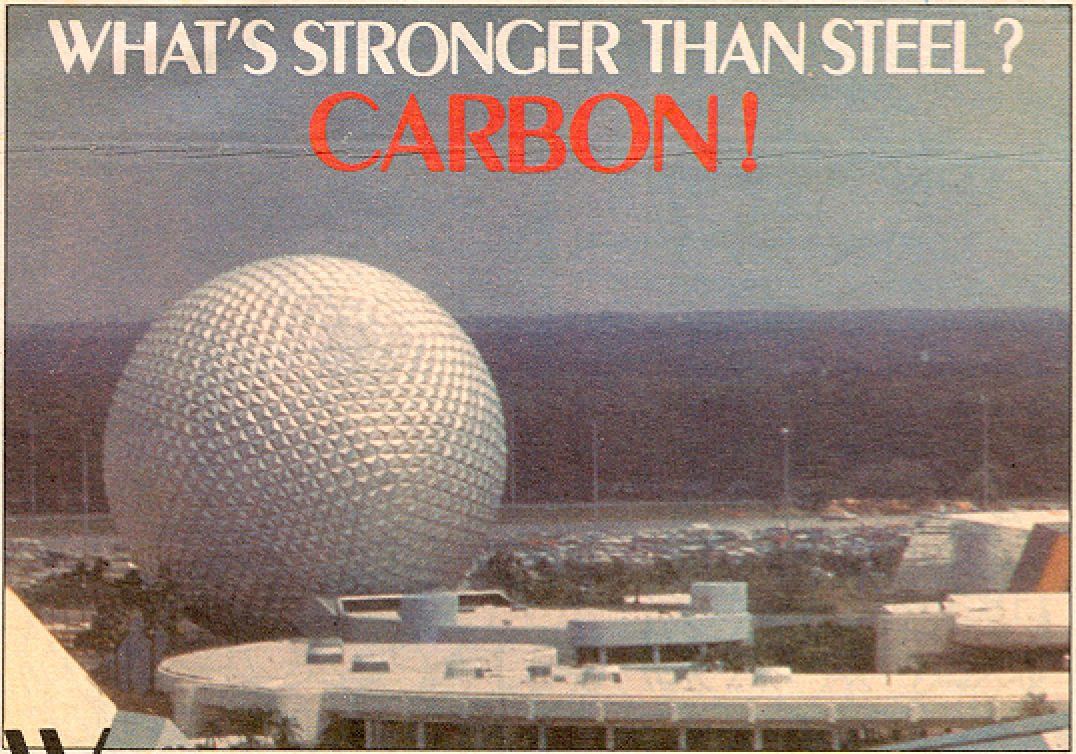
WHAT'S STRONGER THAN STEEL? CARBON!



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The newly discovered third form of carbon offers exciting possibilities for carbon chemistry and material science

WHO ever imagined that carbon can form supermolecules which can vapourize! The detection of clusters of carbon atoms in soot, numbering as many as 60, 70 and 540, have created an excitement in the scientific world, comparable only to that of high temperature superconductors in early 1987. These clusters consisting of only an even number of carbon atoms are arranged in closed cages; structurally very different from the other two forms of carbon we are familiar with, namely, graphite and diamond (Figs 1 and 2). Hence they clearly constitute a new form (or allotrope) of carbon hitherto unknown.

The story of this new species of carbon starts with the detection of long-chain molecules of carbon in the interstellar region, a few years ago. Haruld Kroto of the University of Sussex in England and Richard Smalley of the University of Houston in USA and their co-workers, attempted to generate these chain molecules in the laboratory in the mid-eighties. Their method consisted of ablating graphite crystals with high energy lasers to produce carbon vapour, which was then analysed with a mass spectrograph (Fig.3). To their surprise, they found peaks in the mass spectra corresponding to clusters of carbon atoms, the most abundant being a cluster containing 60 carbon atoms, as seen in Fig.4. The remarkable stability of this species is attributed to its elegant closed structure, a spheroidal cage formed of 12 pentagons and 20 hexagons resembling the surface of a football (Fig.1). Since geodesic domes of a similar shape (shown above here) had earlier been designed by the famous American architect Buckminster Fuller, the C_{60} molecule was named buckminsterfullerene. Some called it footballene, but this name has not caught on. Popularly C_{60} is known as the bucky-ball. Along with buckminsterfullerene, C_{60}, the other prominent carbon cluster molecules found in graphite vapours is C_{70}, containing 70 carbon atoms. It has the shape of a rugby ball. This entire family of carbon molecules is referred to as fullerenes. One of the large fullerenes, one can visualize is, C_{60} made up of 540 carbon atoms.

Preparation of C_{60} and C_{70}

The stability of C_{60} has been attributed to its icosahedral framework. In spite of its stability, it was not possible

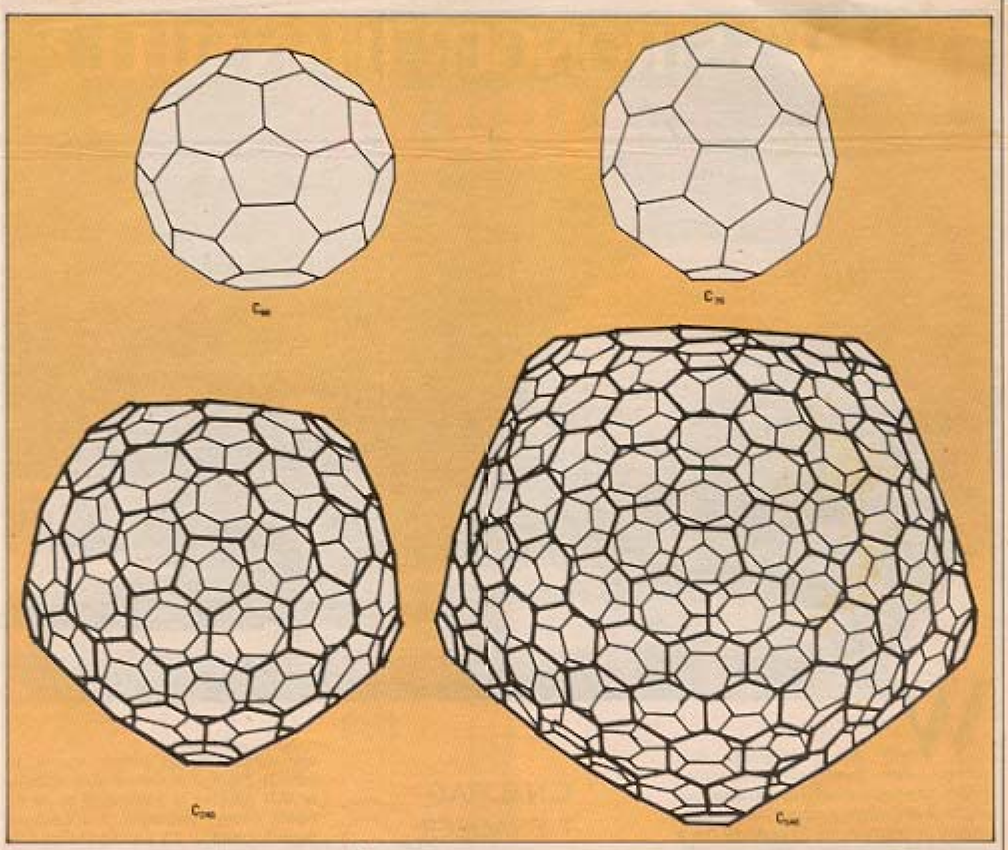
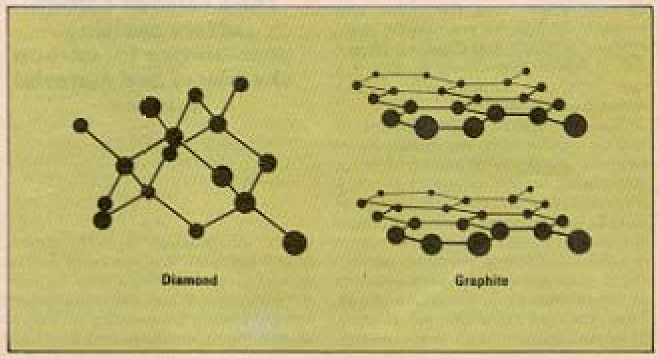


Fig.1 Shapes of supermolecules of carbon

Fig.2 Structures of the two-well known crystalline forms of carbon, diamond and graphite. While diamond is three-dimensional, graphite is two- dimensional



to study C_{60} in the laboratory until recently, since it could not be obtained in sufficient quantities. Theoreticians predicted some properties based on various types of calculations. The situation however changed towards the end of 1990, when Huffman, Kratschmer and co-workers in Germany found a simple laboratory method to prepare sufficient quantities of C_{60} and C_{70}.

Their method involves vaporizing graphite in a conventional bell jar by passing high current through two graphite electrodes in an atmosphere of helium. The soot collected from the arc is digested with an organic solvent (toulene). The solid obtained after removing the solvent from the toulene solution was subjected to mass spectrometry. The mass spectrum showed the presence of C_{60} with a minor

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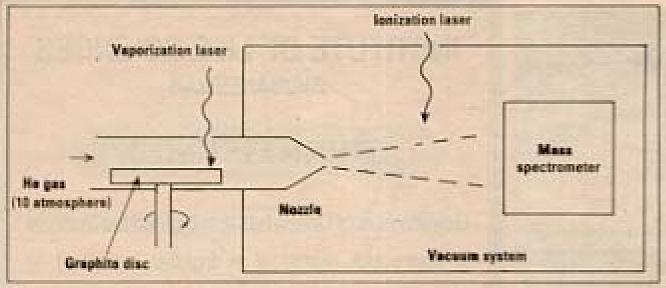

Fig.3 A schematic diagram of the experimental set-up used by Kroto and co-workers in 1985. A high power laser ablates graphite and the resulting vapours are expanded through a supersonic nozzle. The supersonic molecular beam is ionized by another laser and the resulting ions are analysed by a time-of-flight mass spectrometer

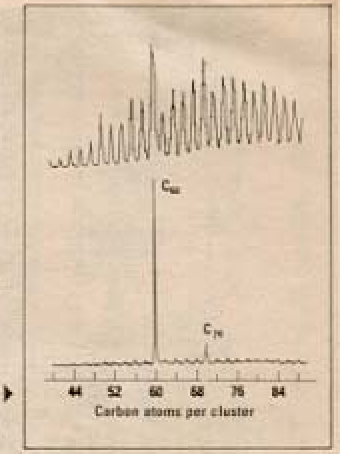

Fig.4 Mass spectra of carbon vapours obtained two experimental conditions. The top one shows a variety of even numbered clusters. The bottom one shows a very strong signal corresponding to carbon 60 (mass number 720) along with a weak feature due to carbon 70 (mass number 840)

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amount of C_{70}. A schematic diagram of a typical graphite arc system to produce soot containing CC_{60}/C_{70} is shown Fig.5.

These two components can be separated by column chromatography (a method of separating subatances using their slow passage through an absorbing medium). C_{60} when dissolved in organic liquids gives a magenta coloured solution, while that of C_{60} is wine red. However, simple aromatic compounds such as benzene, C_6H_6, and naphthalene, $C_{10}H_8$, are colourless. It is really unbelievable that we now have supermolecules of carbon which dissolve in solvents to give colored solutions—a possibility never thought of as we are used to graphite and diamond as the only forms of carbon.

Attempts to isolate C_{60} from natural sources have not been successful. we have found C_{60} and C_{70} to be present in the soot produced by an ordinary spirit lamp using benzene as the fuel. The technique involves quenching a portion of flame by argon coming out from a nozzle and collecting the soot on a cooled surface. The experimental set up is shown in Fig.6. Presence of C_{60} and C_{70} in soot is of relevance not only to understand the origin of these carbon molecules but also the mechanism of formation of soot itself.

New chemistry

The structure and properties of fullerenes is given in the box on p.49. The possibility of incorporating an external atom in their spheroidal cavity (C_{60}, for instance, has a big spherical cavity of 7 A° in diameter) is an interesting aspect of the fullerene chemistry. A variety of metal atoms and ions can, in principle, be trapped in this cavity. Some mass spectrometric studies claim that it is possible to push atoms like lanthanum and caesium inside the spheroidal cavity. It is, however, not completely clear whether these metals are inside or outside.

Recently, energetic C_{60} ions have been used to push helium inside the cavity. A serious experimental difficulty relates to the characterization of such species even if we can make them in measurable quantities. Substitution of the carbon in C_{60} by boron and nitrogen have also been attempted.

Superconductivity

The discovery of superconducting compounds of fullerenes has enhanced the excitement in fullerene research. (Superconductivity means the property of zero resistance exhibited below a particular temperature.) A few months ago, Murphy and co—workers at AT&T Bell Labs in USA, discovered that the potassium derivative of C_{60}, is superconducting at 18 K. The structure of K_3C_{60} is shown in Fig.7. The temperature dependence of its magnetic susceptibility is shown in Fig.8. Rubidium and Caesium analogues of this compound are also superconduct-

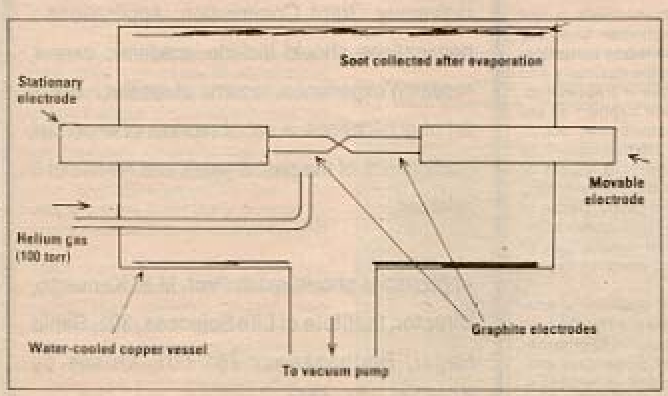

Fig.5 A schematic diagram of the $C_{60}C_{70}$ generator, locally fabricated by the authors. Two graphite rods are in contact and a high current is passed between the two. The vapours are collected on a water-cooled surface. After a couple of hours of vaporization, the soot is removed from the collecting surface and subjected to chemical procedures to separate carbon 60 and 70 from the rest

FULLERENE STRUCTURE AND PROPERTIES

WITH the availability of a method to produce fullerenes in the laboratory, exploring their properties has become the rage of the day. Let us look at some of the important characteristics of $C_{60}$and C_{70}. Mass spectra of C_{60} and C_{70} show peaks at mass numbers 720 an 840 along with less intense fragments. Fig.1 shows a typical mass spectrum of a mixture of C_{60} and C_{70} . Since all the carbon atospectrum ms in C_{60} are similar, the nuclear magnetic resonance (NMR) spectrum shows a single peak. The NMR spectrum provides a confirmation of the spherical shape C_{60} . However, in the case of C_{70} there are five distinct carbon atoms present in the ratio 10:10:20:20:10 and the NMR spectrum shows the expected five peaks with the predicted intensity ratios. Even though there are sixty carbon atoms in C_{60} its high symmetry does not permit many of the vibrations to be active. The Raman spectrum also shows the expected lines.

The X-ray crystal structure of buckminsterfullerene has been solved. At room temperature, C_{60} has a face-centered cubic structure. The X-ray study confirms the spherical structure of C_{60} and shows a intercluster separation of 10 Å in the crystal. The icosahedral hollow cage has a diameter of 7 Å (Fig.2). Since the structure has spherical molecules which can randomly orient themselves, there is considerable disorder at room temperature. On cooling to 250 K (– 20°C) the C_{60} molecules order themselves and give rise to greater crystallinity to the structure.

In diamond, the distance between two carbon atoms is that of a C-C single bond (1.54 Å) while in graphite it is smaller (1.39 Å). In buckminsterfullerene, C_{60} there are two distinct carbon-carbon bond lengths, 1.403 Å and 1.434 Å (Fig.2). These distances are in between those in diamond and graphite. The chemical behaviour of fullerenes would also be expected to be in between that of diamond and graphite. While diamond is a perfect insulator, graphite is a conductor. Buckminsterfullerene is an insulator with a band gap of 2.2 eV. It is difficult to compress C_{60}. In fact, the compressibility of C_{60} is comparable to that of diamond.

We mentioned earlier that C_{60} forms a magenta coloured solution when dissolved in inorganic liquids. This means that there is an electronic transition around 6000 Å in the visible region. This arises from the unique pi electron structure of this molecule. By adding electrons to C_{60} one can make buckide anions. Reduction potentials of C_{60} and C_{70} have been studied. It is easy to add 1,2,3, or 4 electrons to C_{70} to give 1-,2- 3- and 4- anionic species.

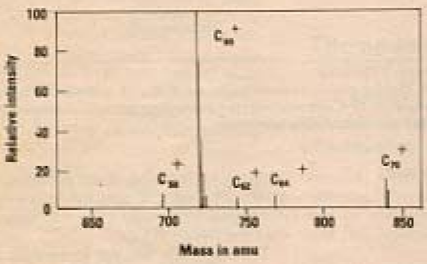

Fig.1 Typical mass spectrum of a mixture of C_{60} and C_{70}. The mass spectrum has peaks at mass numbers at 720 and 840 along with the fragments, C_{58} and C_{62}

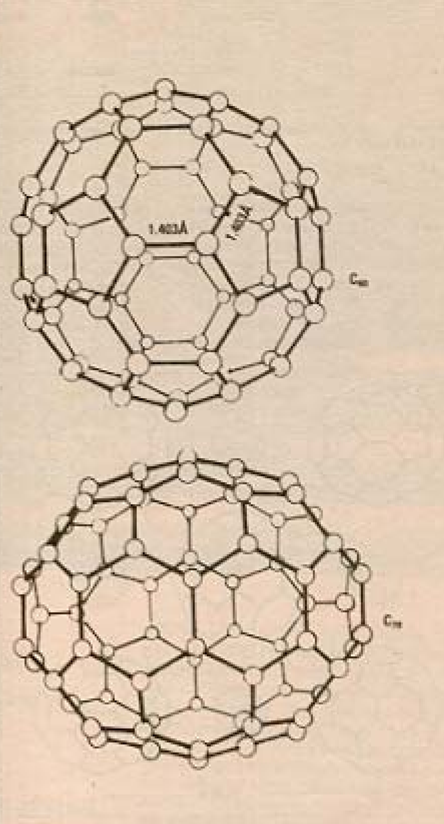

Fig.2 Structures of C_{60} and C_{70} . Note that the C_{60} structure has 12 regular pentagons and 20 irregular hexagons.There are two different carbon-carbon distances, while the distances in the pentagons are equal, the hexagons have two equal bond lengths

C_{60} is a reactive molecule and can undergo several types of reactions. It has been reduced to give $C_{60}H_{18}$ and $C_{60}H_{36}$ and methylated to get $C_{60}(CH_3)_6$. Complete fluorination gives $C_{60}F_{36}$. One of the interesting problems being tackled is to functionalise C_{60} , say with a carboxyl group, and use it for other reactions. A problem that one faces while functionalizing C_{60} is the large number of isomers that are possible in these derivatives. For example, $C_{60}H_2$ can have 59 isomers. The separation and characterization of the isomers would be a formidable task.

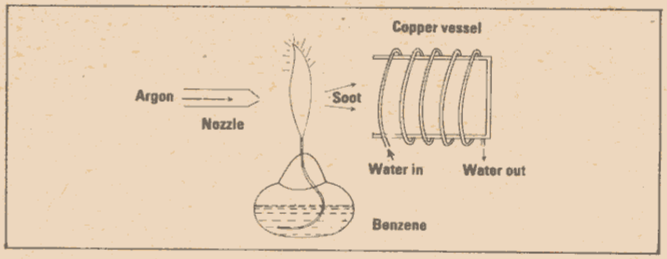

Fig. 6 *Set-up used by the authors to obtain carbon 60 and carbon 70 from the soot of an ordinary benzene flame*

ing with higher transition temperatures (up to 35 K). One of the important differences between these carbon superconductors and the high-temperature cuprate superconductors is that the latter are two-dimensional oxides while the C_{60} derivatives are three-dimensional molecular solids. The other organic molecular superconductors show superconductivity below 10 K unlike C_{60} compounds.

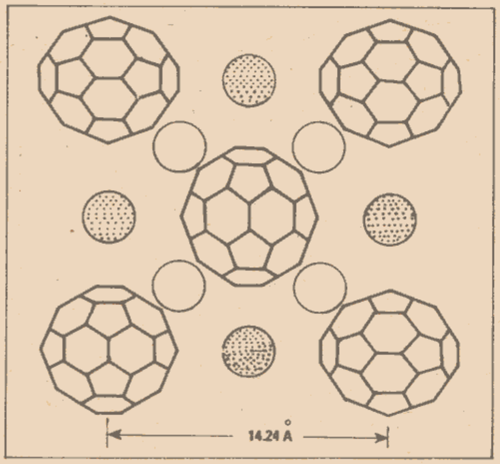

Fig.7 X-ray crystal structure of superconducting K_3C_{60}. Only one face of the face-centred cubic structure is shown

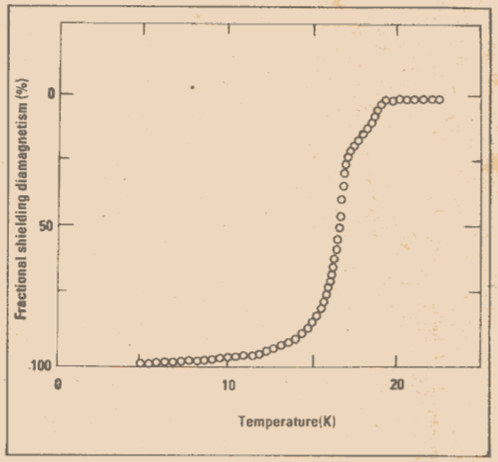

Fig.8 The magnetic susceptibility of K_3C_{60} as a function of temperature. At 18 K, the material becomes diamagnetic corresponding to the superconducting transition

Work at Bangalore

At the Indian Institute of Science, Bangalore, C_{60} and C_{70} have been generated in quantities by employing a novel generator fabricated locally (Fig.5). Spectroscopic studies, functionalization of C_{60} and C_{70}, superconductivity and determination of other solid state parameters form the important aspects of the fullerene research undertaken. Studies with films of C_{60} have shown that nitrogen interacts with C_{60} unlike with other forms of carbon. Transition metals such as nickel bond strongly to C_{60} suggesting that C_{60} may have a role in catalysis. High-pressure studies have shown evidence for metallization of C_{60} under pressure. This has relevance to the superconducting properties of the alkali-doped fullerens.

A new compound of C_{60} containing iron in the spheroidal cage has been prepared. Nitrogen and ammonia react with C_{60} to give yellow nitrogenous compounds. Reactions of C_{60} with reagents such as diborane and diazomethane are being examined. Interaction of C_{60} with organic molecules as well as electron acceptors such as iodine and antimony chloride is being examined, in relation to the electronic and magnetic properties of the adducts. Detailed theoretical studies are being carried out to explain the unique properties of C_{60}.

Regarding the future of fullerenes, a variety of problems related to C_{60} and others will occupy the interest of chemists, physicists, material scientists and others in the next few years. In addition to high-temperature superconductivity, the possibility of making molecular magnets, molecular traps, and molecular bearings would be of interest to material scientists. Use of C_{60} as a veritable storehouse of organic reagents throws up immense possibilities in synthetic organic chemistry. Use of C_{60} in catalysis and organometallic chemistry is equally exciting. Its use as part of polymeric structures is yet to be explored. Meanwhile, synthesis of higher order clusters such as C_{60}, is attracting some attention. There is also the interesting possibility of placing a C_{60} molecule inside the cavity of C_{540}.

Theoreticians are yet to explain the many amazing properties of fullerenes. Though potential applications are many, it is difficult to predict which will become feasible. Applications aside, the science of fullerenes promises to be exciting for some time to come. MMI