FULLERENE CHEMISTRY

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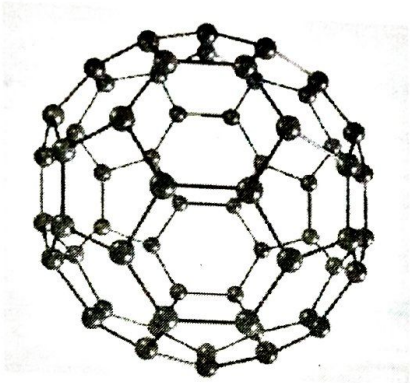
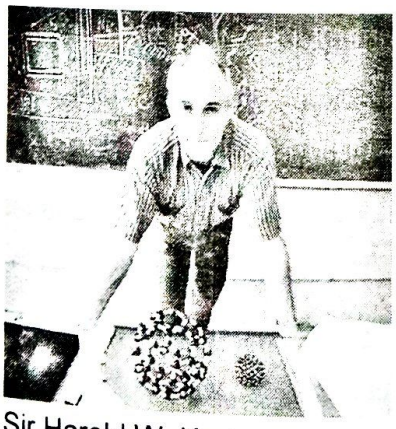
INTRODUCTION :

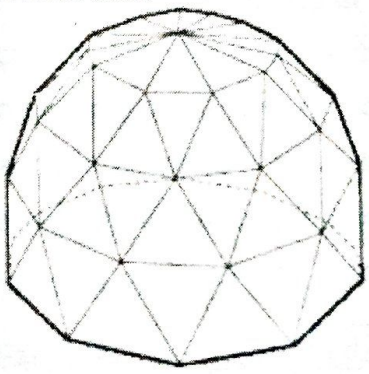


Fullerene, also called **buckminsterfullerene,** is an Allotrope of carbon which consists of 60 carbon atoms, linked together to form either a closed cage ("buckyballs") or a cylinder (carbon "nanotubes"), with the molecular formula C_{60}. The C_{60} molecule was named buckminsterfullerene (or, more simply, the buckyball) after the American architect R. Buckminster Fuller, whose geodesic dome is constructed on the same structural principles. Sixty carbon atoms (C_{60}) joined together by single and double bonds to form a hollow sphere with 12 pentagonal and 20 hexagonal faces-a design that resembles a football, or soccer ball.



Sir Harold W. Kroto

Geodesic dome



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PREPARATION OF FULLERENE

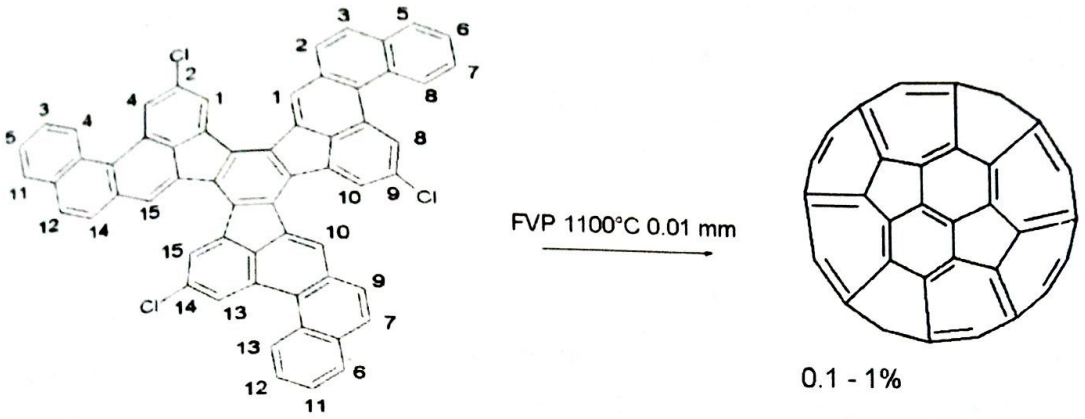
The first fullerene was discovered in 1985 by Sir Harold W. Kroto of the United Kingdom and by Richard E. Smalley and Robert F. Curl, of the United States. Using a laser to vaporize graphite rods in an atmosphere of helium gas, these chemists and their assistants obtained cagelike molecules composed of 60 carbon atoms (C_{60}) which they named Fullerene.

In 1990 physicists Donald R. Huffman of the United States and Wolfgang Krätschmer of Germany announced a simple technique for producing macroscopic quantities of fullerenes, using an electric arc between two graphite rods in a helium atmosphere to vaporize carbon. The resulting condensed vapours, when dissolved in organic solvents, yielded crystals of C_{60}.

MULTISTEP FULLERENE SYNTHESIS

Although the procedure for the synthesis of the C_{60} fullerene is well established (generation of a large current between two nearby graphite electrodes in an inert atmosphere) a 2002 study described an organic synthesis of the compound starting from simple organic compounds.

In the final step a large polycyclic aromatic hydrocarbon consisting of 13 hexagons and three pentagons is submitted to flash vacuum pyrolysis at 1100°C and 0.01Torr. The three carbon chlorine bonds serve as free radical incubators and the ball is stitched up in a no-doubt complex series of radical reactions. The chemical yield is low: 0.1 to 1%. A small percentage of fullerenes is formed in any process which involves burning of hydrocarbons, e.g. in candle burning. The yield through a combustion method is often above 1%. The method proposed above does not provide any advantage for synthesis of fullerenes compared to the usual combustion method, and therefore, the organic synthesis of fullerenes remains a challenge for chemistry.



Properties of Fullerene

The properties of fullerene molecules are versatile which has led to a great deal of research. One potentially useful property is that atoms of different elements can be placed inside the molecular cage formed by the carbon atoms, producing a "shrink wrapped" version of these elements. When metal atoms are introduced into fullerene tubes, the resulting material is like a one-dimensional insulated wire. Another important property is that certain compounds of buckminsterfullerene (notably K_3C_{60}) are superconducting at low temperatures. Compounds made by adding thallium and rubidium ions (electrically charged atoms) to fullerenes become superconducting at -228° C (-378° F). This temperature is relatively high compared to the cooling required by other superconducting materials. Derivatives of buckminsterfullerene have been found to be biologically active and have been used to attack cancer. It is believed that the molecules can enter the active sites of enzymes and block their action.

Fullerene Purification

Fullerene purification is the process of obtaining a fullerene compound free of contamination. In fullerene production, mixtures of C_{60}, C_{70} and higher homologues are always formed. The first available purification method for C_{60} fullerene was by HPLC from which small amounts could be generated at large expense.

A practical laboratory-scale method for purification of soot, enriched in C_{60} and C_{70} starts with extraction in toluene followed by filtration with a paper filter. The

solvent is evaporated and the residue (the toluene-soluble soot fraction) redissolved in toluene and subjected to column chromatography. C_{60} elutes first with a purple color and C_{70} is next displaying a reddish-brown color.

Carbon Nanotubes

In 1991 Iijima_Sumio of NEC corporation's Fundamental Research Laboratory, Tsukuba_Science city, Japan, investigated material extracted from solids that grew on the tips of carbon electrodes after being discharged under C_{60} formation conditions. Iijima found that the solids consisted of tiny tubes made up of numerous concentric "graphene" cylinders, each cylinder wall consisting of a sheet of carbon atoms arranged in hexagonal rings. The cylinders usually had closed-off ends and ranged from 2 to 10 micrometres (millionths of a metre) in length and 5 to 40 nanometres (billionths of a metre) in diameter. High-resolution transmission electron microscopy later revealed that these multiwalled carbon nanotubes (MWNTs) are seamless and that the spacings between adjacent layers is about 0.34 nanometre, close to the spacing observed between sheets of graphite. The number of concentric cylinders in a given tube ranged from 3 to 50, and the ends were generally capped by fullerene domes that included pentagonal rings (necessary for closure of the tubes). It was soon shown that single-walled nanotubes (SWNTs) could be produced by this method if a cobalt-nickel catalyst was used. In 1996 a group led by Smalley produced SWNTs in high purity by laser vaporization of carbon impregnated with cobalt and nickel. These nanotubes are essentially elongated fullerenes.

Individual carbon nanotubes may be metallic or semiconducting, depending on the helical orientation of the rows of hexagonal rings in the walls of the tubes. Rather than conducting electricity via electron transport, a diffusive process that results in electron scattering and conductive heating, SWNTs exhibit ballistic transport, a highly efficient and fast conduction process in which electrons, prevented from diffusing through the wall of the tube or around its circumference by the regular hexagonal array of carbon atoms, propagate rapidly along the axis of the tube. Open-ended SWNTs emit electrons at currents that attain approximately 100 nanoamperes (billionths of an ampere). Owing to such remarkable properties,

electrical conductors made of bundles of nanotubes should exhibit zero energy loss. Aligned MWNTs show promise as field emission devices with potential applications in electronic flat-panel displays. Nanotubes may also be used as highly resilient probe tips for scanning tunneling microscopes and atomic force microscopes.

Carbon nanotubes exhibit faster phonon transport than diamond, which was previously recognized as the best thermal conductor, and the electric current-carrying capacity of nanotubes is approximately four orders of magnitude higher than that of copper. The Young's modulus of MWNTs (a measure of their elasticity , or ability to recover from stretching or compression) is estimated by researchers to be greater than that of carbon fibres by a factor of 5 to 10. MWNTs are capable of readily absorbing loads via a sequence of reversible elastic deformations, such as buckling or kinking, in which the bonds between carbon atoms remain intact.

Applications of Fullerene

The discovery of C_{60} has led to a paradigm shift in the understanding of graphite, in particular graphene sheets on a small scale. It is now known that the most stable form of a carbon aggregate, containing tens to several thousands of atoms, is a closed buckyball or nanotube. Closed fullerene structures, incorporating sulfides of some metals as tungsten and molybdenum, exhibit excellent solid-lubricant properties. Conducting carbon nanotubes may be coated with sheaths of metal sulfides to produce tiny insulated electrical wire.

Fullerenes and nanotubes have engendered much excitement, especially with regard to possible future applications, but so far such applications have been few and far between. Nanotubes in particular may well bring about a revolution in materials science. For example, if SWNTs can be made in bundles of 100 billion, then a material will be produced that may approach the limits of tensile strength possible for any known material involving the chemical bond.

In practice, no material approaches its theoretical "intrinsic strength," because of breakdowns brought on by the propagation of microscopic defects through the material. A bundle of nanotubes, however, may bypass this problem, as microscopic defects may anneal along the length of a particular tube and certainly should not

propagate across the bundle—thus avoiding the problems that occur in conventional materials. Estimates of potential tensile strength vary, but it is predicted that a 1-metre rod may reach 50 to 100 times the strength of steel at one-sixth the weight. The impact of such a material on civil engineering, building construction, aircraft, and automobiles would be spectacular. In order to realize this potential, however, new processes will have to be discovered that can produce long (more than 1 metre), perfectly ordered bundles in which all 100 billion nanotubes preferably have the same diameter and atomic arrangement. At present the technology to achieve this does not exist; indeed, it is not even obvious what strategy might be used to reach this goal. In addition, applications on a small scale should be feasible for medical purposes—for instance, the strength of individual nanotubes may prove useful in microsurgery or nanosurgery.

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