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**A Cucurbituril-based Gyroscane: a new supramolecular
form****

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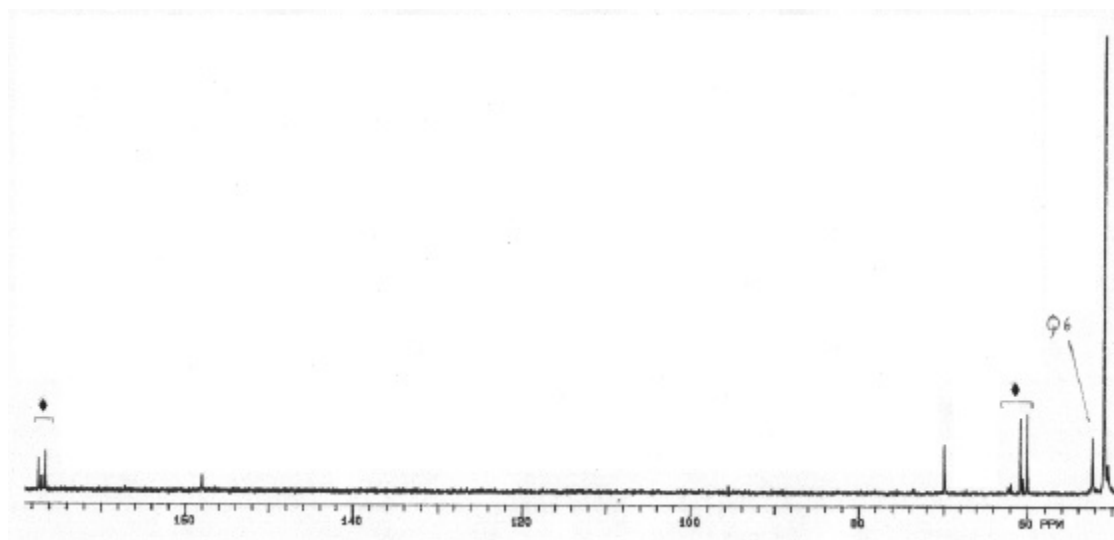


Figure S1. The ^{13}C NMR spectrum of ^{13}C enriched Q5 in 35% $\text{DCl}/\text{D}_2\text{O}$. This sample was prepared on a 20 mg scale using ^{13}C enriched paraformaldehyde (reference 5b, main article). Impurities marked by \blacklozenge are ^{13}C enriched impurities derived from side reactions of the ^{13}C enriched paraformaldehyde. Note the presence of a small amount of ^{13}C enriched Q6.

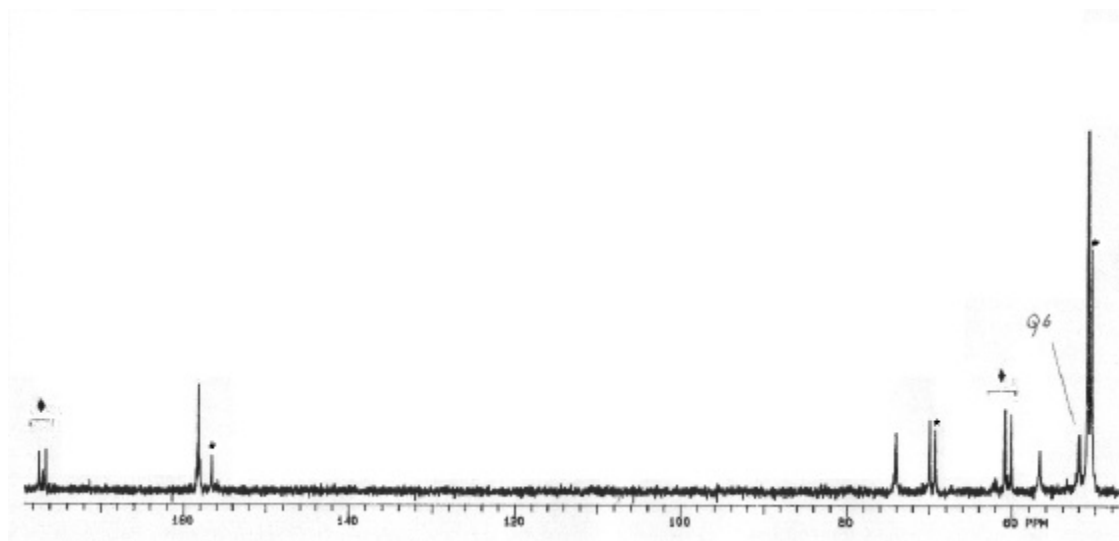


Figure S2. The ^{13}C NMR spectrum of ^{13}C enriched Q5 added to Q5@Q10 in 35% DCl/D₂O. The same impurities indicated in Figure S1 by ♦ are also indicated in this spectrum. The use of 35% DCl/D₂O increases the separation between the resonances for the ^{13}C enriched methylene carbons of Q5, and Q5 bound in Q10. The Q5 bound in Q10 is indicated by *.

**Structure refinement details of
(H₂O)₂(HCl)@Q5@Q10]·10HCl·23.75H₂O (1)**

The crystal structure of **1** was solved by direct methods, and refined using full-matrix least-squares against F^2 using the SHELXTL¹ program on a Silicon Graphics O2 computer. Complex neutral-atom scattering factors were taken from reference 2.

The two organic cages are well defined and ordered, with the Q5 ring located inside the Q10, with Cl⁻ (possibly protonated) [Cl(1)] located at the center of the Q5 cage. Two water (or H₃O⁺) molecules are situated at either end of the Q5 cage [O(31) and O(32)]. Hydrogen atoms associated with the portal water molecules of the central Cl of Q5 were not located on difference maps. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. The anisotropic displacement parameters and errors in atomic coordinates are small. Hydrogen atoms for Q5 and Q10 were included in idealized positions with isotropic displacement parameters constrained to 1.2 times the U_{equiv} of their attached carbon atoms.

A significant amount of residual electron density was smeared through the spaces between the Q5@Q10 components of the asymmetric unit. Substantial difficulties were encountered whilst endeavoring to best model this diffuse electron density, as a large number of water molecules and some HCl as

indicated by the elemental analysis of the crystals. Residual electron density peaks in the asymmetric unit could be assigned as 10 further chlorine atoms [Cl(2)-Cl(11)] and the oxygen atoms of 44 further water molecules. All of these non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. It is evident from the thermal parameters that many of these positions are disordered. Therefore, 8 of the oxygen sites are assigned full occupancy [O(33)-O(40)], 13 are assigned half occupancy after refinement [O(41)-O(47), O(71)-O(75)], the remaining 23 positions assigned occupancy of 0.25 after refinement [O(48)-O(70)]. Many of the oxygen sites have large anisotropic displacement parameters in one direction (U_{11}), implying that the atom is split over two sites. However, for all but 5 atoms, attempts to model this disorder were unsuccessful, leading to refinement instability. These 5 split atoms were assigned two positions [O(71)-O(75) and O(712)-O(752)], with an occupancy ratio of 0.5:0.5 assigned for the two parts after refinement.

In the final model, there are no further isolated features in the difference map, and the highest peaks ($< 1.6 \text{ e}\text{\AA}^{-3}$) are close to identified atom sites. However, the final residual indices remain high, suggesting that the atom sites assigned thus far are further disordered, or there are additional highly disordered atoms in the asymmetric unit. Calculation of the solvent accessible void gives a value of 128 \AA^3 ,

emphasizing the 'unoccupied' space in the model. From inspection of the molecules and their crystal packing, there appear to be two perpendicular two-fold rotation axes, which intersect at the position of Cl(1), *i.e.* in the centre of the Q(5) cage. However, a search for higher crystal symmetry using PLATON,³ or analysis of the reduced cell, did not indicate that the space group has been incorrectly assigned. It is possible that the crystal is partially twinned, exacerbating the disorder in the crystal. Despite the chronic disorder in the crystal the cucurbit[n]uril molecules, Q10 and Q5, are well defined with consistent and normal bond lengths and angles. Thus the problems with the lattice solvation do not detract from the description and interpretation of the features described.

Crystal packing

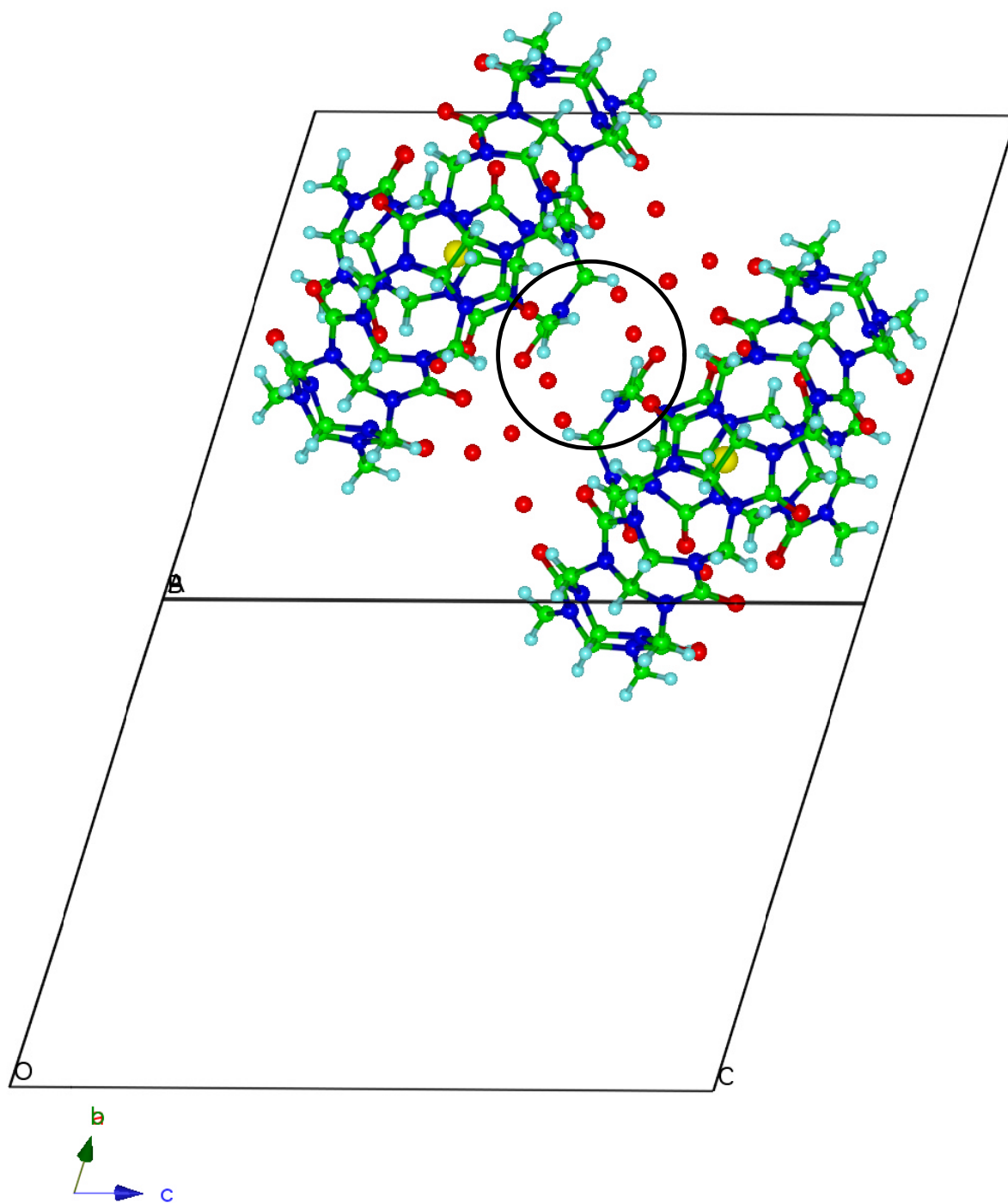


Figure S3. Part of the crystal lattice of **1**, showing a pair of host-guest complexes Cl@Q5@Q10 related by a center of inversion, and some of the intervening water molecules (red). Two 2-imidazolidinone faces of adjacent Q5 molecules form an offset-face-to-face motif (circled, plane separation 3.50Å) across the center of inversion.

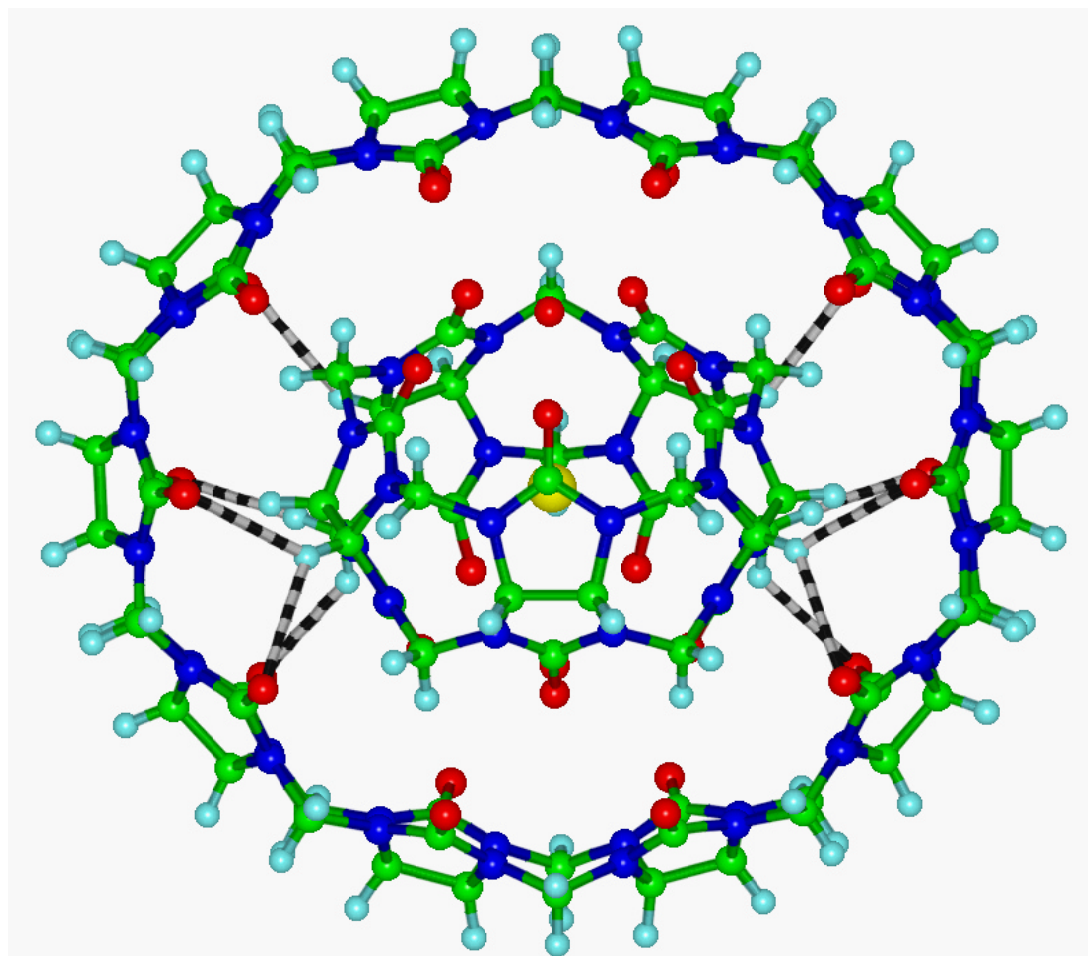


Figure S4. The C-H...O hydrogen bonds from Q5 to Q10.

Portal diameters for Q10

12.477, 13.171, 13.705, 13.156, 12.474, 12.080, 12.067,
14.733, 14.054, 13.373Å

range 12.07 to 14.73Å, mean 13.13Å

References

1. SHELXTL, Rev. 5.0, Siemens Analytical X-ray, Madison, WI, USA.
2. *International Tables for Crystallography*, Kluwer, Dordrecht, **1992**, Vol. C.
3. PLATON, A.L. Spek, Utrecht University, Netherlands.