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The Third Allotrope of Carbon: Fullerene an Update

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Abstract: There were only three known forms or allotropes of carbon molecules - diamonds (tetrahedral arrangement which is the strongest making it a very hard substance), graphite or pencil lead (lattice sheets) and soot or charcoal which has no crystalline structure. The newly discovered allotrope of carbon i.e, fullerene family, are extremely useful in modern as well as biological applications such as nanotechnology, electronics, architecture, construction, optics, enzyme inhibition, antiviral activity, DNA cleavage, photodynamic therapy, electron transfer, and other in vitro and in vivo biological effects. Fullerenes are graphitic cage structures incorporating exactly twelve pentagons and undergo various chemical reactions. This review deals with various progresses in studies of fullerenes and their applications.

Keywords: Third Allotrope, Carbon: Fullerene.

Introduction

Ever since their experimental discovery in 1985,[1] fullerenes have attracted considerable attention in different fields of sciences. The keen interest in fullerenes is due to much of unusal physical and chemical properties as well as diversity of their behavior at various conditions. The discovery and availability in large quantity of fullerenes have stimulated their extensive research in a wide variety of fields such as physics, chemistry, material science, biology etc. Their unique carbon cage structure coupled with immense scope for derivatization makes fullerenes a potential therapeutic agent.[2] Initially fullerenes are viewed as aromatic and quite chemically inert molecules, fullerenes can actually undergo various chemical reactions[3] such as nucleophilic addition, Diel's Alder reaction, 1,3-dipolar cycloaddition, radical addition, oxidation, reduction etc.

Various solvent free mechanochemical reactions of fullerenes have also been investigated. Most of the studied mechanochemical reactions of fullerenes were done by high energy high speed vibration milling technique (HSVM), and many fewer reactions were done by low energy ball milling and hand grinding.[4]

The discoveries of single-walled carbon nanotubes have provided the opportunity to study their mechanical, optical and electronic properties. Specifically, their electronic characteristics are predicted to vary depending upon the nanotube symmetry and diameter, thus giving either metallic or semiconducting behaviour. It is very important for the creation of novel materials for nanoengineering.

Various extraction and chromatographic techniques are currently employed for the isolation of fullerenes because of their immense applications in various fields.[5,6]

Fullerenes include -

Fullerenes: The classical definition of a fullerene is a compound composed solely of an even number of carbon atoms which form a cage-like fused-ring polycyclic system with 12 five-membered rings and the rest six-membered rings; the archetypal example is the 60-atom structure, where the atoms and bonds delineate a truncated icosahedron. However, the term has been broadened to include any closed-cage structure having 20 or more carbon atoms consisting entirely of 3 coordinate carbon atoms.

Fulleranes: Fulleranes are fully saturated fullerenes, for example, the hydrocarbon $C_{60}H_{60}$.

Fulleroids: Heterofullerenes, norfullerenes, homofullerenes, and secofullerenes have been called fulleroids (fullerene-like) because they resemble fullerenes in structure but do not conform to the definition of a fullerene as given above. It is convenient to refer to them as fulleroids and name them as modified fullerenes.

Nomenclature

The general problem of fullerene nomenclature has been first considered by R. Taylor. He proposed the numbering of atoms in those fullerene isomer that were isolated so far. However the proposal was intended mainly to bring some order into naming fullerene derivatives which were being produced at an increasing rate. An approved IUPAC recommendations for naming and numbering the C60-I_h and C_{70}-$D_{5h(6)}$ fullerenes and their derivatives was prepared in year 2002. There are two system for naming-

a) **Systematic names** The recommended systematic names for the icosahedral C_{60} and the $D_{5h(6)}$-C_{70} fullerenes are (C_{60}-I_h)[5,6]fullerene and (C_{70}-$D_{5h(6)}$)[5,6]fullerene. The parenthetical prefix gives the carbon content and the point group symbol; and the bracketed numbers indicate the ring sizes in the fullerene. The latter is important in fullerenes with rings other than five- and six-membered. The subscript parenthetical (6) following the point group symbol *D*5h in the latter name indicates that the five-membered ring on the five-fold symmetry axis is surrounded by six-membered rings. This differentiates this fullerene from an isomeric (C_{70}-D_{5h})[5,6]fullerene, which has five-membered rings surrounding the five-membered ring on the five-fold symmetry axis, which would have the name (C_{70}-$D_{5h(5)}$)[5,6]fullerene. This technique is being further evaluated to determine its value for differentiating among other fullerenes with degenerate point group symbols.

b) **Trivial names** The names [60-I_h]fullerene and [70-D_{5h}]fullerene given in the IUPAC Preliminary Survey are names first introduced into the literature for the C_{60}-I_h and C_{70}-$D_{5h(6)}$ fullerenes. Since important structural information is omitted from these names, they are to be considered as trivial names to be used only for these specific compounds.[7-12]

Classification

Several topological descriptors have been proposed to evaluate and classify the topological structure of fullerene isomers: the pentagon adjacency index NP, the Wiener index WI, the resistance distance RT, the Kekulé structure count, the graph independence number, the number of spanning trees, the combinatorial curvature, the bipartivity measure of fullerene graphs, the occurrence number of different structural motifs in fullerenes.

In the majority of cases, for the stability prediction of lower fullerene isomers C_n with $n \leq 70$ the pentagon adjacency index N_P (the so-called minimal-N_P criterion) is used and according to the minimal-N_P rule it is supposed that fullerenes which minimize N_P are more likely to be stable than those that do not. Consequently, it is believed that the buckminsterfullerene is the most stable C_{60} fullerene, because this is the only one for which N_P has a minimum value ($N_P = 0$).[13,14]

Types of fullerene

Structural variations on fullerenes have evolved well beyond the individual clusters themselves. Examples include-

a) Buckyball clusters: smallest member of these groups include C_{20} and the most common is C_{60}.

b) Nanotubes: hollow tubes of very small dimensions, having single or multiple walls.

c) Megatubes: larger in diameter than nanotubes and prepared with walls of different thickness.

d) Polymers: two-dimensional and three-dimensional polymers are formed under high-pressure high-temperature conditions.

e) Nano"onions": spherical particles based on multiple carbon layers surrounding a buckyball core; proposed for lubricants.

f) Linked "ball-and-chain" dimers: two buckyballs linked by a carbon chain.

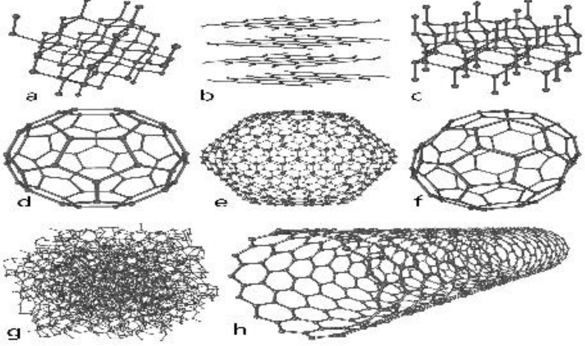
g) Fullerene rings.[15]

Structure

Carbon bonds undergo catenation and give rise to different shapes, demonstrating different properties. One of the famous substances containing carbon is diamond, a carbon allotrope, the bounds form an inflexible three-dimensional lattice, and this unique shape accounts for the strength displayed by diamond. Another carbon allotrope is graphite, in which carbon atoms are planimetrically arranged but are stacked in layers. The third carbon allotrope is fullerene, it is a family of caged compounds composed of only carbon elements. A fullerene C_n consists of 12 pentagonal rings[16] and any number of hexagonal ones, m, such that $m = (C_n - 20)/2$ (Euler's Theorem)[17] linked together to form a geodesic dome. Structure of these fullerenes resembles as a soccer ball and the typical diameter of a fullerene molecule is 0.7 nm.[18]

Fig- Allotropes of carbon

a) Diamond b) Graphite c) Lonsdaleite d) C60 (e) C540 f) C70
g) Amorphous carbon h) single-walled carbon nanotube



Solubility

A deeper understanding of the interaction of fullerenes with various solvents will allow rational choice of solvents capable of purifying fullerenes by cheaper and scalable methods.

Solubility of fullerenes in various solvents-[19]

Solvent	**Solubility (mg/ml)**
n-pentane	0.005
n-hexane	0.043
Cyclohexane	0.036
Choloroform	0.16
Dichloromethane	0.26
1,2-dibromomethane	0.50
Methanol	0.000
Acetone	0.001
Benzene	1.7
Xylenes	5.2
1-methylnaphthalene	33
1-pheylnaphthalene	50

Physical properties[20]

Appearance	Black/brown powder
Odor	odorless
Density	1.65 g/cm^3
Standard heat of formation	9.08 k cal/mol
Refractive index	2.2 (600nm)
Boiling point	Sublimes at 800K
Resistivity	1014 ohms/m
Crystal form	Hexagonal cubic
Vapour pressure	5 × 10^{-6} torr at room temperature
Compressibility	6.9 × 10^{-12} cm^2dyn
Young's modulous	15.9 GPa
Debye temperature	100 K
Bulk modulous	8.8 GPa

Chemical properties

At an early stage of investigations it was supposed that fullerenes ought to be chemically inactive and relativity stable. However it has been later proved that fullerenes participate in various chemical reactions. Fullerenes are also proved to be strong acceptor of electrons in presence of many organic and inorganic donors. There chemical activity results from an easy breakage of one of the double bond. In later experiments a way to break single bond has been found thus allowing preparation of various types of C_{60} adducts compound. Regioselective formation of multiple adducts has allowed study of the changes in chemical and physical properties that occur when the conjugated fullerene chromophore is reduced during an increase in functionalization. Functionalized fullerenes are divided into two classes: exohedral with substituents outside the cage and endohedral fullerenes with trapped molecules inside the cage.

Nucleophilic addition

Fullerenes react as electrophiles with a host of nucleophiles in nucleophilic additions. The intermediary formed carbanion is captured an electrophile. Examples of nucleophiles are Grignard reagents and organolithium reagents. For example the reaction of C_{60} with methylmagnesium chloride.[21,22]

Hydroarylation reaction

Fullerene reacts with chlorobenzene and aluminium chloride in a Friedel-Crafts alkylation type reaction. In this hydroarylation the reaction product is the 1,2-addition adduct (Ar-CC-H).[23]

Cycloaddition

The [6,6] bonds of fullerenes react as dienes or dienophiles in cycloadditions for instance Diels-Alder reactions. 4-membered rings can be obtained by [2+2]cycloadditions for instance with benzyne.

An example of a 1,3-dipolar cycloaddition to a 5-membered ring is the Prato reaction.[24]

Hydrogenation

Fullerenes are easily hydrogenated by several methods with $C_{60}H_{18}$ and $C_{60}H_{36}$ being most studied hydrofullerenes. However, completely hydrogenated $C_{60}H_{60}$ is only hypothetical because of large strain. Highly hydrogenated fullerenes are not stable, prolonged hydrogenation of fullerenes by direct reaction with hydrogen gas at high temperature conditions results in collapse of cage structure with formation of polycyclic aromatic hydrocarbons. [25-27]

Hydroxylation

Fullerenes can be hydroxylated to fullerenols or fullerols by various methods. One method is fullerene reaction in diluted sulfuric acid and potassium nitrate to $C_{60}(OH)_{15}$. Another method is reaction in diluted sodium hydroxide catalysed by TBAH adding 24 to 26 hydroxyl groups.[28]

Electrophilic additions

Fullerenes react in electrophilic additions as well. The reaction with bromine can add up to 24 bromine atoms to the sphere. The record holder for fluorine addition is $C_{60}F_{48}$. According to in silico predictions the as yet elusive $C_{60}F_{60}$ may have some of the fluorine atoms in endo positions (pointing inwards) and may resemble a tube more than it does a sphere.[29]

Oxidation reaction

Although more difficult than reduction, oxidation of fullerene is possible for instance with oxygen and osmium tetraoxide.[30]

Method of production

Pure graphitic carbon soot with a few per cent by weight of C_{60} molecules is produced by evaporating graphite electrodes in an atmosphere of about 100 torr of helium. The resulting black soot is gently scraped from the collecting surfaces inside the evaporation chamber and dispersed in benzene. The material giving rise to the spectral features attributed to C_{60} dissolves to produce a wine-red to brown liquid, depending on the concentration. The liquid is then separated from the soot and dried using gentle heat, leaving a residue of dark brown to black crystalline material. Other non-polar solvents, such as carbon disulphide and carbon tetrachloride, can also dissolve the material.

An alternative concentration procedure is to heat the soot to 400°C in a vacuum or in an inert atmosphere, thus subliming the C_{60} out of the soot. The sublimed coatings are brown to grey, depending on the thickness. The refractive index in the near-infrared and visible is about two. To purify the material, remove the ubiquitous hydrocarbons before the concentration procedure is applied (for example, by washing the initial soot with ether). Thin films and powder samples of the new material can be handled without special precautions and seem to be stable in air for at least several weeks, although there does seem to be some deterioration with time for reasons that are as yet unclear. The material can be sublimed repeatedly without decomposition. Using the apparatus described, one person can produce of the order of 100 mg of the purified material in a day.[31]

Application

Starting soon after the production of fullerenes in 1990, many efforts have been devoted to the application of C_{60} and its derivatives. In fact, fullerene possesses a variety of interesting biological properties, such as HIV-P inhibition, DNA photocleavage, neuroprotection, apoptosis, etc.[32] Unfortunately, the low solubility in biological fluids limits the use of these compounds as new pharmacophores for structure-activity relationship studies in medicinal chemistry.[33] Fullerenes are also used in electronic, optic, medical, and cosmetic applications.

- Earlier experiments performed by Wudl and coworkers demonstrated that there is inhibition of the HIV-P in the presence of C_{60} and are therefore useful in fighting the HIV virus that leads to AIDS.
- Easy photoexcitation of fullerenes results in formation of various species which helps in DNA photocleavage.
- C_{60} could produce membrane disruptions by insertion into phospholipidic bilayers and hence have antibacterial activity.[34]
- Fullerenes are powerful antioxidants, reacting readily and at a high rate with free radicals, which are often the cause of cell damage or death.[35]
- Fullerenes have a property of neuroprotection, they control the neurological damage of diseases such as Alzheimer's disease and Lou Gehrig's disease (ALS).
- Fullerenes and fullerenic black are chemically reactive and can be added to polymer structures to create new copolymers with specific physical and mechanical properties.
- Fullerenes are used in formation of organic photovoltaics (OPVs). The most commonly used fullerene derivative in OPV applications is PCBM.[36,37]
- Fullerenes have marked ability to accept and to transfer hydrogen atoms, so they can be used as catalyst in hydrogenation and hydrodealkylations.

- Fullerenes are used in water purification & bio-hazard protection due to singlet oxygen catalysis of organics properties of C_{60}.
- Fullerenes are more sensitive MRI contrast agents.
- Fullerenes are exceptional free radical scavengers.
- Fullerene derivatives are critically affects Mast cell responses and used in allergy treatment.[38]
- Fullerene black/rubber compounds enhanced durability of vehicles, lower the heat build-up and give better fuel economy.

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