

# Syntheses of two kinds of dimeric hemicarcerand systems

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The first dimeric hemicarcerand systems are reported, whose synthesis allows either identical or nonidentical cavities and their guests to be tethered at designed distances from one another.

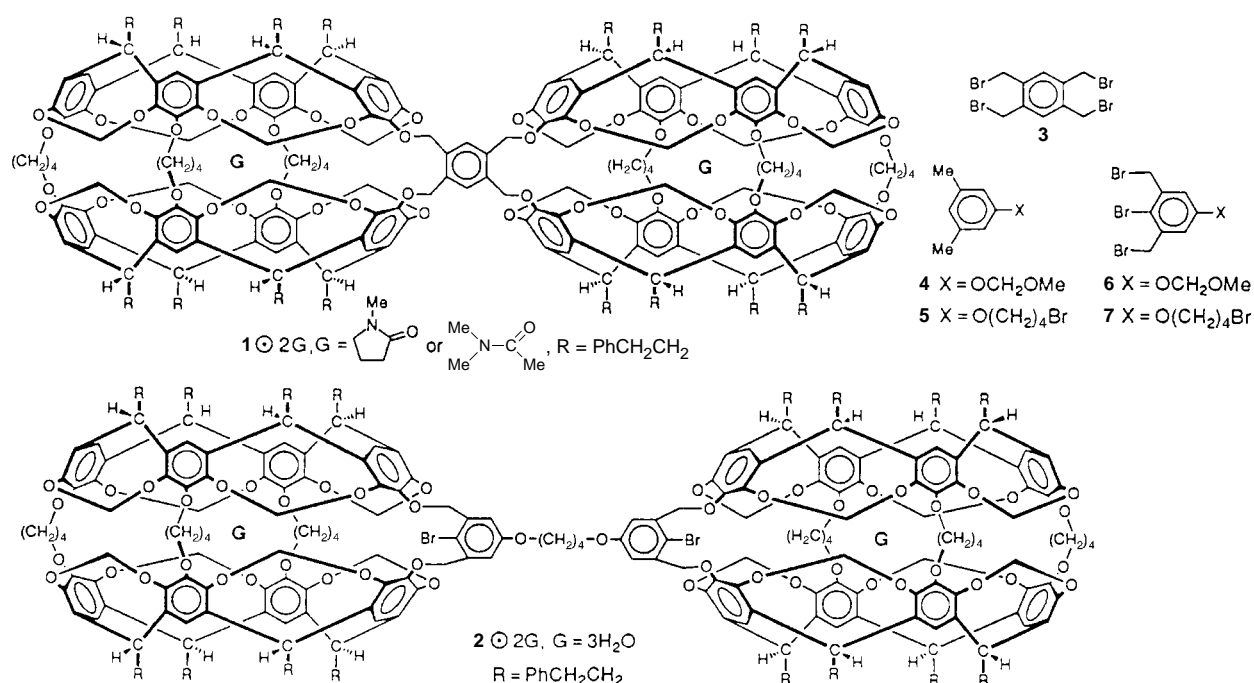
The objective of this research was to establish synthetic feasibility for the synthesis of hemicarcerands covalently attached to one another through groups of designable lengths and saturation, of which **1** and **2** are examples. We reported earlier that appropriate guests incarcerated in **9** underwent oxidation and reduction reactions in bulk solution containing a variety of reducing and oxidizing agents. Electron and water transfers through shells without physical contact between guest and reagent were demonstrated.<sup>1</sup> These results suggest the possibility of electron transfers occurring between two or more designable guests whose hosts of appropriate character are located at controllable distances from one another. We imagine the possibility of ultimately preparing robust polymer chains whose core of guests is conducting, whose proximate shells are electron-permeable, and whose R groups are insulating. Earlier papers report the easy synthesis of diol **8**,<sup>2</sup> and its convertibility to eight different hosts of general structure **9** that differ only in their A groups.<sup>2-4</sup> This family of hosts forms stable complexes with over 50 characterized guests representing a wide variety of structural types.<sup>2-5</sup>

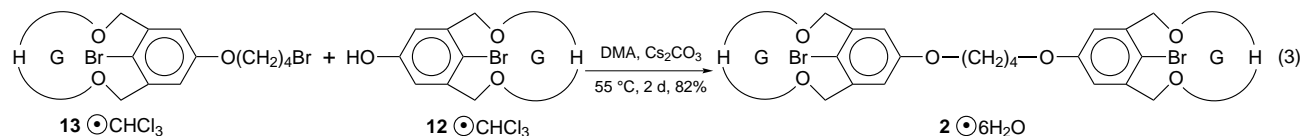
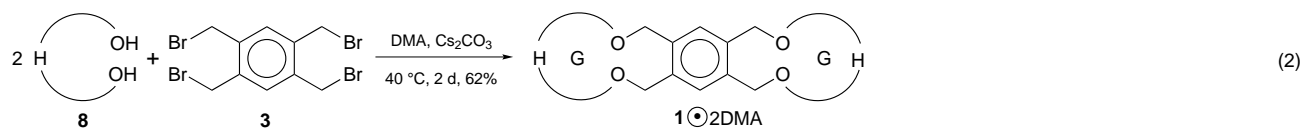
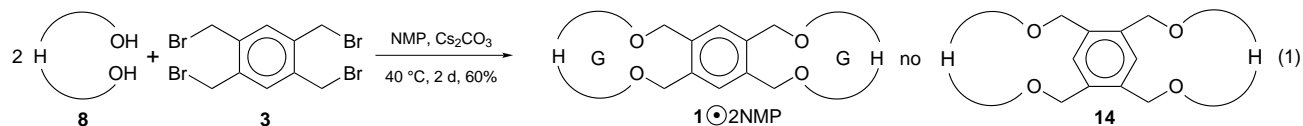
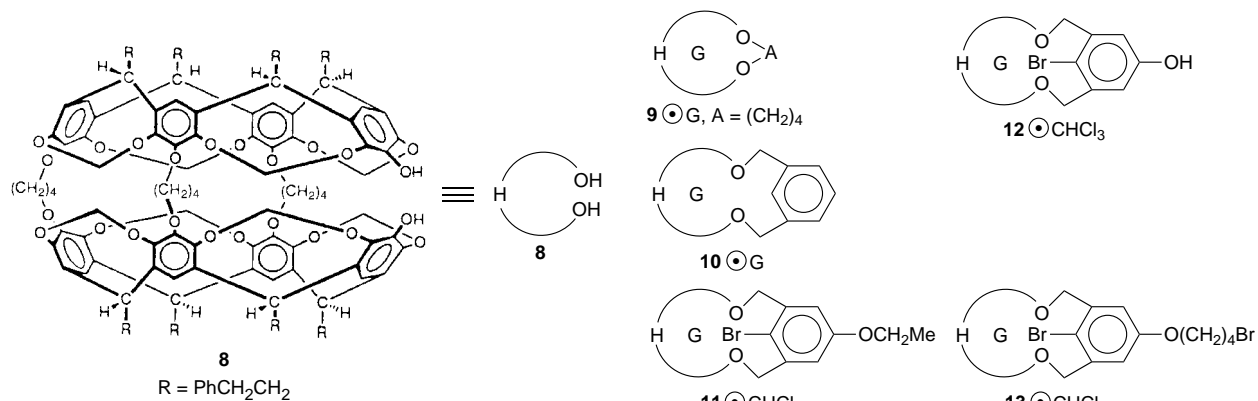
The synthesis of **1**⊙NMP<sup>+</sup> (NMP = *N*-methylpyrrolidone) and of **1**⊙DMA<sup>+</sup> (DMA = dimethylacetamide) was accomplished by the reaction of tetrabromide **3** with two moles of diol **8** under the conditions of eqns. (1) and (2), respectively.<sup>‡</sup> Earlier, **8** had been shown to react with 1,3-(BrCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> to give **10**⊙G, suggesting the possibility that a dimer might be

formed in which each of the two shell closures involved *m*-xylyl rather than *o*-xylyl type reactions, as in **14**.<sup>2</sup> No evidence for formation of **14** was obtained. The rates of the product-determining steps involve formation of the second ether group which closes to form a 26-membered ring leading to **1** or to form a 27-membered ring to provide **14**. Apparently the former rate is faster than the latter.

The final step in the synthesis of **2**⊙6H<sub>2</sub>O<sup>+</sup> is formulated in eqn. (3). The two hemicarceplexes, **12**⊙CHCl<sub>3</sub><sup>+</sup> and **13**⊙CHCl<sub>3</sub><sup>+</sup>, were prepared as follows. The hydroxy group of 3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH was protected by treating it with BrCH<sub>2</sub>OMe–NaH–THF to give **4**<sup>†</sup> (95%), which was brominated with *N*-bromosuccinimide (NBS)–CH<sub>2</sub>Cl<sub>2</sub>–AIBN to give **6**<sup>†</sup> (40%). Shell closure of diol **8** with **6** in NMP–Cs<sub>2</sub>CO<sub>3</sub> (40 °C, 2 d) gave **11**⊙CHCl<sub>3</sub><sup>+</sup> (NMP exchange with CHCl<sub>3</sub> solvent occurred during chromatography). Deprotection of the ArOCH<sub>2</sub>OMe group of **11**⊙CHCl<sub>3</sub><sup>+</sup> (THF–HCl, 35 °C, 4 h) gave **12**⊙CHCl<sub>3</sub><sup>+</sup>. Alternatively, 3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH was treated with excess Br(CH<sub>2</sub>)<sub>4</sub>Br–K<sub>2</sub>CO<sub>3</sub>–DMF (50 °C, 4 h) to provide **5** (60%) (characterized only by <sup>1</sup>H NMR), which was brominated with NBS–CH<sub>2</sub>Cl<sub>2</sub>–AIBN to give **7**<sup>†</sup> (40%). Shell closure of diol **8** with **7** in NMP–Cs<sub>2</sub>CO<sub>3</sub> (30 °C, 2 d) resulted in **13**⊙CHCl<sub>3</sub><sup>+</sup> (72%), NMP again being exchanged for CHCl<sub>3</sub> as guest during chromatography. As indicated in eqn. (3), the DMA–Cs<sub>2</sub>CO<sub>3</sub> catalyzed coupling of **13**⊙CHCl<sub>3</sub><sup>+</sup> and **12**⊙CHCl<sub>3</sub><sup>+</sup> gave **2**⊙6H<sub>2</sub>O<sup>+</sup> (82%), the CHCl<sub>3</sub> guest of the starting materials being replaced by water during chromatography with CH<sub>2</sub>Cl<sub>2</sub>, drying and absorbing water from the atmosphere.<sup>‡</sup>

Corey–Pauling–Koltun model examinations of **1**, **2** and **14** provide the following estimates for the respective maximum and minimum distances the centres of the two cavities can be





from one another: **1**, 13–15; **2**, 13–26; **14**, 12.5–16 Å. For all three models, low-energy conformations appear to exist in which the outsides of the two shells contact one another. We believe it is more likely for electrons to pass from an appropriate guest in one shell of **1** to a second appropriate guest in the other shell of **1** than it is for electrons to pass between oxidizing or reducing agents and incarcerated guests dissolved in dilute solvent, an observed phenomenon.

#### Footnotes and References

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† These new compounds gave C and H elemental analyses within 0.30% of theory,  $M^+$   $m/z$  signals of 80–100% intensity (including guest) in their FAB-MS and  $^1\text{H}$  NMR spectra consistent with their structures.

‡ The procedures were patterned after those that are standard in the literature. All products were purified by chromatography (E. Merck silica

gel 60, 70–230 mesh). The shell closures required reagent grade DMA or NMP, freshly distilled and stored over 3 Å molecular sieves (activated at 320 °C) and degassed just prior to use. The shell closures involved medium dilution and inert atmospheres, and were similar to those reported in refs. 2 and 5.

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