

A covalent way to stuff fullerenes

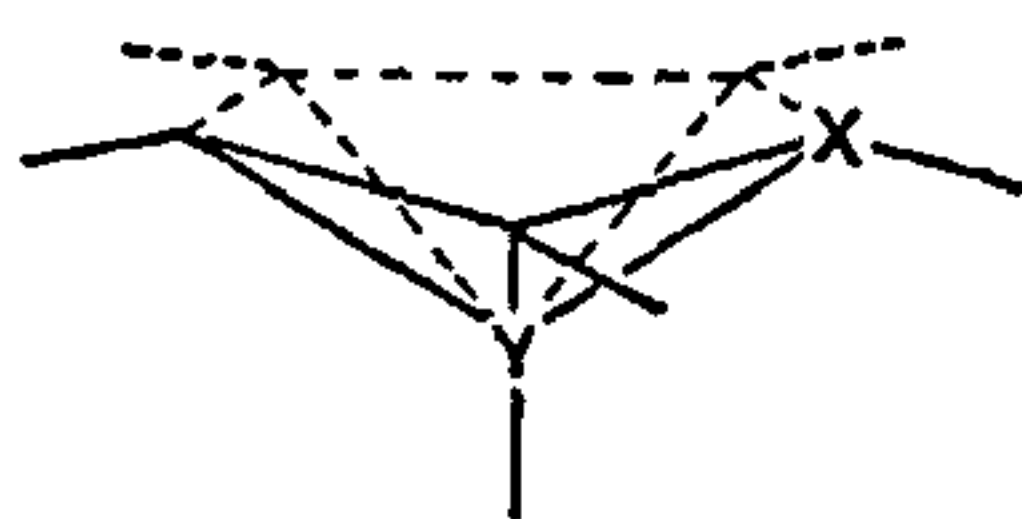
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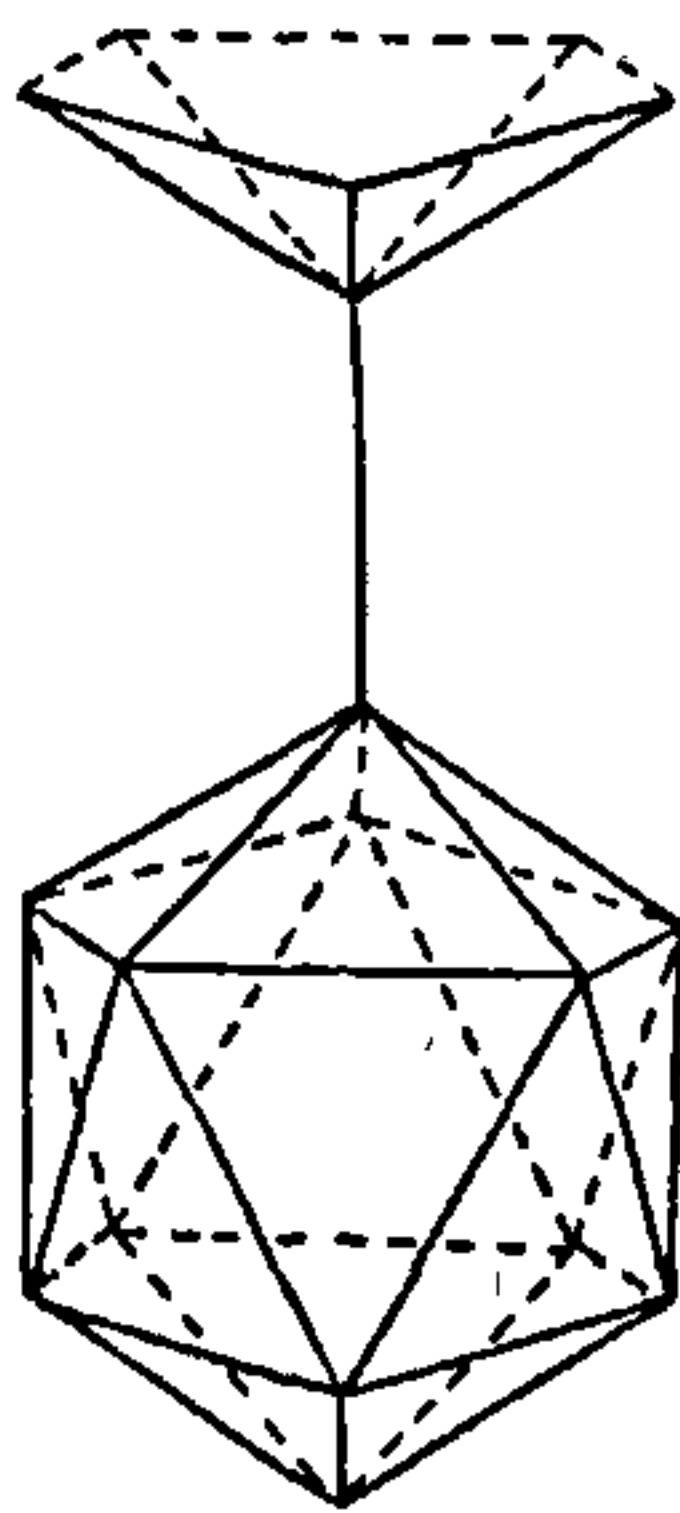
A novel direction in endohedral chemistry of fullerenes is proposed where empty space may be stuffed by covalently bound units.

An intriguing aspect of fullerenes^{1,2} is the large empty space within³. It has been possible to use this space as a molecular container encapsulating neutral atoms and metal ions⁴⁻⁶. 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 electrons⁷. Thus $C_6H_6^{2+}$ (1) has six delocalized electrons, five π electrons from the C_5H_5 ring and one from the $C-H^{2+}$ group⁸. Other familiar isoelectronic analogs are $C_5H_5BH^+$ (2) (ref. 9) and $C_4B_2H_6$ (3)¹⁰. Pentahapto attachment of $C-H^{2+}$ or $B-H^+$ on the



	X	Y
1	C	C^{2+}
2	C	B^+
3	B	B



4

12 five-membered rings inside C_{60} is not practical due to the charge build-up. If one carbon atom in each five-membered ring of C_{60} is replaced by a boron atom, 12 B-H groups can profitably bind in a pentahapto fashion to give a three-dimensionally delocalized structure akin to 3. This now corresponds to $H_{12}B_{12}@C_{48}B_{12}$, following the terminology of Smalley and co-workers¹¹⁻¹³. The hydrogens of the C_4BH_5 ring in the pyramidal $C_4B_2H_6$ are bent towards the capping BH by an average of 22° to

optimize the ring cap interactions^{7, 10, 14}. 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 C_{60} and one of the C-C bonds emanating from this ring is 31.2° (ref. 15). The rigid C_4B pentagons in $H_{12}B_{12}@C_{48}B_{12}$ may have a similar angle. These two angles are not far apart so that the interaction of the H-B unit with the C_4B 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 $B_{12}H_{12}^{2-}$ (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 $B_{12}@B_{12}@C_{48}B_{12}^{2-}$. A neutral analog, $C_2B_{10}@B_{12}@C_{48}B_{12}$, is obtained by replacing the inner core of B_{12} by the carborane motif. The 12 three-dimensionally delocalized pentagonal pyramid units around the C_2B_{10} icosahedron should be a favoured system. An electron deficient equivalent of this structure, viz. $B_{12}@B_{12}@B_{60}$ is seen as a part of the most stable polymorph of elemental boron¹⁷.

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_{60} and are not large enough to accommodate icosahedral $B_{12}@B_{12}$ unit. The distance between the centroid to the centre of five-membered rings in C_{60} is about 3.33 \AA ¹⁸. The radius of icosahedral B_{12} (1.68 \AA)¹⁹, the B-B single bond length (1.76 \AA)²⁰, and the standard ring cap distance in $B_2C_4H_6$ (1.29 \AA)¹⁰ add up to 4.73 \AA . Minor advantages may be obtained by reorganizations such as $B_{12}@C_{12}@C_{38}B_{22}$. 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 size²¹. The $B_{12}@Si_{12}@Si_{38}B_{22}$ structure has the component distances adding up to the required value for Si_{60} . The radius of B_{12} icosahedron (1.68 \AA)¹⁶, B-Si bond length (2.22 \AA)²² and the boron apex to the Si_4B ring distance (1.50 \AA)²³ add up to 5.40 \AA , a distance not far from the distance between the centroid to the centre of five-membered ring in Si_{60} (5.15 \AA)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_{80} can be stuffed by the same motif as described above because of its large radius, leading to $B_{12}@B_{12}@C_{70}B_{10}$. 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 $B_{12}X_{12}^{-2}$ and a thermal reaction of BF_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.

24 Picqueras, M. C., Crespo, R., Orti, E. and Tomás, F., *Chem Phys. Lett.*, 1993, **213**, 509–513.

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- 1 Taylor, R. and Walton, D. R. M., *Nature*, 1993, **363**, 685–693.
- 2 Rao, C. N. R. (ed), Special issue on fullerenes, *Indian J. Chem.*, 1992, **31**
- 3 Kroto, H. W., Allaf, A. W. and Balm, S. P., *Chem. Rev.*, 1991, **91**, 1213–1235
- 4 Weiske, T., Wong, T., Kraitschmer, W., Terlou, J. K. and Schwarz, H., *Angew Chem Int Ed Engl.*, 1992, **31**, 183–185.
- 5 Saunders, M., *Science*, 1993, **259**, 1428–1430.
- 6 Saunders, M., Jimenez-Vazquez, H. A., James Cross, R., Mroczkowski, S., Freedberg, D. I. and Anet, F. A. L., *Nature*, 1994, **367**, 256–259
- 7 Jemmis, E. D. and Schleyer, P. V. R., *J. Am. Chem. Soc.*, 1982, **104**, 4781–4788.
- 8 Giordano, C., Heldeweg, R. F. and Hogeveen, H., *J. Am. Chem. Soc.*, 1977, **99**, 5181–5184
- 9 Jutz, P. and Seufert, A., *Angew Chem.*, 1977, **89**, 330–332
- 10 Pasinski, J. P. and Beaudet, R. H., *J. Chem. Phys.*, 1974, **61**, 683–691
- 11 Hammond, G. S. and Kuck, V. J. (eds), *Fullerenes Synthesis, Properties and Chemistry of Large Carbon Clusters*, ACS Symposium Series, vol 481, American Chemical Society, Washington, DC, 1992
- 12 Guo, T., Jin, C. and Smalley, R. E., *J. Phys. Chem.*, 1991, **95**, 4948–4951.
13. Also see Sevov, 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
- 14 Jemmis, E. D. and Pavan Kumar, P. N. V., *Proc Indian Acad Sci (Chem Sci)*, 1984, **93**, 479–489.
- 15 Fajan, P. J., Calabrese, J. C. and Malone, B., *Acc. Chem. Res.*, 1992, **25**, 134–139
- 16 Wunderlich, J. A. and Lipscomb, W. N., *J. Am. Chem. Soc.*, 1960, **82**, 4427–4428
- 17 Hughes, R. E., Kennard, C. H. L., Sullenger, D. H., Weakliem, H. A., Sands, D. E. and Hoard, J. L., *J. Am. Chem. Soc.*, 1963, **85**, 361–362.
- 18 Bakowies, D. and Thiel, 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 Si_{60} is 5.15 Å²⁴
- 19 Similarly centroid to the boron distance in $B_{12}H_{12}^{-2}$ is calculated to be 1.68 Å from ref. 16.
- 20 B–B distance in planar B_2H_4 (D_{2h}) calculated at the 6-31G* level is 1.76 Å.
21. Mass spectrometrically Si_{60}^+ was characterized to have a layered structure, see Zybill, C., *Angew Chem. Int. Ed Engl.*, 1992, **31**, 173–174 Even though fullerene-like Si_{60} has not been realized experimentally, theoretical predictions gave an impetus to take advantage of its size for stuffing, see ref 24
- 22 B–Si distance in planar BI_2SiI_3 is estimated as 2.22 Å see Mains, G. J., Bock, C. W. and Trachtman, M., *J. Phys. Chem.*, 1989, **93**, 1745–1748
- 23 MNDO calculations on $B_2Si_4H_6$ gives the distance as 1.50 Å Dewar, M. J. S. and Thiel, W., *J. Am. Chem. Soc.*, 1977, **99**, 4899–4906