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A Double Concave Hydrocarbon Buckycatcher

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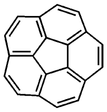
The design and synthesis of molecular receptors able to form stable complexes with guest molecules has been a major challenge of supramolecular chemistry.[1] Association of the receptors, sometimes referred to as molecular tweezers or clips,[2] with guest molecules depends on weak specific interactions such as hydrogen bonding, ion pairing, and dipole−dipole and arene−arene ($\pi-\pi$) interactions in addition to nonspecific van der Waals forces. Since the discovery of fullerenes and related materials the interactions of their curved conjugated carbon networks with properly assembled aromatic rings have been recognized as a significant motif for the formation of inclusion complexes.[3] Buckybowls, bowl-shaped polycyclic aromatic hydrocarbons with carbon networks related to fullerenes, appear to be ideal candidates for molecular receptors with the ability to recognize curved-surface fullerene cages through concave-convex "ball-and-socket" $\pi-\pi$ interactions.[4] Corannulene (**1**) is the smallest and best studied buckybowl. However, even though concave−convex interactions between C_{60} (**2**) and corannulene have been previously proposed in the observed gas-phase formation of $[C_{60}$-**1**$]^{+1}$ complex,[5] no experimental evidence exists to unequivocally prove this stereochemical arrangement between buckybowls and fullerenes.



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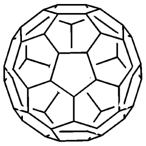

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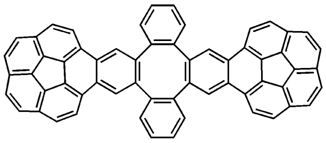

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Thus, lack of experimental confirmation for this phenomenon led to the conclusion that "the attractive force of the concave−convex interactions is not so significant, if at all" for these systems.[3] Herein we report the synthesis of **3**, a $C_{60}H_{24}$ molecular tweezers with two corannulene subunits that can be positioned to embrace a molecule of C_{60} forming a 1:1 inclusion complex through "pure" concave−convex $\pi-\pi$ interactions. Complexation was confirmed by NMR titration and a X-ray structure determination of the complex (Figure 1). These results provide evidence for the importance of concave−convex $\pi-\pi$ interactions in the supramolecular chemistry of fullerene carbon cages and buckybowls.

The synthesis of the molecular clip **3** is outlined in Scheme 1. It starts with isocorannulenofuran **4** which was recently synthesized in our laboratory and shown to be a useful synthon for the synthesis of large conjugated systems containing corannulene subunits by its Diels−Alder reactions with dienophiles.[6] Thus, 2 equiv of **4** react with dibenzocyclooctdiyne **5** producing a ca. 2:1 mixture of two isomeric adducts **6a** and **6b** with an excellent combined yield of 92%. The major adduct **6a** exhibits C_s symmetry as demonstrated by ^{1}H and ^{13}C NMR spectra, while **6b** has C_{2v} symmetry. X-ray crystal structure determination of **6a** confirms that the major adduct results from anti bis-addition of **4** to diyne **5** (Figure 2). As a result, one of the bridging oxygen atoms (O1 in Figure 2) as well as the two bridgehead hydrogen atoms connected to carbon atoms C1 and C4 lie under the concave face of one of the corannulene subunits. These protons are therefore strongly magnetically shielded by the corannulene fragment giving a broad NMR singlet at 3.21 ppm while the resonance of the other two bridgehead hydrogen atoms at C13 and C16 is observed at 6.44 ppm. The four symmetry equivalent bridgehead hydrogen atoms in the more symmetrical **6b** absorb at the usual range of 6.33 ppm.

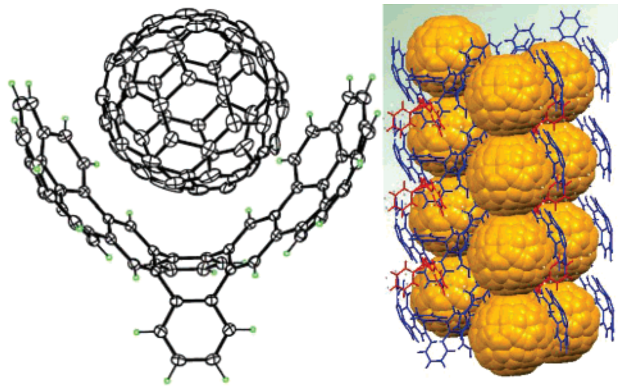
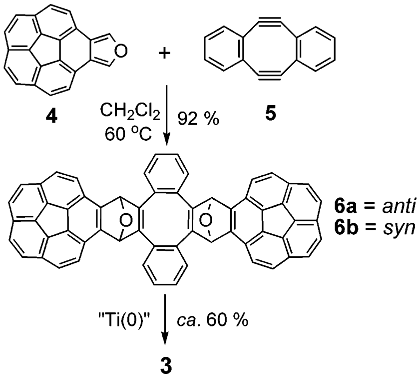


Figure 1. (left) Ortep representation of the crystal arrangement between **2** and **3**. Two toluene molecules are omitted for clarity. Only one of the two disordered orientation of C_{60} is shown. (right) Crystal packing pattern of **2** (gold) with **3** (blue) and toluene (red), showing a linear columnar arrangements of fullerene C_{60}.

Scheme 1. Synthesis of Molecular Tweezers **3**



Deoxygenation of the endoxides **6a** and **6b** is achieved by the low-valent titanium method[7] providing the desired hydrocarbon

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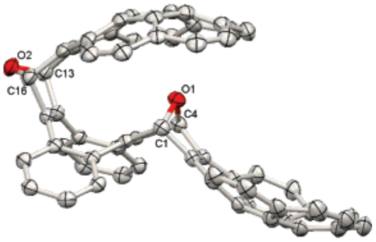

Figure 2. Crystal structure of the adduct **6a**. Hydrogen atoms and a solvating toluene molecule are omitted for clarity.

3a 0.00 **3b** 0.06 **3c** 0.19

Figure 3. Relative energies (kcal mol^{-1}) for the conformers of **3** calculated at the Becke3/LYP//6-31G(d) level with ZPE correction.

$C_{60}H_{24}$ (**3**) with a modest yield of ca. 60%. Molecular modeling calculations[8] at the Becke3LYP/6-31G(d) level of theory predict that all three possible conformations of **3** have quite comparable stabilities with the concave−concave conformer **3a** being only very slightly preferred over **3b** and **3c** (Figure 3). Of course **3a** would appear to be the best candidate as a molecular receptor for buckminsterfullerene since it exhibits two properly oriented concave surfaces of the corannulene subunits with a significant cleft in between. Inspection of the calculated structure shows that the distances between symmetry related carbon atoms of the hub five-membered rings of corannulenes are in the range of 9.84−11.86 Å. The effective van der Waals radius of C_{60} in both the pristine state and in several of its inclusion complexes is found to be in the range of 9.8−10.2 Å,[9] so **3** should be able to accommodate it easily inside the concave−concave cavity. All three conformations are in rapid equilibrium owing to the low inversion barrier of the corannulene bowl.[4]

Slow evaporation of ca. 1:1 solutions of **2** and **3** in toluene produces dark red crystals of X-ray quality. Crystal structure determination shows the crystals to be the inclusion complex **2*3** with two solvating toluene molecules (Figure 1). Both **2** and **3** lie on a crystallographic mirror plane which relates the two corannulene subunits. C_{60} and toluene molecules exhibit disorder in the crystal. The fullerene molecule is placed nicely in the center of a doubly concave cleft with most of the corannulene subunits carbon atoms being in van der Waals contact with the fullerene cage with the shortest distance of 3.128 Å. This confirms that **3** indeed acts as a molecular receptor for **2**. Both **3** and the solvating toluene molecules wrap around C_{60} in its “equatorial” region but allow close contacts of the carbon cages in the “polar” regions which results in a formation of linear columns in which each molecule of fullerene is in a contact with two other fullerenes with the centroid-to-centroid distance of 9.7730 (15) Å (the length of the *a* crystallographic axis), at the lower end of the usual 9.80−10.20 Å range.[9,10]

The complexation of **3** with buckminsterfullerene also takes place in solution as evidenced by changes in the chemical shifts of the hydrogen atoms of **3** upon addition of C_{60}. An NMR titration experiment in deuterated toluene shows systematic downfield shifts for the four symmetry independent protons in the corannulene subunits with increasing concentrations of **2**. The maximum changes in their chemical shifts defined as $\Delta\delta_{\mathrm{max}} = \delta_{\mathrm{bound}} - \delta_{\mathrm{free}}$ are 0.118, 0.134, 0.102, and 0.099 ppm, while the $\Delta\delta_{\mathrm{max}}$ of the remaining three protons are only ca. −0.06, −0.01, and −0.01 ppm. This suggests that the complexation of C_{60} takes place in the expected concave−concave cleft of **3**. We estimated the binding constant K_a by nonlinear curve fitting of the NMR data with K_a and $\Delta\delta_{\mathrm{max}}$ treated as parameters. The evaluations gave the averaged value of $K_a = 8600 \pm 500$ M^{-1}. That value is at the upper limit of the generally accepted reliability of NMR titrations (10^4 M^{-1}).[11]

While unsubstituted corannulene **1** does not show any evidence for complexation with C_{60} in solution, K_a values of 350−450 M^{-1} were found for *sym*-pentakis(arylthio) corannulenes in toluene and 1400 M^{-1} for decakis(arylthio) derivative in CS_2, clearly indicating the importance of the substituents for the binding of fullerenes by these systems.[12] In the case of **3** no heteroatoms or polar substituents can contribute to the binding of the receptor with the fullerene host. Therefore we believe the strength of the binding comes from “pure” $\pi-\pi$ interaction between the convex fullerene and the concave faces of the two properly oriented corannulene subunits of **3**.

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Supporting Information Available: Complete ref 8; experimental procedures and ^{13}C NMR spectra for the new compounds; NMR titration data; CIF files for **6a** and **2*3** complex. This material is available free of charge via the Internet at http://pubs.acs.org.

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