A covalent way to stuff fullerenes

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A novel direction in endohedral chemistry of fullerenes is proposed where empty space may be stuffed by covalently bound units.

An intriguing aspect of fullerenes is the large empty space within. It has been possible to use this space as a molecular container encapsulating neutral atoms and metal ions. A few atoms do not fill the available space. To stuff fullerenes a systematic chemical binding of atoms or molecules to the endohedral surface is needed. In this communication we propose a novel way to achieve this.

Stuffing should be anchored to the five- or six-membered rings. Hapto-five or hapto-six binding would be ideal. Five-membered carbon rings are known to form pentagonal pyramidal compounds if there are six interstitial electrons. Thus C₅H₅⁺ (1) has six delocalized electrons, five π electrons from the C₅H₅ ring and one from the C–H⁺ group. Other familiar isostructural analogs are C₅H₂BH⁺ (2) (ref. 9) and C₄B₂H₅ (3). Pentahapto attachment of C–H⁺ or B–H⁺ on the optimize the ring cap interactions. The amount by which the terminal groups bend depend on the particular ring and cap combination. The angle made between a five-membered ring in C₆₀ and one of the C–C bonds emanating from this ring is 31.2° (ref. 15). The rigid C₅B pentagons in H₁₂B₁₂@C₄₈B₁₂ may have a similar angle. These two angles are not far apart so that the interaction of the H–B unit with the C₅B ring may not be far from optimum. The 12 B–H bonds should ideally be tied to an icosahedron so that the nonbonded H–H interactions are minimized and the overall symmetry is preserved.

One of the most stable icosahedral molecules is B₁₂H₁₂⁻² (ref. 16). If the apical boron atoms of the 12 pentagonal pyramids are connected to a central B₁₂ unit by B–B single bonds as in 4 (only one pentagonal pyramid is shown), we have a stuffed fullerene B₁₂@B₁₂@C₄₈B₁₂, a neutral analog, C₁₀B₁₀@C₁₂B₁₂, is obtained by replacing the inner core of B₁₂ by the carborane motif. The 12 three-dimensionally delocalized pentagonal pyramidal units around the C₁₀B₁₀ icosahedron should be a favored system. An electron deficient equivalent of this structure, viz. B₁₂@B₁₂@B₆₀, is seen as part of the most stable polymorph of elemental boron.

The only problem with this stuffed fullerene structure is lack of space. The dimensions of C₆₀ or C₄₈B₁₂ cage are considerably smaller than that of B₆₀ and are not large enough to accommodate icosahedral B₁₂@B₁₂ unit.

The distance between the centroid of the five-membered rings in C₆₀ is about 3.33 Å. The radius of icosahedral B₁₂ (1.68 Å), the B–B single bond length (1.76 Å), and the standard ring cap distance in B₂C₄H₆ (1.29 Å) add up to 4.73 Å. Minor advantages may be obtained by reorganizations such as B₁₂@C₁₀@C₃B₂₂. However these are still not sufficient. There are several ways to proceed at this stage. Atoms larger than carbon in the outer surface can accommodate the inner boron units. Fullerenes based on silicon turned out to be of the right size. The B₁₂@Si₁₂@Si₃B₁₂ structure has the component distances adding up to the required value for Si₆₀. The radius of B₁₂ icosahedron (1.68 Å), B–Si bond length (2.22 Å) and the boron apex to the Si₃B ring distance (1.50 Å) add up to 5.40 Å, a distance not far from the distance between the centroid to the center of five-membered ring in Si₆₀ (5.15 Å).

There are many other ways to stuff carbon-based fullerenes. For example instead of an icosahedral B₁₂ unit, smaller clusters may be tried. A linear three atom unit such as Fe–O–Fe that bind two five-membered rings facing each other in a hapto-5 fashion may be practical. Larger fullerenes may be stuffed more easily with the icosahedron-based systems. For example C₆₀ can be stuffed by the same motif as described above because of its large radius, leading to B₁₂@B₁₂@C₆₀B₁₀. Studies along these lines are underway. A modified arcing method where the electrode material may have
appropriate ratios of the elements, a stepwise synthesis based on B$_2$X$_{12}$ and a thermal reaction of B$_3$ in the presence of Si are experimental possibilities towards stuffed fullerenes. We refrain from speculating on the properties of these highly dense molecules.

In summary, it should be possible to stuff fullerenes by covalently bound units. Electron counting and overlap arguments help in selecting the right stuffing.


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Direct numerical simulation of a complex turbulent flow

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Direct numerical simulations (DNS) have been carried out of the viscous, unsteady flow in a three-dimensional cavity generated by the motion of one of its walls. These flows are known to be complex and difficult to compute even when the Reynolds numbers are low enough to permit steady, laminar flow in the cavity. We have now been successful in computing unsteady, transitional and turbulent flows in this geometry. At Reynolds numbers of 3200 and 10,000 our computations show excellent agreement with the experimental data of Prasad and Koseff.

Although the equations governing the motion of a viscous, incompressible fluid, the Navier-Stokes equations, have been known for almost two centuries, very few complete solutions of these exist for realistic geometries. The difficulties stem from the essential nonlinearity of the equations and the wealth of possible phenomena, including turbulence, that can take place as a parameter re, the Reynolds number, varies from zero to infinity. Till recently one could only resort, apart from experiments, to approximate methods, perturbation techniques and empirical and semi-empirical analysis. The availability of fast computers has, however, changed the scenario and it is now possible to accurately compute some complex, realistic flows for modest Reynolds numbers. This communication is to report such a computation which is somewhat special as detailed experimental results exist for this case with which the computational results can be compared.

We consider a viscous liquid completely filling a cubical cavity of side $l_0$; the fluid is set in motion by the uniform motion, at speed $v_0$, of the top wall along the direction of one of the generators of that wall, the $y$-direction. Let $x$ be the depthwise coordinate and $z$ the lateral or spanwise coordinate. Then the motion of the initially quiescent fluid is governed by the continuity equation and the $N$-$S$ equations in dimensionless form.