectrum of 3-EtCOEt gives only one pattern of  $H_a$  and  $H_b$  signals. The EtCOEt guest is like-ended, and its long axis must be coincident with the long polar axes around which this guest must rotate rapidly. Since EtCOEt is a longer molecule than

MeCOEt, rotation of the former about the host's shorter equatorial axes must also be slow or non-existent. The spectra of the other carcerplexes each contain only one  $H_a$  and  $H_b$  pattern, suggesting that the guests are rotating rapidly on the  $^1\text{H}$  NMR time scale around both the equatorial and polar axes. This interpretation is consistent with expectations based on molecular model examinations.

The guest-proton signals moved 1–4 ppm upfield from their normal positions. For example, the  $\text{CH}_3$  signals'  $\delta$  values were: 2-2 $\text{CH}_3\text{OH}$ ,  $-0.75$ ; 2- $\text{CH}_3\text{CN}$ ,  $-1.64$ ; 2-2 $\text{CH}_3\text{CN}$ ,  $-2.16$ ; 3- $\text{CH}_3\text{CH}_2\text{OH}$ ,  $-1.18$ ; 3-( $\text{CH}_3$ ) $_2\text{NCHO}$ ,  $-0.10$  and  $-0.33$ ; 3- $\text{CH}_3\text{CH}_2\text{COCH}_3$ ,  $-1.94$  and  $-3.08$ ; 3- $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$ ,  $-3.39$ . The fact that the protons of 2-2 $\text{CH}_3\text{CN}$  occur at higher field than 2- $\text{CH}_3\text{CN}$  suggests that the two methyl groups of the former are located in the temperate zones of the host in a dimeric structure 19. The high



upfield shifts of the  $2\text{CH}_3\text{OH}$  suggest these Me groups also occupy the temperate zones in a dimeric structure **20**, which places the hydrogen-bonded hydroxy groups in the torrid zone. In variable temperature  $^1\text{H}$  NMR experiments, the OH signal moved monotonically from  $\delta = -0.48$  at  $-50^\circ\text{C}$ , to  $-0.72$  at  $22^\circ\text{C}$ , to  $-1.05$  at  $110^\circ\text{C}$ . The relative lower field resonances of the OH proton at lower temperatures are consistent with increased association of the methanol molecules at lower temperatures.<sup>5</sup>

The first-order rate constants ( $k/\text{min}^{-1}$ ) were measured for  $2\cdot 2\text{MeCN} \rightarrow 2\cdot\text{MeCN} + \text{MeCN}$  at various temperatures ( $\pm 1\text{ K}$ ) in  $\text{CDCl}_2\text{CDCl}_2$  by following the disappearance of the  $\delta -1.15$  signal for the  $2\cdot 2\text{CH}_3\text{CN}$  carceplex and growth of the  $\delta -1.64$  signal for  $2\cdot\text{CH}_3\text{CN}$  for solutions of the initially obtained mixture of  $2\cdot 2\text{CH}_3\text{CN}$  and  $2\cdot\text{CH}_3\text{CN}$  produced in the shell closure. Values obtained were as follows: at 383, 1.8; 373, 0.13; 363, 0.05; and at 353 K,  $0.02\text{ min}^{-1}$ . A plot of  $\log k$  vs.  $1/T$  provided  $E_a = 20\text{ kcal mol}^{-1}\ddagger$  for the unimolecular decomplexation process. A sample of  $2\cdot\text{MeCN}$  proved to be stable for five days when heated to  $215^\circ\text{C}$  in 1,2,4-trichlorobenzene. We conclude from molecular model examination that  $2\cdot 2\text{MeCN}$  is somewhat strained, and that the expelled MeCN molecule escapes through the small portals between the four phenylethyl groups at the north and south polar regions. Possibly the expelled molecule is driven out by

collisions between thermally excited pairs of the two prisoner molecules (a billiard-ball effect). Attempts failed to expel a molecule of MeOH from  $2\cdot 2\text{MeOH}$  by heating the substance dissolved in  $\text{C}_2\text{D}_2\text{Cl}_4$  at  $110^\circ\text{C}$  for five days. Attempts failed to introduce a molecule of MeCN by refluxing the carceplex in 2:1 MeCN– $\text{MeC}_6\text{H}_5$  for four days. Similar attempts failed to introduce  $\text{H}_2\text{O}$  into the same carceplex by heating it in a solution of 9:1 (v)  $\text{Me}_2\text{NCH}-\text{H}_2\text{O}$  at  $100^\circ\text{C}$  for seven days.

These carceplexes in the solid state contain immobile hosts but confined mobile guests, not dissimilar in this respect to liquid crystals. We are examining these and other carceplexes for possible material science applications suggested by those of liquid crystals.

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$\ddagger$  1 cal = 4.184 J.