Discovery of Fullerenes

Giving a New Shape to Carbon Chemistry

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The 1996 Chemistry Nobel prize has been awarded jointly to Robert F Curl Jr and Richard E Smalley of Rice University, Houston, U S A and Harold W Kroto of Sussex University, Brighton, U K for the discovery of fullerenes. Fullerenes constitute a new form of the element carbon. This remarkable discovery has opened up exciting new avenues in multidisciplinary research involving chemistry, physics, materials science and even biology.

Fullerenes belong to a fundamentally new class of molecules and also constitute a new allotrope of carbon. Unlike graphite and diamond (which are the only two structurally well characterised allotropes of carbon), this new allotrope is made of hollow carbon cages. Because of its discrete molecular nature, it is the only pure form of carbon. The number of carbon atoms in each fullerene cage can vary and for this reason numerous new structures can be imagined. Generally, they are represented by the formula C_n, where n denotes the number of carbon atoms present in the cage. C_{60} (fullerene containing 60 carbon atoms) is the most abundant and well characterized member of the fullerene family and is currently dominating fullerene research.

Story Behind the Discovery

The story of the discovery of fullerenes is fascinating because the discovery came about during an investigation into a problem of interest to astronomers. Kroto was interested in radioastronomy. In order to determine whether carbon containing molecules present in interstellar clouds were responsible for some of the signals, he began making and characterizing new carbon species in the laboratory, using microwave spectroscopy as his main tool. Interstellar cyanopolynes (HC_nN, n = 5-11) were discovered by Kroto and coworkers through a synergistic combination of laboratory microwave spectroscopy experiments, theoretical analysis, and observational radioastronomy. Curl, a fellow spectroscopist on the other side of the Atlantic, suggested that collaboration with Smalley would be beneficial. Smalley was interested in cluster chemistry. He had designed and built a special laser-supersonic cluster beam apparatus which could vaporize almost any known material into a plasma of atoms and lead to precise information about the pattern and distribution of the clusters. In an action packed fortnight in September 1985, Curl, Kroto and Smalley along with graduate students J R Heath and S C O'Brien began to carry out some experiments on laser vaporization of carbon.

Generally vaporized carbon is obtained by directing an intense beam of laser onto a graphite or any other carbon surface. The carbon atoms produced in this way in an inert atmosphere combine to form a series of clusters where the size varies from a few atoms to many hundreds. These experiments were aimed at synthesizing long chain carbon molecules, since the conditions might reproduce those existing in red giant stars, which give off large amounts of carbon. This would then provide good evidence to show how such molecules originate in the interstellar medium.

During the course of the experiments which probed the behaviour of the pure carbon clusters, a striking observation was made. Under some clustering conditions the peak corresponding to 720 mass units appeared extremely strong. The intensity of this peak relative to adjacent peaks varied dramatically under different clustering conditions. Under a particular condition, the mass spectrum was totally dominated by the 720 peak, corresponding to sixty carbon atoms.

The next difficult task was to assign a structure for the 720 mass peak which could explain its unique stability. Kroto, Smalley and Curl came up with a brilliant resolution to the problem. Using handmade models, they found that the planar graphite sheet structure curls up on the introduction of a few pentagons. For a 60 atom cluster with 12 pentagons, the structure closes in on itself, forming a beautiful cage (*Figure 1*). The shape is identical to that of a soccer ball. But the inspiration for the remarkable proposal of C_{60} having a spheroidal cage structure came from the geodesic domes designed by the renowned architect R Buckminster Fuller. The stability of geodesic structures was realized and exploited by this architect earlier, for example in the American pavilion in the 1967 Montreal Expo. But it was not suspected that such structures could be realized on a molecular scale until 1985. Since the geodesic dome concept played an important role in arriving at the structure of C_{60}, it was given the name *Buckminster-fullerene.*

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The whole family of hollow cage carbon clusters are now called fullerenes. The most important member of the family, apart from C_{60}, is C_{70}. It is usually a major contaminant

Figure 1 Structure of C_{60}.

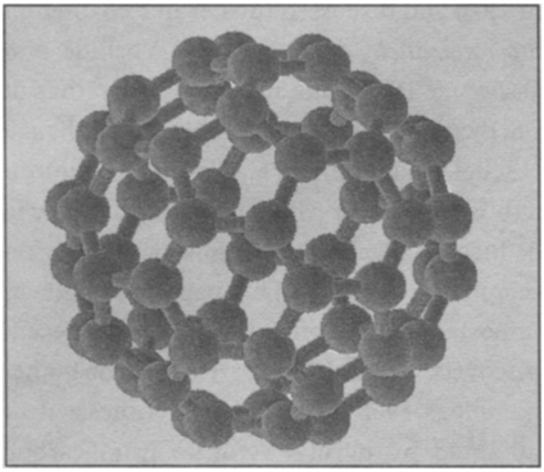
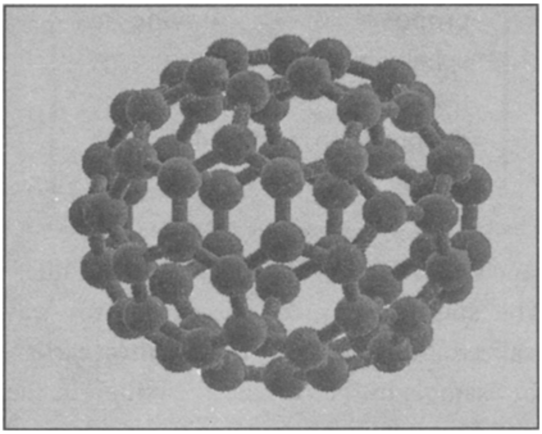


Figure 2 Structure of C_{70}



in the production of C_{60}. The rugby ball shaped structure of C_{70} is shown in *Figure 2.*

Predictions Prior to Discovery

There were many conjectures on the possible existence of fullerenes prior to the actual discovery of these molecules. A hollow cage structure for carbon was first mentioned in an imaginative way by Jones in 1966 in a 'semi-popular' journal. The structure of C_{60} molecule was seriously suggested by Osawa in 1970 and discussed further in a chapter on *superaromaticity* in a book by Yoshida and Osawa in 1971. The next paper was that of Bochvar and Gal'pern in 1973 who published Hückel calculation on C_{60}. In 1980 Davidson published a paper which used graph theory to deduce an algebraic solution of the Hückel calculation for C_{60}. This paper contains an important paragraph in the light of the recent discovery: "Should such structures or higher homologs ever be rationally synthesized or obtained by pyrolytic routes from carbon polymers, they would be the first manifestations of authentic, discrete three dimensional aromaticity".

On the experimental front, there are many early papers on carbon clusters. But the most important ones which actually stimulated the key experiments are those published by Hintenberger and coworkers in 1959-63 in which it was shown that species containing up to 33 carbon atoms could be formed in a carbon arc. The next important advance was made by Rohlfing, Cox and Kaldor in 1984 who found that much larger carbon clusters C_n with n= 30-190 could be produced by vaporization of graphite.

Synthesis and Confirmation of the Structure

Even though the discovery of C_{60} through mass spectrometry was achieved in 1985, many chemists were not fully convinced of the existence of fullerenes. The substance had been inferred in an exotic instrument, but was not made in a bottle. Kroto, Smalley and Curl followed up their original proposal with many additional experiments. They provided evidence for the cage structure by incorporating metal ions in C_{60}. But the breakthrough in synthesis came almost five years after the original discovery, from a group of physicists.

Krätschmer, Lamb, Fostiropoulos, and Huffman, in following up their earlier infrared spectral observations, discovered that at 300-

400° C, a solid material could be sublimed from the deposit obtained from arc-processed graphite. They were able to crystallize the material and the X-ray and electron diffraction analyses showed that it consisted of arrays of 7 Å diameter spheroidal molecules. They also reported IR, UV/VIS, and mass spectra of this extracted material which provided the first confirmation of the Buckminsterfullerene structural proposal. Later a single line ^{13}C NMR spectrum was reported, confirming the equivalence of all carbon atoms of the highly symmetrical cage. Conclusive evidence for the remarkable cage structural proposal was obtained by the chemical derivatization of C_{60} by Hawkins and others. They synthesized OsO_4(4-tert-butylpyridine) adduct with C_{60}. Further they obtained crystals of this complex and showed by X-ray analysis that rotation of the free C_{60} in solid phase can be frozen by derivatization. This study provided the first reliable measure of carbon-carbon bond lengths for the C_{60} cage. Later many derivatives have been synthesized and characterized.

Since the discovery of the procedure by Krätschmer and Huffman for the macroscopic production of C_{60}, methods to prepare and purify fullerenes have been further developed and improved by many research groups.

Even though C_{60} is available in macroscopic quantities, conventional organic synthesis of the molecule is yet to be achieved. This is currently one of the greatest challenges of synthetic organic chemistry. Of course, there have been a few efforts in this direction involving carbon rings, smaller polycyclic condensed aromatics like corannulene, sumanene, etc. Success may not be very far.

Higher Fullerenes

Ever since C_{60} and C_{70} were first detected by Kroto and others by laser vaporization of graphite, much effort has been directed to answer why C_{60} and C_{70} are so stable and what kinds of other fullerenes, with different sizes and shapes, can be formed as stable entities. Theoretical calculations on the higher fullerenes have predicted that all even-numbered fullerenes with the sizes larger than C_{70} can exist, at least in the sense of a hollow-closed cage structure. Until now, eight fullerenes comprised of 60, 70, 76, 78, 82, 84, 90, 96 carbon atoms have actually been isolated and confirmed to exist as stable clusters. Further, for C_{60}, C_{70}, and C_{84}, the proposed structures have been confirmed by conventional spectroscopic tools as well as by chemical derivatization. For C_{76} and C_{78}, the structures have been proposed by ^{13}C NMR spectroscopy in solution.

Several variations in the fullerene cluster shapes have been observed. Long cylindrical nanotubes, cage enclosed in a cage, onion-like shapes have all been made. Usually, carbon tubules consist of hexagonal sheets folded as long cyclindrical shapes capped with pentagons. These represent a range of structures bridging fullerenes and graphite.

A general formula for fullerenes is C_{20+2n}, made up of 12 pentagons and n hexagons. For the larger fullerenes, several isomeric forms can be derived with pentagons and hexagons exclusively.

Electronic Structure and Properties of Fullerenes

The spheroidal geometry of fullerenes is their most arresting feature, and it directly determines their singular electronic structure. According to Euler's theorem, a closed structure can be constructed with 12 pentagons. A general formula for fullerenes is C_{20+2n}, made up of 12 pentagons and n hexagons. For the larger fullerenes, several isomeric forms can be derived with pentagons and hexagons exclusively. If smaller and/or larger rings are accommodated, many other structures are possible. Conventional chemical knowledge indicates that unsaturated organic compounds with adjacent pentagons are unstable. The fact that C_{60} is the smallest possible fullerene with all pentagons isolated was one of the reasons for the original rationalization that it might be stable. Further, analysis of the problem of pentagon isolation in the general context of fullerene cages of any kind uncovered the surprising result that, not only was C_{60} the first isolated pentagon fullerene but most significantly the second was C_{70}. As C_{70} was known to be the second magic number in the original beam experiments, this discovery yielded the first strong support for the original fullerene structure proposal and gave rise to the 'pentagon isolation rule', governing general fullerene stability. To date all fullerenes that have been isolated follow this rule.

Initially C_{60} was expected to be extremely unreactive. This prediction was based on the fact that 12500 resonance structures are theoretically possible. Many of these forms apparently do not contribute to the stability of the molecule. Consequently, C_{60} behaves like an alkene rather than as an aromatic compound. In general, fullerenes undergo all the reactions associated with poorly-conjugated, electron-deficient alkenes. But their unique feature is the vast number of products possible from the addition of just one reagent.

Future Directions

The electronic structure of fullerenes, and of C_{60} in particular, has fuelled the expectation that they will find unique applications. Remarkably, a few alkali metal salts of C_{60} are found to be superconducting. The fact that C_{60} can undergo reversible electrochemical reduction to various anions suggests possible

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use in rechargeable batteries. They may be of some use in cancer therapy since they can encapsulate radioisotopes. The ability to trap and retain solvents between the cages may also have some applications. Water soluble fullerene derivatives have been made for possible biological use.

One important point to be mentioned is that the successful exploration of the chemistry, physics and material properties of fullerenes requires a highly interdisciplinary approach. Research in this area needs the breaking of artificial barriers of communication between various disciplines.

Suggested Reading

- **H W Kroto, J R Heath, S C O'Brien, R F Curl and R E Smalley. *Nature*. Vol 318. p 162, 1985.**
- **F Diederich and Y Rubin. *Angew. Chem. Int. Ed. Engl.* Vol 31. p 1101, 1992.**

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Fullerene Research in India

Many aspects of physics and chemistry of fullerenes are being studied in various research laboratories in the country. Theoretical and experimental work is going on in the Indian Institute of Science (Bangalore), BARC (Mumbai), Indira Gandhi Centre for Atomic Research (Kalpakkam), and University of Hyderabad, to name a few institutions. An entire laboratory equipped with state-of-the-art microscopy techniques is dedicated to carbon research in Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore.

Two journals, *Indian Journal of Chemistry* (Volume 31A, B, May 1992) and *Fullerene Science and Technology* (Volume 3, No.6, 1995) have published special issues covering Indian contributions to fullerene research.