

Arrayed CH- π hydrogen bonds in a circle for single-axis rotation of a bowl in a tube

Designing unique molecules is one of the most indispensable roles of chemists, who strive to understand physical science through the language of molecules. Through the molecular design of rigid cylindrical molecules, we previously discovered unique behaviors of cylindrical molecules such as the intense circularly polarized luminescence and the solid-state, inertial rotational motion of a spherical guest in the cylinder [1,2]. With the aid of crystallographic analyses associated with another supramolecular complex with cylindrical molecules, we have now revealed the presence of CH- π hydrogen bonds [3]. As has been described by one of the reviewers of our paper [4], the CH- π hydrogen bond has “hovered around the border between a true hydrogen bond and a nonspecific dispersive interaction for some years,” “but conclusive evidence has been elusive.” The 2011 version of the International Union of Pure and Applied Chemistry (IUPAC) definition of hydrogen bonds states that “the evidence of bond formation” is indispensable for any type of hydrogen bond [5], and we are pleased to “supply strong evidence” (comment by the same reviewer) “with solid quantitative evidence for the strength of the complexation and for the conclusion that complexation is enthalpy driven” (by another reviewer). Additional findings of solid-state, single-axis rotation of bowl-shaped guests in a cylindrical host further highlight the uniqueness of the weak yet directional forces of CH- π hydrogen bonds.

The unique CH- π supramolecular complex was assembled with a cylindrical host molecule, (*P*)-(12,8)-[4]cyclo-2,8-chrysenylene ([4]CC), and a bowl-shaped guest, corannulene (COR) (Fig. 1 (a)). Through thermodynamics analyses with NMR and isothermal titration calorimetry (ITC), we obtained an association constant of $K_a = 2.94 \times 10^3 \text{ M}^{-1}$ for the 1:1 complex, which was driven by favorable enthalpy with $\Delta H = -6.76 \text{ kcal}\cdot\text{mol}^{-1}$. There are 10 hydrogen atoms at the periphery of the bowl guest, and we estimate the enthalpy gain to be $-0.7 \text{ kcal}\cdot\text{mol}^{-1}$ for one CH- π contact.

Theoretical studies further deepened our understanding of the chemical bonds in our bowl-in-tube supramolecular system. Density functional theory (DFT) calculations and atoms-in-molecule (AIM) analyses were useful for this investigation. The DFT calculations first reproduced experimental results such as association energetics and NMR chemical shifts. The subsequent AIM analyses then clarified the presence of the “CH- π hydrogen bonds.” As can

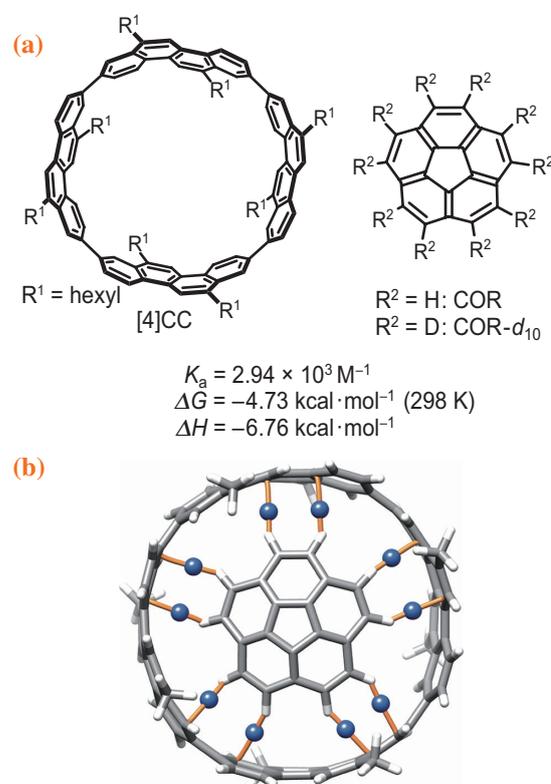


Fig. 1. Bowl-in-tube complex assembled with CH- π hydrogen bonds. (a) Molecular structures. (b) AIM analysis of the DFT structure of [4]CC \supset COR: bond critical points (blue) and bond paths (orange) are shown.

be seen in Fig. 1(b), the AIM analyses showed the presence of bond critical points (blue) and bond paths (orange), which anchor the bowl in the cylindrical space of the host. “For systems of this sort, this type of analysis is probably among the best evidence that can be expected” (by the reviewer).

The solid-state structure of the bowl-in-tube complex was then revealed by crystallographic analysis. The diffraction analysis was carried out at SPing-8 BL38B1. Unexpectedly, in the crystalline solid state, the [4]CC guest and the COR host were present at a 1:2 ratio in the form of [4]CC \supset (COR) $_2$ (Fig. 2(a)). In this complex, one COR molecule occupied the central position of the cylindrical host (COR $_{\text{cent}}$) and the other molecule was stacked above it (COR $_{\text{edge}}$). These COR molecules were solved as disordered structures of three different orientations (Fig. 2(b)). The electron density mapping of COR indicates concentric distributions of electrons, indicating single-axis rotation of the COR guests. The

structural parameters from the crystal data of the CH- π contacts were within the expected range for the CH- π hydrogen bonds.

One of the most intriguing findings of this study was the presence of dynamic motion of the COR guests. Anomalous single-axis rotation of the bowl-shaped guests was spectroscopically observed in the solid state. We prepared a crystalline solid of a complex composed of [4]CC and deuterated COR (COR- d_{10}) and measured solid-state ^2H NMR spectra under static conditions without magic angle spinning. The typical Pake doublet of ^2H resonance with quadrupolar splitting of 42 kHz was observed (Fig. 3(b)). This small splitting indicated the dynamic motion of COR- d_{10} , because the splitting for a static molecule should be 135 kHz. Simulation of the ^2H NMR line shape revealed that the COR guest rotated along a single C_5 axis of the molecule within the cylinder (Fig. 3(b)). The rotational frequency of this single-axis rotation was estimated to be 2.26 GHz at 298 K. Moreover, the precise energetics for the rotation was disclosed: the energy barrier ΔG^\ddagger was $+4.67 \text{ kcal}\cdot\text{mol}^{-1}$, which originated from the enthalpy barrier $\Delta H^\ddagger = +1.40 \text{ kcal}\cdot\text{mol}^{-1}$ and the entropy barrier $-T\Delta S^\ddagger = +3.27 \text{ kcal}\cdot\text{mol}^{-1}$ (298 K). The energetics showed the unique weak yet directional characteristics of the CH- π hydrogen bonds.

We found a novel CH- π complex in the form of a bowl-in-tube complex. This unique supramolecular system supplied the first firm evidence for the

presence of CH- π hydrogen bonds with quantitative measures. The uniqueness of this weak yet directional force was noted with the dynamic motion within the complex, which, we believe, should provide a new design concept for molecular machinery.

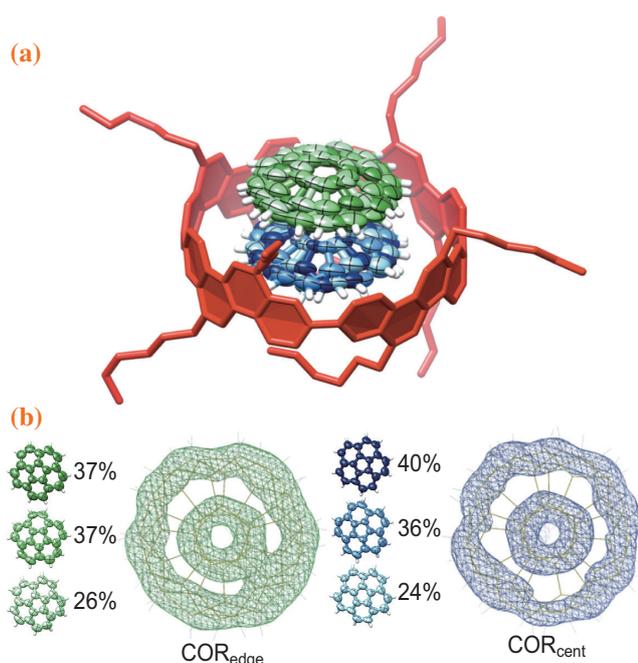


Fig. 2. Crystal structure of the bowl-in-tube complex, [4]CC \supset COR. (a) Molecular structures. (b) Contour electron density mappings ($2F_o - F_c$ contoured at 1.5σ , root mean square deviation) and disordered structures of COR.

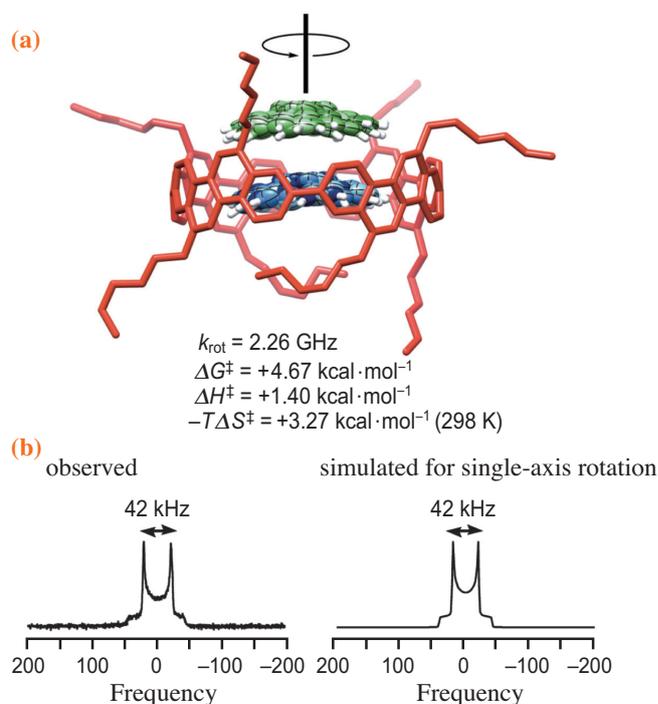


Fig. 3. Solid-state single-axis rotation of the bowl guests in a cylindrical host. (a) Axis of the single-axis rotation and kinetic parameters. (b) Observed and simulated solid-state ^2H NMR spectra under static conditions without magic angle spinning.

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References

- [1] S. Sato *et al.*: Proc. Natl. Acad. Sci. USA **114** (2017) 13097.
- [2] T. Matsuno *et al.*: Nat. Commun. **9** (2018) 1907.
- [3] M. Nishio: Phys. Chem. Chem. Phys. **13** (2011) 13873.
- [4] T. Matsuno, M. Fujita, K. Fukunaga, S. Sato and H. Isobe: Nat. Commun. **9** (2018) 3779.
- [5] G.R. Desiraju: Angew. Chem. Int. Ed. **50** (2011) 52.