Crystallographic Characterization of the Molecular Structure and Solid State Packing of the Fullerene-Shaped Hydrocarbon C$_{36}$H$_{12}$

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The importance of $\pi-\pi$ interactions in the solid state organization of planar, conjugated hydrocarbons and related molecules is well recognized, and its effects have been analyzed.[1] With the recent isolation and chemical characterization of the fullerenes,[2] the synthesis and properties of nonplanar, polycyclic hydrocarbons have gathered increasing attention.[3] Work has progressed from the pioneering work of Lawton on corannulene,[4] C$_{20}$H$_{10}$, which is the simplest polycyclic hydrocarbon to assume a fullerene-like shape, to the recent report by Scott and co-workers of a single-step synthesis of a C$_{36}$-fullerene subunit, C$_{36}$H$_{12}$.[5] Understanding and controlling the nature of intermolecular $\pi-\pi$ interactions for nonplanar hydrocarbons represents a significant challenge for supramolecular chemistry. The potential for curved $\pi-\pi$ interactions with fullerene surfaces has been explored by adapting flat aromatic units into curved environments. For example, in $(\eta^2\text{-C}_{60})\text{Ir(CO)Cl(Ph}_2\text{-}$ $\text{PCH}_2\text{C}_6\text{H}_4\text{OCH}_2\text{C}_6\text{H}_5)_2$, the four aromatic rings in the two phosphine ligands encircle the fullerene portion of the adjacent complex so that a linear chain of molecules is formed.[6] In the calix[5]arene/C$_{60}$ adduct, five arene groups encapsulate the C$_{60}$ moiety.[7] Curved or bowl-shaped hydrocarbons have the potential to stack through insertion of the convex surface of one molecule into the concave surface of its neighbor. Such stacking is absent in the solid state structure of corannulene,[8] the simplest curved polycyclic hydrocarbon, but does occur in crystalline cyclopentacorannulene, C$_{22}$H$_{10}$.[9] Related bowl−bowl interactions have been postulated to occur in the gas phase association of corannulene radical cation with corranulene and the fullerene-C$_{60}$ radical cation with corannulene.[10] Here we examine C$_{36}$H$_{12}$ by X-ray crystallography to determine both the molecular and solid state structures. This is the largest fullerene-like hydrocarbon for which there is crystallographic data.

The fullerene fragment, C$_{36}$H$_{12}$, was prepared *via* high-temperature (1250 °C) flash vacuum pyrolysis of decacyclene
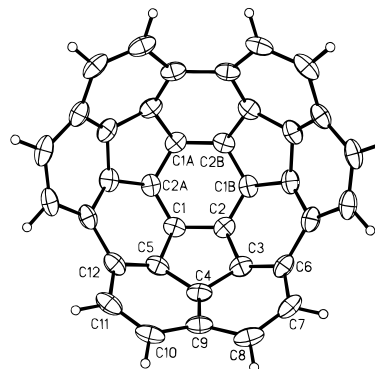
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Figure 1. A perspective view of an isolated molecule of C$_{36}$H$_{12}$ with 50% thermal contours. Bond distances (Å): C(1)−C(2), 1.430(5); C(1)−C(2A), 1.379(5); C(1)−C(5), 1.430(5); C(2)−C(2A), 1.379(5); C(2)−C(3), 1.430(5); C(3)−C(4), 1.438(5); C(3)−C(6), 1.393(6); C(4)−C(5), 1.439(5); C(4)−C(9), 1.382(5); C(5)−C(12), 1.396(5); C(6)−C(7), 1.436(5); C(6)−C(12A), 1.472(5); C(7)−C(8), 1.385(5); C(8)−C(9), 1.430(5); C(9)−C(10), 1.427(5); C(10)−C(11), 1.375(5); C(11)−C(12), 1.445(5); C(12)−C(6A), 1.472(5).

as described by Scott *et al.*[5] and crystallized with difficulty by slow diffusion of *n*-hexane into a chloroform solution of the compound. From the fine, lint-like golden needles, a very small single crystal was found to be suitable for collection of X-ray diffraction data through the use of a Siemens SMART CCD system.[11] C$_{36}$H$_{12}$ crystallizes in the uncommon rhombohedral space group *R*3*c*. The fully ordered molecules reside at sites of C_3 symmetry, whereas the ideal molecular point symmetry is C_{3v}. Figure 1 shows a drawing of the individual molecule. The bowl shape is clearly apparent in Figures 2−4. The depth of the bowl, as measured by the perpendicular distance from the center of the hexagonal base to the center of the plane defined by C(8), C(10), C(8A), C(10A), C(8B), and C(10B) is 3.107 Å, and the radius, as defined by the distance from the center of the group C(8), C(10), C(8A), C(10A), C(8B), and C(10B) to C(8) is 4.128 Å (the corresponding distance to C(10) is 4.068 Å). As the parameters given in the caption to Figure 1 show, there is significant alternation in the C−C distances with the 6:6 ring junctions shorter than the 6:5 ring junctions. This arrangement is analogous to the situation in C$_{60}$ where the average C−C distance at a 6:6 ring junction is 1.383(4) Å while at a 6:5 ring junction it is 1.453(5) Å.

Figure 2 presents a comparison of the structure of the fullerene fragment, C$_{36}$H$_{12}$, with that of the fullerene, C$_{60}$.[12] In these drawings, in which the two structures are superimposed, it is clear that the two structures are similar at the base of the C$_{36}$H$_{12}$ bowl, but that the bowl splays outward at its rim. Thus, the deviation from C(8) to its counterpart in C$_{60}$ is 0.67 Å, and the corresponding distance for C(10) is 0.60 Å. As a consequence of the outward opening at the rim of the bowl, the pyramidalization of the carbon atoms nearest to the edge is less than that for the carbon atoms nearer to the bottom of the bowl. The pyramidalization at C(1) and C(2) as defined by the π-orbital axis vector (POAV)[13] is 101.91° and 102.38°, and the pyramidalization decreases: 99.70° for C(3), 99.81° for C(5), 98.81° for C(4), 96.33° for C(6), and 96.32° for C(12). Earlier

(11) Golden needles of C$_{36}$H$_{12}$ crystallize in the rhombohedral space group *R*3*c* with $a = b = 18.1583(14)$ Å, $c = 10.3231(12)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 2947.8(5)$ Å^3, and $Z = 6$. Refinement of 1057 reflections (based on F^2) with 109 parameters converged to $wR_2 = 0.1007$. A conventional R_1 (based on 855 reflections with $I > 2\sigma(I)$) is calculated to be 0.0506.

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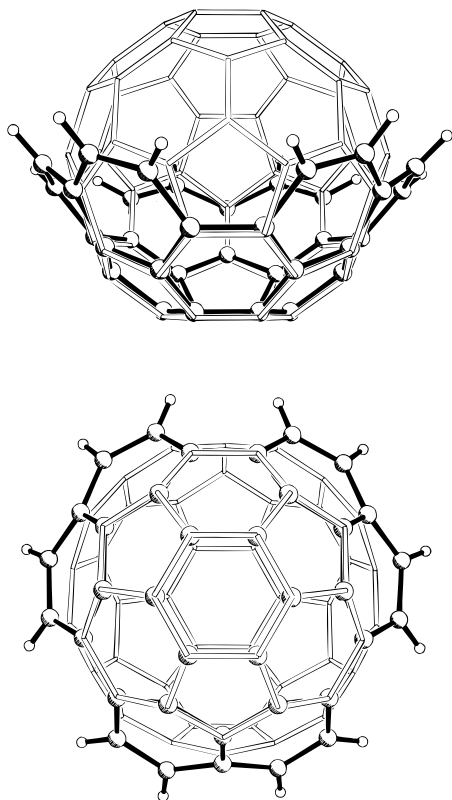*J. Am. Chem. Soc., Vol. 119, No. 24, 1997* 5767

Figure 2. Two orthogonal views of a superposition of the structure of $C_{36}H_{12}$ (represented by circles for atoms with solid lines as bonds) and C_{60} (with open lines connecting the atomic positions). The open lines of the C_{60} molecule obscure the bonds of the $C_{36}H_{12}$ when the open lines are closer to the viewer. The coordinates for C_{60} are taken from the crystallographic data on $C_{60} \cdot 6SbPh_3$ in ref 12.

theoretical work predicted a POAV in the range 102.37−102.42° for C(l) of $C_{36}H_{12}$.[5] For the corresponding carbon atom of corannulene the POAV is much smaller, 98.72°, while for C_{60} the POAV is 101.64°.[13]

In the solid state, $C_{36}H_{12}$ forms linear stacks in which the convex bottom of one bowl is nestled within the concave surface of the next bowl below it. The arrangement of three bowls within an infinite stack is shown in Figure 3. These stacks occur along a crystallographic 3-fold axis that is parallel to the *c* axis. Three *c*-glide planes at 60° to one another pass through this axis. Since the glide planes do not bisect the C−C bonds of the base hexagon of the bowl, and since this is not a regular hexagon reflection through these planes, 1/2 translation along the *c* direction generates a molecule that is staggered by a 15.5° rotation with respect to the first molecule. However, every other bowl in a stack is arranged in a perfectly eclipsed fashion. The separation between the bottoms of adjacent bowls is 5.162 Å. This packing produces rather close C···C contacts between the rim of one bowl and bottom of the adjacent bowl. The shortest of these are 3.356 Å from C(8) in one bowl to C(5) in the next bowl, 3.428 Å from C(8) in one bowl to C(1) in the adjacent one, and 3.505 Å from C(11) to the neighboring bowl's C(2).

The arrangement of stacks of bowls relative to the unit cell is shown in Figure 4 which shows a stereo view of the extended intermolecular organization of the solid. Note that all of the stacks of bowls are aligned in one direction. Thus, the dipoles of all bowls are also aligned, so crystalline $C_{36}H_{12}$ should exhibit pyroelectric properties.[14] A related, bowl-shaped molecule, 4,8,-12-trioxa-12c-phospha-4,8,12,12c-tetrahydrodibenzo[*cd,mn*]-
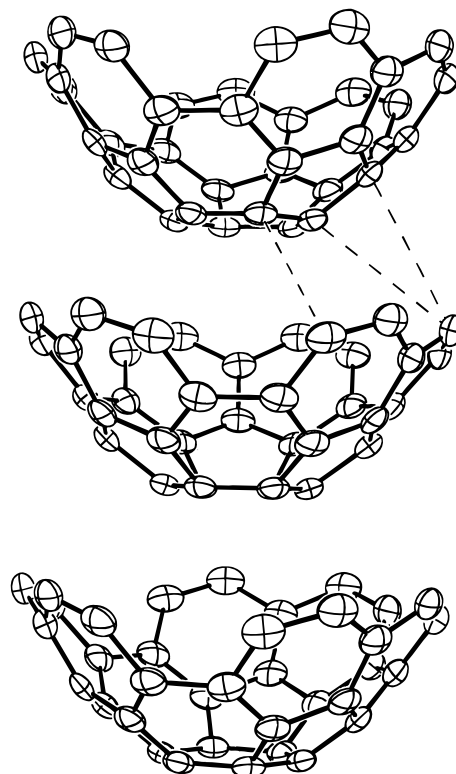

Figure 3. A drawing showing the columnar stacking of bowls along the *c* axis. The dashed lines indicate the closest contacts between bowls.
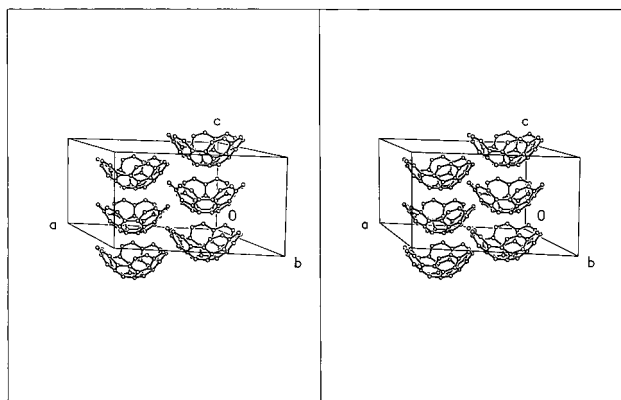

Figure 4. A stereo view of the solid state packing in $C_{36}H_{12}$.

pyrene, has also been found to crystallize in similar stacks with all bowls aligned along the polar axis and to show significant pyroelectric properties.[15]

Supporting Information Available: Details of data collection and structure refinement, tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom positions for $C_{36}H_{12}$ (6 pages). See any current masthead page for ordering and Internet access instructions.

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