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Novel Concave Building Block for the Synthesis of Organic Hosts

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Natural hosts frequently contain a cavity or cleft whose inner concave surface matches the convex surface of a guest. Recently, synthetic hosts that mimic this feature (cavitands) have been designed. If new and more elaborate host-guest systems are to be developed, versatile and readily accessible building blocks must be available. Here, we describe a novel building block, 2, that meets these requirements. Compound 2 contains two fused 2-imidazolidone rings, which are flanked by two o-xylene units. Its overall shape is concave and its convex side is shielded by two phenyl substituents. The use of 2 in the synthesis of three new cavitands is demonstrated.

Diphenylglycouluril (1a) was treated with paraformaldehyde and NaOH in Me2SO to yield the tetrakis(hydroxymethyl) derivative 1b (85%). Refluxing 1b in benzene with 4 equiv of p-toluenesulphonic acid gave 2a in 35% yield. Similarly, treatment of 1b with an excess of hydroquinone or 1,4-dimethoxybenzene in 1,2-dichloroethane gave 2b (75%) and 2c (50%). Molecular models indicate that the o-xylene units of 2 can have upward (u) or downward (d) orientations, leading to three possible conformers: uu, ud, or dd. Molecular mechanics calculations reveal that conformer uu has the lowest energy. For compound 2b an X-ray structure determination was performed. This

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contains two diphenylglycoluril and two hydroquinone rings linked through eight methylene bridges. The void in 5 (2.5 x 2.0 Å) is not large enough to hold an organic guest. However, higher homologues of 5, e.g., those containing additional diphenylglycoluril and hydroquinone rings, do have large enough voids.10

Starting from 2, hosts that have a metal center next to a cavity are readily accessible. As an example, we prepared 6 by reacting 2b successively with: excess of TOS(OCH2CH2)2Cl and base in Me2SO, excess of benzimidazole (Bz) and NaH in DMF, and 1 equiv of RhCl in Me2SO (overall yield 70%). Compound 6 has two trans-coordinated Cl ligands, one being inside the cavity, the other outside. The binding and catalytic properties of hosts 4-6 are currently being investigated and will be published in forthcoming papers.

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(1) In addition to 5 a compound is isolated which contains three diphenylglycoluril and three hydroquinone rings, linked through 12 methylene bridges (symmetry P31). The cavity of this cavitand has a diameter of ~5 Å. Sibbersma, R. P.; Smeets, J. W. H.; Notte, R. J. M., unpublished results.

Observation of a Nonconcerted Double Proton Transfer in the Solid State by 15N CPMAS NMR

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We present here for the first time NMR spectroscopic evidence of a nonconcerted double proton transfer. The double proton motion studied occurs along slightly asymmetric double-minimum potentials in solid TTAA2 according to Scheme I. For H-chelates of the malonaldehyde type like TTAA, it has been very difficult to establish the double-minimum character of the proton potential using different spectroscopic techniques including NMR.4 Goedken et al.5 have performed an X-ray crystallographic analysis of solid TTAA, have postulated the "diagonal" tautomerism 1 = 3 shown in Scheme I, and have further suggested that the degeneracy of this process is lifted due to a rhombic distortion of the unit cell. However, the X-ray method cannot reveal details such as the nonconcerted character of the double proton motion in TTAA or if the tautomerism is static or dynamic.

Since solid-state proton transfers between nitrogen atoms are most directly probed by 15N CPMAS NMR,6,6 we have performed such experiments on 95% 15N-enriched TTAA.8 Figure 1 shows some of the 15N CPMAS spectra obtained with an apparatus described previously.9 We observe four lines, a-d, of equal intensity. Between 100 and 80 K, the lowest temperature where experiments were performed, no spectral changes occur, indicating that the chemical shifts are temperature independent within experimental error. Taking into account 15N solution NMR data,10 we assign the overlapping lines a and d to NH atoms and the two resolved lines b and c to two inequivalent =N- atoms in solid TTAA. As the temperature is increased, lines d and c move toward each other without coalescing, as do lines a and b. The low-field shift of line a from 96 to 288 K matches the high-field shift of line b over the same temperature range. The same is true for lines d and c. Since the intrinsic chemical shifts are temperature independent, these changes can only be explained by fast proton transfer from atom a to b and from atom d to c. In other words, the position of line n depends on the average proton density pn on atom n. The observed chemical shift difference \( \delta_m - \delta_n \)

Figure 1. 15N CPMAS NMR spectra of 95% 15N-enriched TTAA at 6.082 MHz as a function of temperature: 10-Hz line broadening, 1K-4K zero filling, 25-ns cross-polarization time, 4000-Hz sweep width, 1.5-s repetition time, 9-µs 1H-1/2 pulses, quadrature detection, 1000 scans on the average; reference, external 15NH4NO3.

Scheme I

\[
\begin{array}{c}
\text{R} \\
\text{=N} \\
\text{R}
\end{array}
\]

\[
\begin{array}{c}
\text{R} \\
\text{=N} \\
\text{R}
\end{array}
\]