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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.

Diphenylglycyluril (1a) was treated with paraformaldehyde and NaOH in Me$_2$SO to yield the tetrakis(hydroxyethyl) derivative 1b (85%). Refluxing 1b in benzene with 4 equiv of p-toluene sulfonic 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%), respectively. 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 structure determination (3) confirms the uu conformation of 2 in the solid state.

The $^1$H NMR spectrum of fully acetylated 2d in CD$_2$Cl$_2$ and in Me$_2$SO-$d_4$ displays one pair of well-defined doublets for the CH$_2$ protons at $d$ 5.05 and 3.85 ($J$ = 16 Hz). The position and splitting pattern of the doublets did not change over a temperature range as large as ~95 to 150 °C. This led us to believe that either one conformer (uu or dd) is present or that all three conformers interconvert rapidly. To solve this question we synthesized compound 2d. The (CH$_3_2$)$_2$ bridges of this compound do not allow for any other conformation than uu. As the $^1$H NMR spectra of 2d and its nonbridged analogue 2e show identical pairs of doublets for the CH$_2$ protons (±0.05 ppm), we conclude that compounds 2 also adopt the uu conformation in solution.

Basket-shaped cavitand 4 was prepared (75%) by treating 2b with 2 equiv of 1,11-dichloro-3,6,9-trioxoantranilic acid and K$_2$CO$_3$ in Me$_2$SO. The oxygen atoms of the urea units and the oxyethylene bridges form two receptor sites at the far ends of the molecule. These receptor sites bind alkali metal ions with affinities peaking for K$^+$. Cavitation 4 forms strong 1:1 complexes with protonated diamines e.g., [H$_2$N(CH$_2$)$_2$NH$_3$]$^+$ in these complexes the guest CH$_2$ protons in the $^1$H NMR spectrum at 130 °C. Refluxing 1b and hydroquinone (molar ratio 1:1) in 1,2-dichloroethane in the presence of 4 equiv of p-toluene sulfonic acid produced cavitand 5 (3%, yield not optimized).
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 MeSO4, excess of benzimidazole (Bz) and NaH in DMF, and 1 equiv of RhCl in MeSO4 (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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(10) In addition to 5 a compound is isolated which contains three diphenylglycoluril and three hydroquinone rings, linked through 12 methylene bridges (symmetry D3h). The cavity of this cavitand has a diameter of ~5 Å. Sibbesma, R. P.; Smeets, J. W. H.; Noote, 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.

Such solid-state proton transfers between nitrogen atoms are most directly probed by 15N CPMAS NMR.6 We have performed such experiments on 95% 15N-enriched TTAA. 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 p(a) on atom n. The observed chemical shift difference 6, = 6, - 6,

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-ms cross-polarization time, 4000-Hz sweep width, 1.5-s repetition time, 9-µs 1H-2 pulses, quadrature detection, 1000 scans on the average; reference, external 15NH4NO3.

Scheme I

R = CH3
