

Buckyball C₆₀ – The Story so Far.

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Introduction

'Are there, in nature, behaviours of whole systems unpredicted by the parts? This is exactly what the chemist has discovered to be true.'

Richard Buckminster Fuller

(reputed architect famous for his geodesic dome structures)
in J Baggot's *Perfect Symmetry*.

In the pre-1985 era, only two allotropic forms of carbon viz. diamond and graphite was known. Diamond is a polycyclic aliphatic system known for its extreme hardness. On the other hand graphite can be considered as a layered system of fused aromatic rings and is known for its lubricating properties. The notion of creating hollow graphite balloons in 1966 was dismissed as being merely 'amusing and interesting', but the search for newer cluster forms of carbon formed one of the major research activities of chemists, astrophysicists and biologists to account for the formation of the Universe. The third allotrope was first reported by H W Kroto, R E Smalley, R F Curl and co-workers in 1985. This marked the advent of the fullerene science, which equally enthused chemists, physicists and material scientists.

The Great Accidental Discovery

Harold Kroto, an astrophysical chemist at the University of Sussex, UK had studied the formation of long chain carbon clusters that are formed in the interstellar medium. Using laboratory simulations of the conditions in the atmosphere of cool N-type red giant stars, he had successfully established the production of certain interstellar species like HC₇N and HC₉N. In order to investigate the mechanism, through which carbon

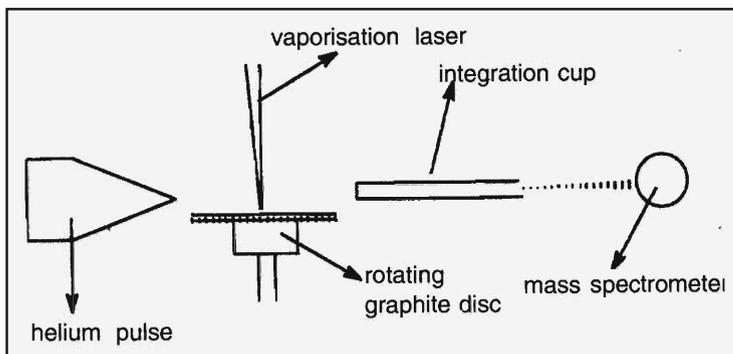


Figure 1.

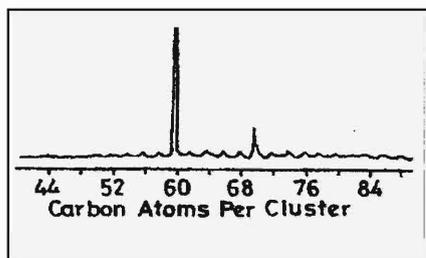
These experiments were based upon the principle that any refractory material can be vaporised when placed at the focus of an intense laser pulse. The vaporized material was entrained into an inert gas (helium) pulse flowing over the surface during vaporization. It was cooled by the carrier gas to allow formation of clusters containing a few to several hundred atoms. After clustering, the gas mixture underwent supersonic expansion into a vacuum with resulting cooling to a few degrees Kelvin. The experimental set-up is shown in *Figure 1*.

Under optimised experimental conditions, the mass spectrum confirmed the presence of C_{60} in extremely large ratio as compared to other fullerene clusters. It also showed the presence of C_{70} (*Figure 2*).

Rationalisation of the Structure

Kroto and others proposed in laser vaporisation, graphite disseminates into pieces of six-membered rings. In terms of many fused ring systems, with unsatisfied valences at the edges, there was not much choice left. A diamond type (tetrahedral) structure would have many unsatisfied valences. Kroto had vivid

Figure 2.



memories of walking through a Fuller's structure at Expo'67 in Montreal. Thus Buckminster Fuller's studies were consulted and the only structure which would satisfy all the sp^2 valences was that of a *truncated icosahedron* (an icosahedron with its vertices chopped off) (*Figure 3*). The striking resemblance of C_{60} with Buckminster Fuller's geodesic domes, and with the

ubiquitous soccer ball has earned it the nickname of 'buckyball'. In fact Kroto's student Jim Heath purchased a football from a nearby sports store to demonstrate to their research group the feasibility of having a ball like structure with sixty vertices.

The possible structure of a spherical shell of sp^2 hybridised carbon atoms can be worked out by Euler's formula. It was noted that it is impossible to construct a spherical structure using only hexagonal faces. As suggested by Jones, pentagonal faces were introduced to distort the structure out of its perfectly spherical symmetry and thus the truncated icosahedron was found suitable for C_{60} . The six-membered rings are stabilised by aromaticity, and the strains of bending the poly-aromatic system out of planarity are uniformly distributed over the surface. Moreover, about 12,500 Kekulé structures existed for this molecule offering further stabilization through resonance. An alternate structure called 'graphitene' consisting of two sheets of seven hexagonal rings, six arranged symmetrically about one, linked by six pairs of carbon atoms connecting pairs of pentagonal rings was put forward by Maier. However it had lesser resonance energy than the truncated icosahedron structure and so it was rejected.

Euler's formula gives an easy way to predict the structure of any C_n cluster (n even and greater than 22). For such clusters there exists at least one closed hollow cage consisting of 12 pentagons and $(n-20)/2$ hexagons. Thus for C_{60} , number of pentagons is equal to twelve and the number of hexagons is equal to twenty.

By 1990, two astrophysicists Kratschmer (Heidelberg) and Donald Huffman (University of Arizona), in an attempt to produce laboratory analogue of interstellar dust, succeeded in synthesizing macroscopic quantities of fullerenes. This greatly facilitated the ongoing research in the field.

Structure and Aromaticity

The proposed structure of C_{60} by Kroto and others perfectly fitted the spectroscopic data. For symmetry reasons, the infra-

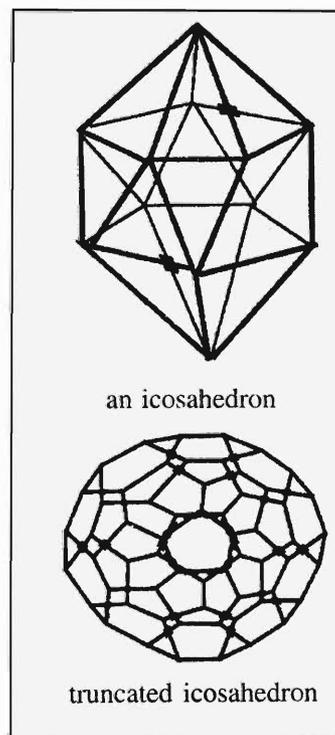


Figure 3.

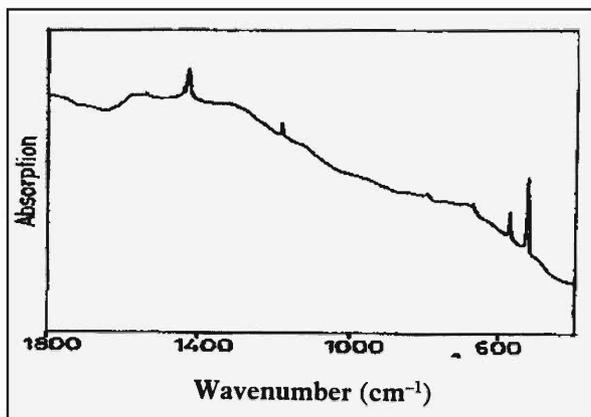


Figure 4.

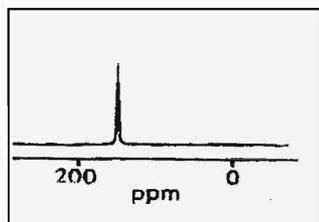


Figure 5.

red spectrum of the soccerball C_{60} should exhibit only four absorptions and indeed this was found to be the case. Out of the 174 vibrational modes giving rise to 42 fundamentals of various symmetries, only four have t_{1u} symmetry and are IR active (1429cm^{-1} , 1183cm^{-1} , 577cm^{-1} , 528cm^{-1}) (Figure 4).

The ^{13}C NMR (Figure 5) of pure C_{60} showed the presence of only one peak at 143 ppm downfield of TMS correspond-

ing to freely rotating molecules. This confirmed the equivalence of all carbon atoms. Despite the aforementioned supporting evidence there lacked definite proof for the soccer ball framework. For example, the single peak of ^{13}C NMR spectrum could arise from coincident peaks or of a fluxional structure. Also the possibility of dodecahedral structure (which too has a I_h symmetry) could not be ruled out. A crystal structure of underivatized C_{60} could not be obtained due to extensive disorder in the crystals. The ball-like molecules were packed in an ordered *fcc* lattice, but due to almost spherical symmetry there was enormous degree of orientational disorder. Hawkins and others (Berkeley) reasoned that if the apparent spherical symmetry of C_{60} was destroyed by its derivatization, it could crystallize with orientational order and hence allow a detailed crystallographic analysis. They succeeded in anchoring the C_{60} molecule in its proper orientation by osmylating it in the presence of pyridine, and thus obtained the first proof of the actual structure of C_{60} (Figure 6).

The spherical shape of the unsaturated carbon network causes the carbon atoms to pyramidalise. This has several consequences:

1. A large amount of strain energy is introduced due to deviation from planarity.
2. The conjugated carbon atoms of fullerenes respond to the

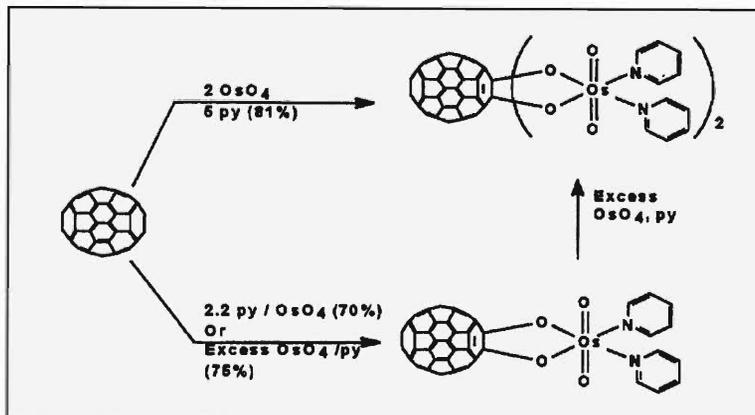


Figure 6.

deviation from planarity by rehybridisation of the sp^2 σ and π -orbitals is applicable only to strictly planar systems.

3. The bonds at the junctions of two hexagons are shorter than the bonds at the junctions of a hexagon and a pentagon. A—B bond length (1.46 Å) is greater than B—C bond length (1.35 Å) (Figure 7). This shows that the pi-delocalisation is not extensive as in case of purely planar systems.

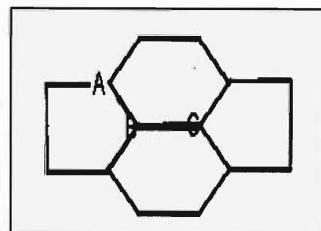


Figure 7.

It is evident (from Figure 8) that C₆₀ has a closed electronic shell and the delocalisation of pi-electrons is sufficient to offset the strain, which anyway is uniformly distributed throughout the spherical structure. Since all its electrons are paired, it is expected to be diamagnetic. More sophisticated *ab initio* calculations have added details to the picture of sixty long (roughly single) and 30 short (roughly double) carbon-carbon bonds. However, the inclusion of C₆₀ in the class of graphite as well as that of benzene complicates the picture and further investigation is required to explain the observables.

Superconductivity in Doped (intercalated) C₆₀

In organic conductors, the presence of pi-electrons is responsible for the electronic transport properties. This is exemplified by the high conduction observed in extended system like polymers and graphite. In molecular systems, the transport properties depend upon the overlap between the pi-orbitals on adjacent molecules. Since the nature of this overlap is crucial, so the



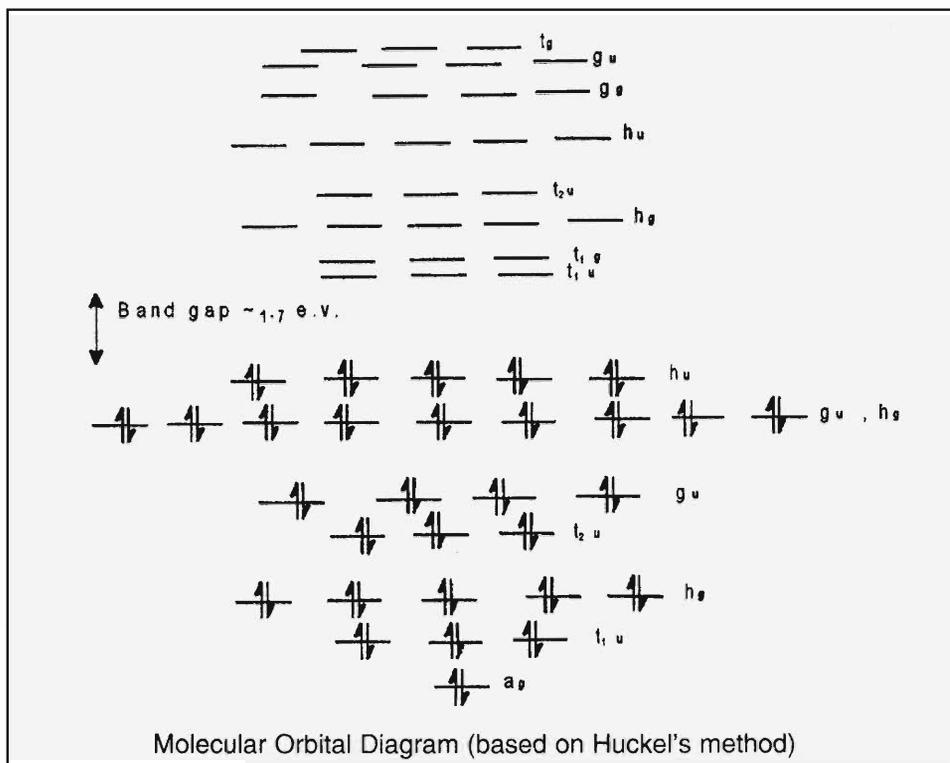
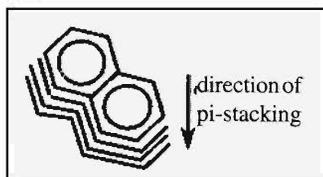


Figure 8.

directionality of the pi-orbitals exerts a profound effect on the resultant electronic properties. For example, in systems like naphthalene, pi-stacking would enhance conductivity (Figure 9). This leads to anisotropy as the conduction band is made up of only those pi-orbitals, which are directed perpendicular to the plane. However, in C_{60} the pi-orbitals are radiating in all directions. Thus if at all an isotropic 3-D molecule conductor could be constructed, C_{60} would be the ideal system. Crystalline films of pure C_{60} are *fcc* lattices having band gap of 1.7 eV which at room temperature is much more than the average thermal energy (kT). Thus at room temperature C_{60} behaves like an insulator. But like silicon, it is possible to dope C_{60} by giving/taking extra electrons and hence forming *n/p type* semiconductors. Due to large size and high electron affinity, C_{60} can be easily doped with alkali metals (the most common ones being potassium, cesium, rubidium, osmium and lanthanum).

Figure 9.



Reactivity of C₆₀

The reactions of C₆₀ are governed by the fact that it is not aromatic in the true sense. Due to this:

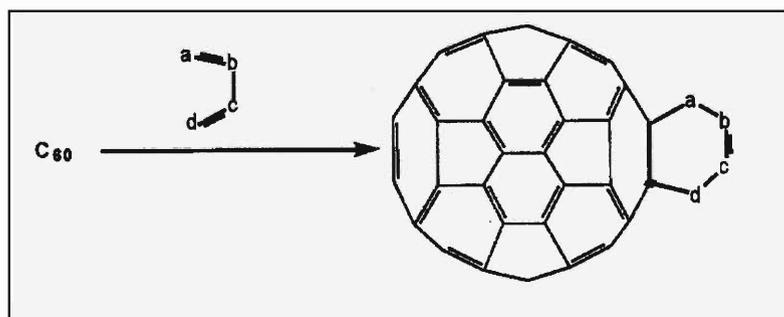
1. The delocalisation of electrons is poor.
2. C₆₀ can be regarded as a huge ball made up of several conjugated alkene units rather than an aromatic molecule.

Since all the carbon atoms are sp^2 hybridised, they exert an $-I$ effect (electron withdrawing) on any double bonds. This makes the molecule electron deficient in nature and hence facilitates nucleophilic attacks on it. This is also reflected in its mild oxidising nature and high electron affinity. Due to these properties, it acts as an excellent electrophile. Owing to its lack of substituents, C₆₀ undergoes addition rather than substitution reactions. The bond at the junction of two hexagons is shorter than the bond at the junction of a hexagon and a pentagon (*Figure 7*). Addition generally takes place at the 6:6 ring junction in an η^2 fashion. The presence of 30 such junctions in C₆₀ leads to a possibility of a wide variety of adducts. The rigidity of C₆₀ introduces eclipsing interactions and thus the C—C bond is strained in its reactions.

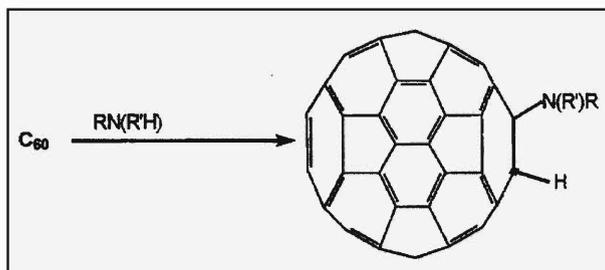
Some typical organic reactions of C₆₀ can be summarised as:

1. Cycloadditions

C₆₀ being an electron deficient molecule proves to be an ideal dienophile for Diels–Alder (2+4) reactions (*Scheme 1*).



Scheme 1.



Scheme 2.

It undergoes retro-Diels–Alder reactions which makes it useful in regio-selective formation of stereochemically defined multiple adducts.

2. Reactions with neutral bases

Neutral nucleophiles like $RN(R)H$ have been found to undergo multiple additions. The reaction appears to occur in a stepwise fashion with electron transfer preceding the covalent bond formation (Scheme 2).

3. Friedel–Crafts fullerication

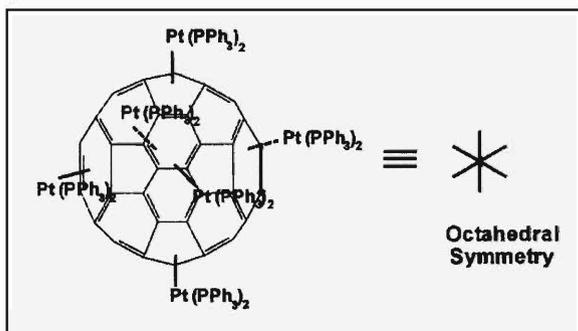
Polychlorinated fullerenes are capable of undergoing Friedel–Crafts reactions with aromatic molecules in presence of catalytic amounts of $AlCl_3$. Weak Lewis acids like BCl_3 , BF_3 , $TiCl_4$ are found to be unreactive.

Organometallic Chemistry of C_{60}

The versatility of organometallic compounds in catalytic and material sciences renders them suitable for possible combinations with C_{60} . The reactivity of C_{60} is comparable to that of electron deficient conjugated olefins, and this is well exemplified by reactions with transition metal complexes.

The first metal complex of the buckyball was synthesised by Paul J Fagan (E I Du Pont de Nemours and Co.) which has an overall octahedral symmetry (Figure 10). It has been observed that the complexations of transition metals to C_{60} take place in a dihapto (η^2) form rather than in η^5 or η^6 binding mode. However, some η^5 -fullerene metal complexes have been synthesised by Sawamura.

Figure 10.



Some typical reactions of C_{60} with transition metal complexes can be classified as:

1. Addition of the metal to the olefinic bond at 6:6 junction.

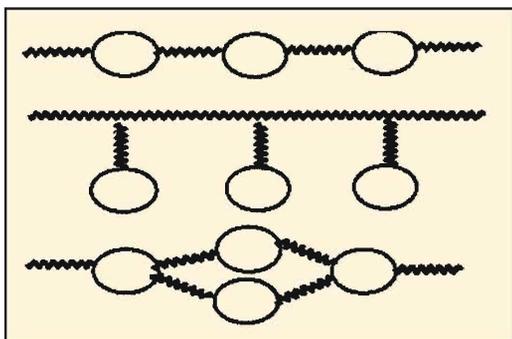


Figure 11.

ever, the toxicity of fullerenes has not been fully established, and this limits their immediate use in biological systems.

c) *Polymers*

Fullerenes have been incorporated in polymers in a variety of modes (Figure 11). The most remarkable properties of such polymers is that they acquire the properties of the fullerenes attached to them. This gives easy access to the design of new materials with varying properties.

d) *Electro-optical materials*

Many donor-acceptor type compounds have been synthesised by making use of the good electron properties of C_{60} . Adducts of C_{60} with pi-conjugated polymers have found extensive applications in photovoltaic devices. Recently 'bucky-light bulbs' have been designed by Rubin and Wudl. Fullerene derivatives have also been reported to exhibit fluorescence at room temperature. This is obviously expected because the rigid structure of C_{60} favours deactivation of the excited state through radiative emission then via internal conversions.

e) *Nanotubes*

Highly diversified technology has come up in the form of carbon nanotubes. These nanotubes can be imagined as elongated fullerenes or 'buckytubes'. Carbon nanotubes are being envisaged as potential shape selective catalysts. Carbon encapsulated materials can be preserved in their pure forms and can be introduced into a chemical reaction in a controlled fashion. These nanotubes are extremely flexible and have extremely high tensile strength. Moreover each nanotube exhibits remarkable conductivity properties ranging from metallic to non-metallic behaviours. Smalley's group is actively working on these lines to develop highly conducting nanowires consisting of large nanotubes doped with metal atoms.



Conclusions

The rich and exciting science of buckyball and related fullerenes has arrived. Its ability to complex with organic as well as inorganic moieties makes it an ideal vehicle for materialising several systems. The abundance of C_{60} amongst other fullerenes reflects the stability rendered by its amazing symmetry. Although several speculations are being made for its vast range of applications, the buckyball has not really reached the industries. However it must be kept in mind that for a fifteen year old molecule to make such a remarkable progress is an achievement by itself. The trio, Harold W Kroto, Robert E Smalley and Robert F Curl have been awarded the Nobel Prize in 1996 for it. The immense potential in this field will continue to pose challenges and entice talented people from all walks of science.

'If God would give me the grace to make one molecule, what would that molecule be?'

Orville Chapman

Acknowledgement

I am thankful to Prof. Pradeep Mathur at IIT, Mumbai for letting me carry out a reaction on the buckyball in his laboratory (in 1998) and in the process, develop a keen interest in me for this field. He was a motivating element in writing of this piece. My thanks are also extended to Prof. Anil K Lala (IIT, Bombay) who encouraged my whim of contributing to this periodical. I am especially grateful to my friends Avinash and Srikanth for helping me in typing the manuscript.

Suggested Reading

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