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Bucky Balls: An Introduction, Discovery and Overview of Their Properties and Applications

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Abstract: **Bucky balls have attracted considerable attention in different fields of science and technology since, 1985. This article reviews Bucky balls and their persistence in science and technology. Investigations of chemical, physical and biological properties of fullerenes have yielded promising information. Many of the practical applications of Bucky balls follow directly from their extraordinary properties. Relevant chemical, physical, biological and optical properties are assessed, which make Bucky balls essential components for the future of Nano electromechanical systems. This paper explores the molecular structure of these molecules and different synthesis methods used nowadays. Also various potential therapeutic applications of fullerenes have been reviewed in this paper. In many cases, the necessity of building organic compounds leads to the exploration of nanostructures like Bucky balls. These molecules bring to the word engineering flexibility and promising applications in electrical, military and medical fields.**

Keywords: **persistence, Bucky ball, Hydrogen Storage, Solar Cells, Synthesis, Molecular Wires, Properties, Structure.**

1. INTRODUCTION

Bucky balls were discovered experimentally for the first time in September 1985. The Buckminsterfullerene, named after the American architect Buckminster Fuller, whose geodesic dome which resembles was observed by a group of scientists including Richard Smalley, Robert Curl and Harry Kroto at Rice University, Huston. For their novel discovery, they shared a Nobel Prize in 1996. [1] Other fullerenes were discovered shortly afterwards with carbon atoms; it ranges from 18 atoms to to hundreds of atoms. Among them, the Bucky ball contains 60 carbon atoms generally. C60 remains the easiest to produce and the cheapest, with prices rising rapidly for other larger fullerenes. In the beginning, the scientists had problem in producing sufficient amount of fullerenes. They had succeeded to prepare only less than 10-15 g. But after 5 years, Kratschmer and Huffmann, [1] and then Kroto developed new high yielding preparative methods for fullerenes.[2] These scientists named the newly found molecule after the architect Richard Buckminster Fuller, who created the dome in 1967 with the same shape as the carbon cluster. Bucky balls generated so much interest and excitement among research scientists that the three scientists who discovered Bucky balls received Nobel Prize in Chemistry in 1996.[3] Fullerenes were later found to exist naturally in interstellar dust as well as in geological formations on Earth, in the ppm-range.. [4][5][6]

2. DISCOVERY

British chemist Harold W. Kroto at the University of Sussex was studying strange chains of carbon atoms found in space through microwave spectroscopy, a science that studies the absorption spectra of stellar particles billions of kilometers away to identify what compounds are found in space. This is possible because every element radiates a specific frequency of light that is unique to that element, which can observed using radio telescopes. The elements can then be identified because a fundamental rule of matter stating that the intrinsic properties of elements apply throughout the universe, which means that the elements will emit the same frequency regardless of where they are found in the universe. Kroto took spectroscopic readings near carbon-rich red giants, or old stars with very large radii and relatively low surface temperatures, and compared them to spectrum lines of well-characterized substances. He identified the dust to be made of long alternating chains of carbon and nitrogen atoms known as cynopolyynes, which are also found in interstellar clouds. However Kroto believed that the chains were formed in the stellar atmospheres of red giants and not in interstellar clouds, but he had to study the particles more closely. At the same time, Richard Smalley was doing research on cluster chemistry, at Rice University in Houston, Texas. "Clusters" are aggregates of atoms or molecules, between microscopic and macroscopic sizes, that exist briefly. Smalley had been studying clusters of metal atoms with the help of Robert Curl, using an apparatus Smalley had in his laboratory. This laser-supersonic cluster beam apparatus had the ability to vaporize nearly any known material into plasma using a laser, which is a highly concentrated beam of light with extremely high energyThrough an acquaintance with Curl, Kroto contacted Smalley and discussed the possibility of using his apparatus to recreate the high-heat conditions of a red giant's atmosphere in order to study the clusters of carbon produced, which might give Kroto insight as to the formation of the carbon chains. Smalley conceded and Kroto arrived in Smalley's laboratory in Rice University on September 1, 1985 whom began working on the experiment along with graduate students J.R. Heath and S.C. O'Brien smalley's apparatus, shown figure 6, fires a high energy laser beams at a rotating disk of graphite in a helium-filled vacuum chamber. Helium is used because it is an inert gas and therefore does not react with the gaseous carbon. The intense heating of the surface of the graphite breaks the CFC bonds because of the intense energy. Once vaporized, the carbon atoms cool and condense in the high-pressure helium gas, colliding and forming new bond arrangements. Immediately upon cooling several degrees above absolute zero in a chamber, the carbon leads to a mass spectrometer for further analysis.

A mass spectrometer uses an atom or molecule's weight and electric charge to separate it from other molecules. This is done by ionizing the molecules, which is done by bombarding the molecules with high energy electrons which then knocks of electrons. If an electron is removed from an otherwise neutral molecule, then the molecule becomes a positively charged ion or cation. The charged particles are then accelerated by passing through electric plates and then altered through a slit. A stream of charged particles exits the slit and is then deflected by a magnetic field into a curved path. Because all the particles have a charge of +1, the magnetic eld exerts the same amount of force on them, however, the more massive ions are deflected less, and thus a separation occurs. By adjusting the strength of the accelerating electric plates or the deflecting magnetic field, a specific mass can be selected to enter the receptor on the end. After adjusting the experiment, it became greatly evident that the most dominant molecule measured was 720 amu (atomic mass units). By dividing this number by the mass of a single carbon atom (12 amu), it was deduced that the molecule was comprised of 60 carbon atoms (720 / 12 = 60).

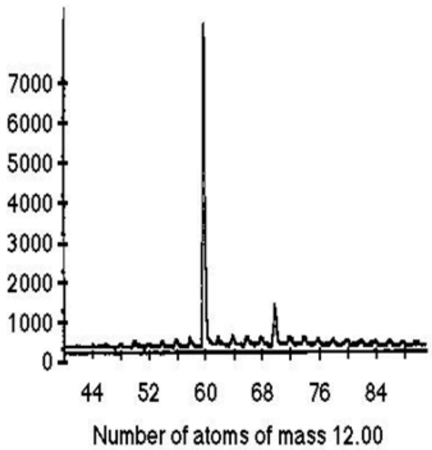

Figure 1: University of Wisconsin [5]

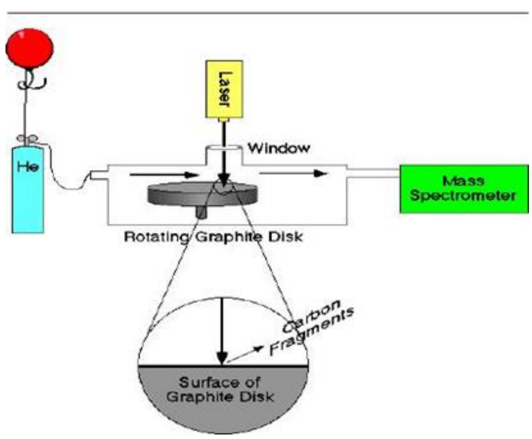

fig 2

The next task was to develop a model for the structure of C60, this new allotrope of carbon. Because it was overwhelmingly dominant, Smalley reasoned the molecule had to be the very stable. The preferred geometry for stable molecule would reasonably be spherical, because this would mean that all bonding capabilities for carbon would be satisfied. If it were a chain or sheet like graphite, the carbon atoms could still bond at the ends, but if it were circular all ends would meet. Another hint as to the arrangement of the molecule was that there must be a high degree of symmetry for a molecule as stable as C60. Constructing a model that satisfied these requirements was fairly dicult and the group of scientists experimented with several models before coming to a conclusion. As a last resort, Smalley made a paper model by cutting out paper pentagons and hexagons in which he tried to stick them together so that the figure had 60 vertices. Smalley found that he create a sphere made out of 12 pentagons interlocking 20 hexagons to make a ball. The ball even bounced. To ensure that the shape fulfilled the bonding capabilities of carbon, Kroto and Curl added sticky labels to represent double bonds. The resulting shape is that of a truncated icosahedron, the same as that of a soccer ball. Smalley, Curl, and Kroto named the molecule buckminsterfullerene after the American architect and engineer Richard Buckminster Fuller who used hexagons and pentagons for the basic design of his geodesic domes. Eleven days after they had begun, the scientist submitted their discovery to the prestigious journal Nature in a manuscript titled "C60 Buckminsterfullerene". The journal received it on the 13th of September and published it on the 14th of November 1985. The controversial discovery sparked approval and criticism for a molecule that was remarkably symmetrical and stable. [7][8][9]

3. STRUCTURE

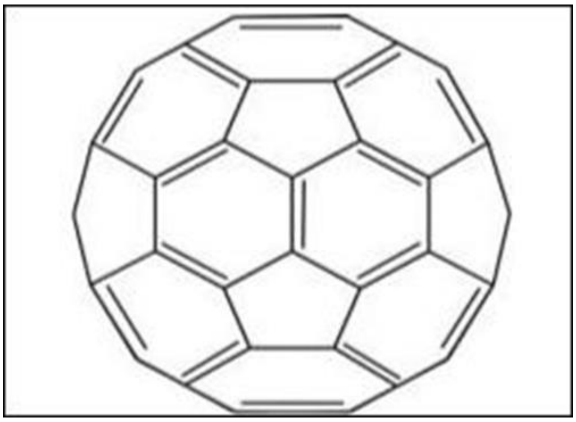

Fig. 3: Bucky ball C_{60} arranged in spherical structure with Carbon at each vertex

Bucky balls are large carbon cage molecules (Fig.3) considered to be three-dimensional analogues of benzene. The most abundant form of fullerenes is Buckminster fullerene (C_{60}) with 60 carbon atoms arranged in a spherical structure. The shape of the molecule, known as truncated icosahedrons, [1] resembles that of a soccer ball, which contains 12 pentagons and 20 hexagons. Fullerenes fulfill the EULER's theorem, i.e., if a polyeder is to build a closed structure from pentagons and hexagons; it has to contain exact 12 pentagons. Following this rule, the smallest stable fullerene is C_{60}, which has no two pentagons side by side, making it the most stable structure

4. SYNTHESIS OF FULLERENES

In 1990, Krätschmer and his colleagues developed a contact arc discharge method for macroscopic production, known as the Krätschmer-Huffman method. They discovered that carbon rods heated resistively in a helium atmosphere cloud generate gram quantities of fullerenes embedded in carbon soot, which was also produced in the process. This method consists of graphite electrodes contact arcs passing alternating or direct current through them in an atmosphere of helium in approximately 200 torr. The evaporated graphite takes the form of soot, which is dissolved in a non polar solvent. The solvent is dried away and the C60 and C70 Bucky balls can be separated from the residue. Optimal current, helium pressure and flow rate leads to yields of up to 70% of C60 and 15% of C70 with this method. Laser vaporization is also used for fullerene production. In a typical apparatus a pulsed Nd:YAG laser operating at 532 nm and 250 mJ of power is used as the laser source and the graphite target is kept in a furnace at 1200 °C. Finally, it should be mentioned that fullerenes have also been produced in soothing flames involving, for example, the combustion of benzene and acetylene, although the yields are low.[10]

PROPERTIES:

Bucky balls' most relevant properties are presented. The study of these properties led scientists to think of the multiple applications that the molecule could have.

Chemical Properties:

The carbon atoms within a Bucky balls molecule are sp^2 and sp^3 hybridized, of which the sp^2 carbons are responsible for the considerably angle strain presented within the molecule. C60 and C70 exhibit the capacity to be reversibly reduced with up to six electrons. This high electron affinity results from the presence of triply-degenerate low-lying LUMOs (lowest unoccupied molecular orbital). Oxidation of the molecule has also been observed; nevertheless, oxidation is irreversible. C60 has a localized pi-electron system, which prevents the molecule from displaying superaromaticity properties.

Physical Properties:

Bucky balls are extremely strong molecules, able to resist great pressures—they will bounce back to their original shape after being subject to over 3,000 atmospheres. Theoretical calculations suggest that a single C60 molecule has an effective bulk modulus of 668 GPa when compressed to 75% its size [3]. This property makes fullerenes become harder than steel and diamond, whose bulk moduli are 160 GPa and 442 Gpa, respectively. An interesting experiment shows that Fullerenes can withstand collisions of up to 15,000 mph against stainless steel, merely bouncing back and keeping their shapes. This experiment resembles the high stability of the molecule.

Optical Properties:

Delocalized pi electrons in Bucky balls are known to provide exceptionally large nonlinear optical responses. Bucky balls have shown particular promises in optical limiting and intensity-dependent refractive index. Additionally, the transfer of electrons from enclosed atom(s) to the Bucky balls enhances the third-order nonlinear optical effect by orders of magnitude compared to empty cage Bucky balls.

APPLICATIONS:

Hydrogen Gas Storage:

Due to its unique molecular structure, fullerene is the only form of carbon, which potentially can be chemically hydrogenated and de-hydrogenated reversibly.[11] When fullerenes are hydrogenated, the C=C double bonds become C-C single bonds and C- C bonds is 83 kcal/mole, and theoretical calculations show that the bond strength of the hydrogenated C-H bond is 68 kcal/mole[11] . This means that for fullerene hydrides, the H-C bond is appreciably weaker that C-C bonds. Therefore, when heat is applied to fullerene hydrides, the H-C bonds will break before the C-C bonds, and the fullerene structure should be preserved. The considerably lower heat of formation for C60H36 indicates that C60H36 as a molecule is thermally more stable than C60. Therefore, hydrogenation of C60 is thermodynamically favored and can be accomplished under the right chemical conditions. The color of the hydrogenated fullerene changes from black to brown, then to red, orange, and light yellow with increasing hydrogen content. Fullerenes with up to 6.1% hydrogen content has been developed experimentally [11]. A potential application of fullerene hydrides is in hydrogen gas storage devices for electric vehicles that would employ a fuel cell. Currently available hydrogen storage technologies like compressed gas or storage as metal hydrides are potentially hazardous and/or have low hydrogen storage densities. Table 1 [11] shows a comparison of the amount of media required for storage when using Bucky balls versus a metal hydride. The metal hydride storage media used in this comparison is Titanium, Zirconium.

Table 1: Comparison of Hydrogen storage capacities for internal combustion engines

Comparison of Hydrogen Storage Capacities for Internal Combustion Engines		
	Fullerenes	Metal Hydride
Hydrogen Required to Operate 250 Miles	12 lbs	12 lbs
Amount of Storage Media Required	197 lbs	1200 lbs

Solar Cells:

The high electron affinity and superior ability to transport charge make Bucky balls the best acceptor component currently available. First, they have an energetically deep-lying LUMO, which endows the molecule with a very high electron affinity relative to the numerous potential organic donors. The LUMO of C60 also allows the molecule to be reversibly reduced with up to six electrons, thus illustrating its ability to stabilize negative charge[.12] Importantly, a number of conjugated polymer–fullerene blends are known to exhibit ultrafast photo induced charge transfer, with a back transfer that is orders of magnitude slower. The state of the art in the field of organic photovoltaic is currently the Bulk Hetero junction (BHJ) solar cells based on Bucky balls derivate phenyl- C61_butryric acid methyl ester (PCBM), whit reproducible efficiencies approaching 5 %[13]. Conventional silicon solar cells exceed 20% efficiency. Therefore, we can ask ourselves, why is it so important to think of organic solar cells? First, the cost of production of organic light-converting devices compared to the corresponding inorganic analogues is lower by more than two orders of magnitude. And second, an important merit of organic solar cells is their flexibility. They can be rolled up, cut, and spread over any surface. Particularly, such plastic can be used for covering both the inner and outer walls of buildings; cells of any color and texture can be manufactured. For example, a cell phone can be painted with this material, thus walking in a sunny day will be enough to charge the device's battery. American military departments actively support projects associated with organic solar cells because these materials demonstrate high capabilities to be used in new armaments and attendant systems[14]. Finally, great expectations are also associated with the use of organic cells in the advertising and packaging business. These involve autonomous luminous banners, large liquid-crystal line displays and packaging for food.

Fullerene Strengthening/Hardening of Metals:

Fullerenes offer unique opportunities to harden metals and alloys without seriously compromising their ambient temperature ductility. This is due to the unique characteristics of fullerenes, namely their small size and high reactivity, which enable the dispersion strengthening of metallic matrices with carbide particles that result from in-situ interactions between fullerenes and metals. In a comparison of the hardness of a popular aerospace intermetallic compound Ti-24.5AI-17Nb, with and without fullerene additives, a 30% hardness enhancement was measured for the material with fuller ne additives [15].

Optical Application of Fullerene:

Optical limiting refers to a decrease in transmittance of a material with increased incident lightintensity. The phenomenon of optical limiting has a significant potential for applications in eye and sensor protection from intense sources of light. Based on the optical limiting properties of Bucky balls, one can make an optical limiter, which allows all light below an activation threshold to pass and maintains the transmitted light at a constant level below the damage threshold for the eye or the sensor [11] Figure 4 shows the typical performanceof an optical limiter.

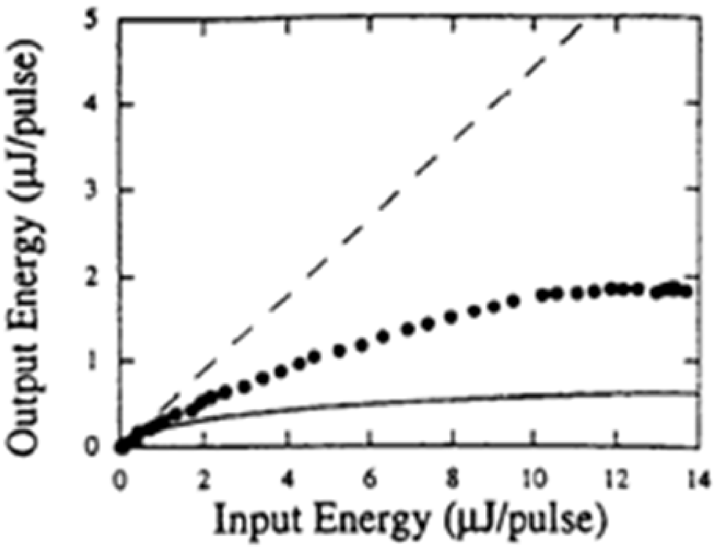

Figure 4: The typical performanceof an optical limiter

Bucky balls Based Sensors:

Bucky balls -based interdigitated capacitors (IDCs) recently have been developed to explore sensor applications. This novel solid-state sensor design is based on the electron accepting properties of fullerene films and the changes that occur when planar molecules interact with the film surface. Bucky balls chemistry provides a high degree of selectivity and the

IDC design provides high sensitivity. The solid-state chemical sensor's small size, simplicity, reproducibility and low cost make them attractive candidates for fullerene applications development. Studies of IDC configurations with fullerene films have able to sense water in isopropanol with a resolution of 40 ppm[11]. These results demonstrate the feasibility of using fullerenes as selective dielectric films for IC chemical sensors.

Bucky balls as Molecular Wires:

Recent experiments have documented electron transport through single molecules. Under certain experimental conditions molecular conduction through a single molecule rather than through an ensemble of molecules is guarantee. This phenomenon is possible due the high electron affinity of Fullerenes. If a molecular computer is ever to be built, then it will need molecular wires in order to connect to its various components. Figure 5 shows a computer created scenario of a possible use of Fullerenes in the manufacture of molecular conductors. When a source of UV light is applied to the system in figure 6, the Fullerene molecules get excited and electrons move from the Porphyrin wire towards the Fullerenes. These electrons leave holes in the Porphyrin through which electrical current can flow from one electrode to the other[16].

Bucky balls in Medicine:

Interest of scientists in water-soluble fullerene compounds is directly related to their biological activity. Dendrimer 4p containing[18]carboxyl groups is the more promising today. The synthesis and the use of this compound in medicine were patented in the U.S. (C-sixty Corporation); at present, this drug undergoes clinical trials as a promising medication for treatment of AIDS [17]. Fullerene derivatives can be used in the photodynamic cancer therapy as antibacterial agents and medications of neuroprotective action. Because of their ability to enclose atoms, Fullerenes promise to be of great use as drug carriers. Additionally, noble gases have been encapsulated in Fullerenes, which have no desire to bond with the surrounding carbon atoms but can be used in applications such as magnetic resonance imaging (MRI). Researchers at Rice University have designed C60 and other fullerenes molecules with an atom of gadolinium inside and with chemical appendages that make them water-soluble. In typical MRI contrast agents, the metal gadolinium is lined to a non-fullerene molecule, which is normally excreted quickly from the body. Fullerenes encapsulated with gadolinium might allow the contrast agent to remain in the body longer, allowing doctors to perform slower studies.

Endohedral Bucky balls:

Endohedral Fullerenes are created when an atom is inserted inside a Fullerene molecule. Figure 4 illustrates an example of a Fullerene containing a non-carbon atom inside.

In one of the methods employed for this purpose, ions are accelerated and implanted to the C60 cage. The first collision should absorb and redistribute a good part of the kinetic energy to ensure that the ions have just enough energy to open the cage and enter, without having sufficient kinetic energy left to escape.

Metallofullerenes made this way include M@C60 with M =Li, Ca, Na, K, Rb. Larger yields can be achieved by co-evaporation of the carbon and the metal in an arc discharge chamber (typical for fullerene production). However, in this process mostly higher endohedral fullerenes, like M@C82, are formed. These Metallofullerenes are very stable molecules and can be use in many applications. For example, it has been shown that the bulk modulus of K@C60 is higher than that of C60, and while C60 rolling dynamics are the same as K @C60 rolling dynamics, the sustaining pressure of K @C60 intercalated between layers was higher than that of C60 intercalated between layers. From this it can be concluded that for nano ball-bearing applications, Metallofullerenes are more effective than fullerene. A crystal of La@C60 is predicted to be an air-stable superconductor since there is a complete charge transfer from La to the C60 cage resulting in a triply charged molecule. Finally, we want to make use of the spin dynamics of the endohedral fullerenes N@C60 and P@C60 in molecular spin electronic devices such as a quantum computer. Because the C60 fullerene shields the incorporated nitrogen or phosphorus atom from the environment, these molecules have exceptional spin properties, notably very long electron spin relaxation times [18].

BIOLOGICAL APPLICATIONS OF FULLERENES:

Fullerenes are inert, hollow and indefinitely modifiable. When administered orally in the water-soluble form, they are not absorbed; while on i.v. injection, they get rapidly distributed to various body tissues. They are excreted unchanged by kidney[19]. Acute toxicity of water-soluble fullerenes was found to be quite low.[20] All these interesting properties offer possibilities of utilizing fullerenes in biology and medicinal chemistry and promise a bright future for fullerenes as medicinal agents. However, this possibility faces a significant problem, i.e., natural repulsion of fullerenes to water. To overcome this limitation, a number of methodologies are being developed. These include synthesis of fullerene derivatives having modified solubility profile, encapsulation of C_{60} in cyclodextrins[21] or in calixarenes [22] or water suspension preparations [23] many derivatives of fullerenes have been synthesized. There have been many patents written on fullerenes, and fullerene patent database is growing rapidly. Fullerenes and their derivatives are being intensively investigated as they exhibited promising preliminary activities in the following medical streams.

Diagnostic applications:

Endohedral metallofullerenes are the fullerenes with metal ion trapped inside fullerene cage. These have shown potential applications in diagnostics. As for example, water solublised forms like $M@C_{82}(OH)_{30}$ are being used as Magnetic Resonance Imaging contrast agents ($M=Gd^{3+}$),[24] X-ray contrast agents ($M=Ho^{3+}$)[25] and radiopharmaceuticals ($M={}^{166}Ho^{3+}$and ${}^{170}Tm^{2+}$)[26,27]. One of these derivatives, i.e., ${}^{166}Ho^{3+}@C_{82}(OH)_{30}$ has been extensively studied as radioactive tracer for imaging of diseased organs and for killing cancerous tumours. The radioactive metal is trapped inside the carbon shell, which is very stable and resistant to metabolism by body. The metallofullerenes have been found to be non-toxic, and they stay in the body for approximately one hour, allowing imaging of circulatory system.[21]

AntiHIV activity:

The enzyme protease specific to HIV-1 has been shown to be a viable target for antiviral therapy. The active site of this enzyme can be roughly described as an open-ended cylinder lined almost exclusively by hydrophobic amino acids except for two catalytic aspartic acids. Wudl *et al* hypothesized that since C_{60} molecule has approximately same radius as the cylinder that describes the active site of HIV-P, an opportunity exists for a strong hydrophobic interaction between C_{60} derivatives and the active site surfaces. Inhibition of HIV-P in presence of C_{60} was demonstrated through molecular modelling studies and experimental observations.[28] Virus inactivation assays confirmed the activity of fullerene derivatives against HIV-1 and HIV-2 [29,30] A water-soluble derivative was found to be active against HIV-1 and HIV-2 (EC_{50} approximately 6 μM) in acute and chronic infected human lymphocytes and also noncytotoxic up to100 μM in peripheral mononuclear cells and H9, Vero and CEM cells.[31]As the binding constant found experimentally was not significant in terms of affinity, structural optimization of C_{60} derivatives for HIV-P interaction was investigated. On this basis, some authors proposed ideal inhibitors, in which two ammonium groups at distance of 5.5 Å or 5.1 Å are directly linked to C_{60}. Molecular modeling studies on these derivatives showed that they could fit well inside the HIV-P cavity and can interact with carboxylic residues of aspartatic acid. [30]

5. CONCLUSION

Bucky balls are the third form of carbon and they have become most important molecules in the field of science and technology. Due to their very practical properties, nowadays bucky balls are a key topic in nanotechnology and industrial research. The applications presented in this paper are possible uses of these molecules due to one or more of their extraordinary properties. Fullerenes are used in today's industry already, mostly in cosmetics, where they play an important role as antioxidants. The cost of Fullerenes is directly related to the feasibility of implementing several of the applications discussed in this paper. As more applications of Fullerenes become available, the demand for these molecules will increase and we will be able to see a significant decrease on the price of Fullerenes per gram compared to today's market value.

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