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 \( C_6H_6 \) (1) has six delocalized electrons, five \( \pi \) electrons from the \( C_6H_6 \) ring and one from the \( C-H^2 \) group. Other familiar isoelectronic analogs are \( C_5H_2BH^+ \) (2) (ref. 9) and \( C_6B_7H_6 \) (3) (10). Pentahapto attachment of \( C-H^2 \) or \( B-H^2 \) on the optimize the ring cap interactions. The amount by which the terminal groups bind depend on the particular ring and cap combination. The angle made between a five-membered ring in \( C_6 \) and one of the \( C-C \) bonds emanating from this ring is 31.2° (ref. 15). The rigid \( C_7B_7 \) pentagon in \( B_12H_{12} \) (ref. 15). The rigid \( C_7B_7 \) pentagon in \( B_12H_{12} \) may have a similar angle. These two angles are not far apart so that the interaction of the \( H-B \) unit with the \( C-B \) ring may not be far from optimum. The \( B-B \) 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 \( B_{12}H_{12}^2 \) (ref. 16). If the apical boron atoms of the 12 pentagonal pyramids are connected to a central \( B_{12} \) unit by \( B-B \) single bonds as in 4 (only one pentagonal pyramid is shown), we have a stuffed fullerene \( B_{12}B_{12}B_{12} \). A neutral analog, \( C_{10}B_{10} \), is obtained by replacing the inner core of \( B_{12} \) by the carborane motif. The 12 three-dimensionally delocalized pentagonal pyramids around the \( C_{10}B_{10} \) icosahedron should be a favoured system. An electron deficient equivalent of this structure, viz. \( B_{12}B_{12}B_{10} \), 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 \( C_60 \) or \( C_{48}B_{12} \) cage are considerably smaller than that of \( B_{12} \) and are not large enough to accommodate icosahedral \( B_{12} \) unit. The distance between the centroid to the centre of five-membered rings in \( C_60 \) is about 3.33 Å. The radius of icosahedral \( B_{12} \) (1.68 Å) (15), the \( B-B \) single bond length (1.76 Å) (20), and the standard ring cap distance in \( B_{12}C_{60} \) (1.29 Å) (10) add up to 4.73 Å. Minor advantages may be obtained by reorganizations such as \( B_{12}B_{12}B_{12} \). 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 \( B_{12}B_{12}B_{12} \) structure has the component distances adding up to the required value for \( Si_{60} \). The radius of \( B_{12} \) icosahedron (1.68 Å) (16), \( B-Si \) bond length (2.22 Å) (22) and the boron apex to the \( Si-B \) ring distance (1.5 Å) (23) add up to 5.40 Å, a distance not far from the distance between the centroid to the centre of five-membered ring in \( Si_{60} \) (5.15 Å) (24).

There are many other ways to stuff carbon-based fullerenes. For example instead of an icosahedral \( B_{12} \) 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 \( C_{60} \) can be stuffed by the same motif as described above because of its large radius, leading to \( B_{12}B_{12}B_{10} \). 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 $B_2X_{12}^-$ 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.

13. Also see Sewov, S C, and Corbett, J D., Science, 1993, 262, 880–883. This is the only example of stuffed fullerene structure that we have come across. In these carbon-free fullerenes the bonding is not predominantly covalent.
18. Bakowes, D and Thiell, W., J Am Chem Soc., 1991, 113, 3704–3714. The distance between the centroid of the $C_{60}$ to the centre of one of the five-membered rings is calculated from the data in the above reference to be 3.33 Å. The corresponding distance in $S_{60}$ is 5.15 Å.
19. Similarly centroid to the boron distance in $B_3H_{12}^-$ is calculated to be 1.68 Å from ref. 16.
20. B–B distance in planar $B_3H_4$ ($D_{3h}$) calculated at the 6–31G* level is 1.76 Å.
21. Mass spectrometrically $Si_{60}^+$ was characterised to have a layered structure, see Zybin, C., Angew Chem. Int. Ed Engl., 1992, 31, 173–174. Even though fullerene-like $Si_{60}$ has not been realised experimentally, theoretical predictions gave an impetus to take advantage of its size for stuffing, see ref. 24.
23. MNDO calculations on $B_3SiH_3$ gives the distance as 1.50 Å.

Received 2 December 1993, revised accepted 5 March 1994.