

# THEORETICAL STUDIES OF STABILITY AND REACTIVITY OF LOWER FULLERENES

A DISSERTATION

*Submitted in partial fulfillment of the  
requirements for the award of the degree*

*of*

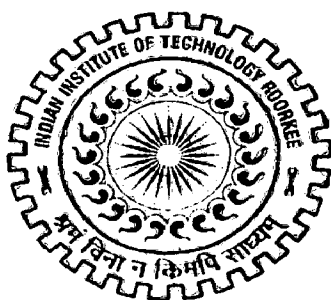
MASTER OF TECHNOLOGY

in

ADVANCED CHEMICAL ANALYSIS

By

**SRIDHARAN SRINATH**



DEPARTMENT OF CHEMISTRY  
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE  
ROORKEE -247 667 (INDIA)  
JUNE, 2007

***DEDICATED***  
***TO***  
***MY FAMILY AND FRIENDS***

## CANDIDATE'S DECLARATION

---

I hereby certify the work which is being presented in thesis entitled "*Theoretical Studies of stability and reactivity of lower fullerenes*" in partial fulfillment of the requirement for the award of the degree of master of technology submitted in the **Department of Chemistry, IIT Roorkee**, is an authentic record of my own work carried out during a period from July 2006 to June 2007 under the guidance and supervision of **Dr.P.P.Thankachan**, Asst.Professor, Department of Chemistry, IIT Roorkee, Roorkee.

The matter embodied in this thesis has not been submitted by me for the award of any other degree.

Date: 25-06-07

*S.Srinath*  
(Sridharan Srinath)

---

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.



**Dr. P.P.Thankachan**

Asst.Professor

Department of Chemistry

Indian Institute of Technology Roorkee

Roorkee – 247667.

Date:

## ACKNOWLEDGEMENT

---

It gives me great honour and pleasure to express my profound sense of gratitude to my guides, **Dr. P.P.Thankachan**, Asst. Professor, Department of Chemistry, Indian Institute of Technology Roorkee, for his meticulous guidance and supervision during the course of present project work.

I am also thankful to **Dr. R. Bhushan**, Professor and Head, Department of Chemistry, Indian Institute of Technology Roorkee, for providing me the infrastructural and necessary facilities to carry out this project work.

My words fail to express my sincere thanks to **Mr. Neeraj Naithani** for his cooperation, encouragement during my work.

I offer my sincere thanks to **Mrs. Vibha Kumar** for her unrelenting help, undetering support and providing a congenial environment in lab.

I highly appreciate the cooperation and affection showed by my **parents** and my sweet **sister** who have been a constant source of inspiration, patience and moral encouragement to me.

I would like to thank my dear friends **Mr.Ramakant Sahu** , **Ms.Payal Tyagi** and **Ms.Nidhi Tyagi** for their all round support.

I would like to thank my friends **Saurabh Aggarwal**, **M.Siva Kumar** and **M.Ramesh** for their help in performing my calculations and documentation on their PC.

Last, but not the least, I wish to acknowledge the **LAN** connection provided by Indian Institute of Technology Roorkee, which helped me a lot throughout my project.

(Sridharan Srinath)

## ABSTRACT

The smallest possible fullerene,  $C_{20}$ , has other isomers of competing energy and the relative stability order has been controversial. In the present work, ring, bowl and cage structures of  $C_{20}$  are optimized at Hartree-Fock, MP2 and DFT/B3LYP levels using D95V(d,p) and cc-pVDZ basis sets. Energetics of hydrogenation of the cage structure ( $C_2$ ) and bowl structure of  $C_{20}$  to yield  $C_{20}H_2$  isomers and completely hydrogenated perhydrofullerene  $C_{20}H_{20}$  are also studied. Preliminary studies in  $C_{24}$  are also reported.

# CONTENTS

CHAPTER	PAGE No
<b>CANDIDATE'S DECLARATION</b>	<b>i</b>
<b>ACKNOWLEDGEMENT</b>	<b>ii</b>
<b>ABSTRACT</b>	<b>iii</b>
<b>CONTENTS</b>	<b>iv</b>
<b>LIST OF FIGURES</b>	<b>vi</b>
<b>LIST OF TABLES</b>	<b>vii</b>
<b>1.0 INTRODUCTION AND LITERATURE REVIEW</b>	<b>1</b>
1.1 Fullerenes	1
1.2 Buckyballs-a new sphere of science	1
1.3 Geometrical aspects of fullerenes	1
1.4 Fullerene structures	4
1.5 Discovery of fullerene C <sub>60</sub>	4
1.6 Structure and physical properties of some higher fullerenes	6
1.7 Production of fullerenes	7
1.8 Lower fullerenes	8
1.9 C <sub>20</sub>	9
1.10 C <sub>24</sub>	10
1.11 Potential uses of fullerenes	11
1.12 Review of literature on theoretical studies	12
<b>2.0 METHODS OF THEORETICAL CALCULATIONS</b>	<b>16</b>
2.1 Molecular orbital theory	16
2.2 Hartree-Fock method	17
2.3 Basis functions	21
2.4 Determination of equilibrium geometry	23
2.5 Moller-Plesset Perturbation theory	23
2.6 Density functional theory	24

<b>3.0</b>	<b>RESULTS AND DISCUSSION</b>	<b>25</b>
	<b>REFERENCES</b>	<b>38</b>

## LIST OF FIGURES

---

Figure No.		Page No.
1.	The Platonic solids	2
2.	Truncated icosahedron	4
3.	Structure of $C_{60}$	6
4.	Kratshmer-Huffmann apparatus used at Widener University	7
5.	Isomers of $C_{20}$	9
6.	Overview of different structures of $C_{24}$	10
7.	The cage isomer of $C_{20}$ ( $C_2$ symmetry)	28
8.	The cage isomer of $C_{20}$ ( $D_{3d}$ symmetry)	29
9.	The cage isomer of $C_{20}$ ( $D_{5d}$ symmetry)	30
10.	Hydrogenated $C_{20}$ bowl structure	31
11.	Hydrogenated $C_{20}$ cage ( $C_2$ symmetry) structure	32
12.	Perhydrofullerene structure	33
13.	$C_{24}$ structures	35



## LIST OF TABLES

---

Table No		Page No
1	Faces, Vertices of regular solids	3
2	Energies of different structures of C <sub>20</sub>	26
3	Relative stabilities of different structures of C <sub>20</sub>	27
4	Bond lengths (Å) of C <sub>2</sub> optimized structure	28
5	Bond lengths (Å) of D <sub>3d</sub> optimized structure	29
6	Bond lengths (Å) of D <sub>5d</sub> optimized structure	30
7	Hydrogenation of C <sub>20</sub>	32
8	Energy, Enthalpy and free energy changes at 298 K	34
9	Activation Energies of C <sub>20</sub> structures	35

***INTRODUCTION***

***AND***

***LITERATURE REVIEW***

## Introduction

### 1.1) Fullerenes

Till 1985 only two forms in which pure carbon occurred, were recognized: **diamond** and **graphite**. Both these substances consist entirely of carbon atoms, but differ greatly in their structure and physical properties. In diamond, each carbon atom is bound to four other carbon atoms in a tetrahedral arrangement. This structure makes diamond extremely hard, where as graphite has a layer structure which makes it soft and conducting.

### 1.2) Bucky balls – a new sphere of science:

Fullerenes are a new class of molecules and may be thought to constitute a new allotrope of carbon. They have the structure of hollow carbon cages. Because of its discrete molecular nature, it is a pure form of carbon. The number of carbon atoms in each fullerene cage can vary and for this reason numerous new structures can be visualised. Generally, they are represented by the formula  $C_n$ , where  $n$  denotes the number of carbon atoms present in the cage.  $C_{60}$  is the most abundant and well characterized member of the fullerene family and is currently dominating fullerene research. It has a closed cage like structure which is based on the family of platonic solids. The 1996 Chemistry Nobel Prize was awarded jointly to Robert F Curl Jr and Richard E Smalley of USA and Harold W Kroto of UK for the discovery of fullerenes. This remarkable discovery has opened up exciting new avenues in multidisciplinary research involving chemistry, physics, materials science and even biology.

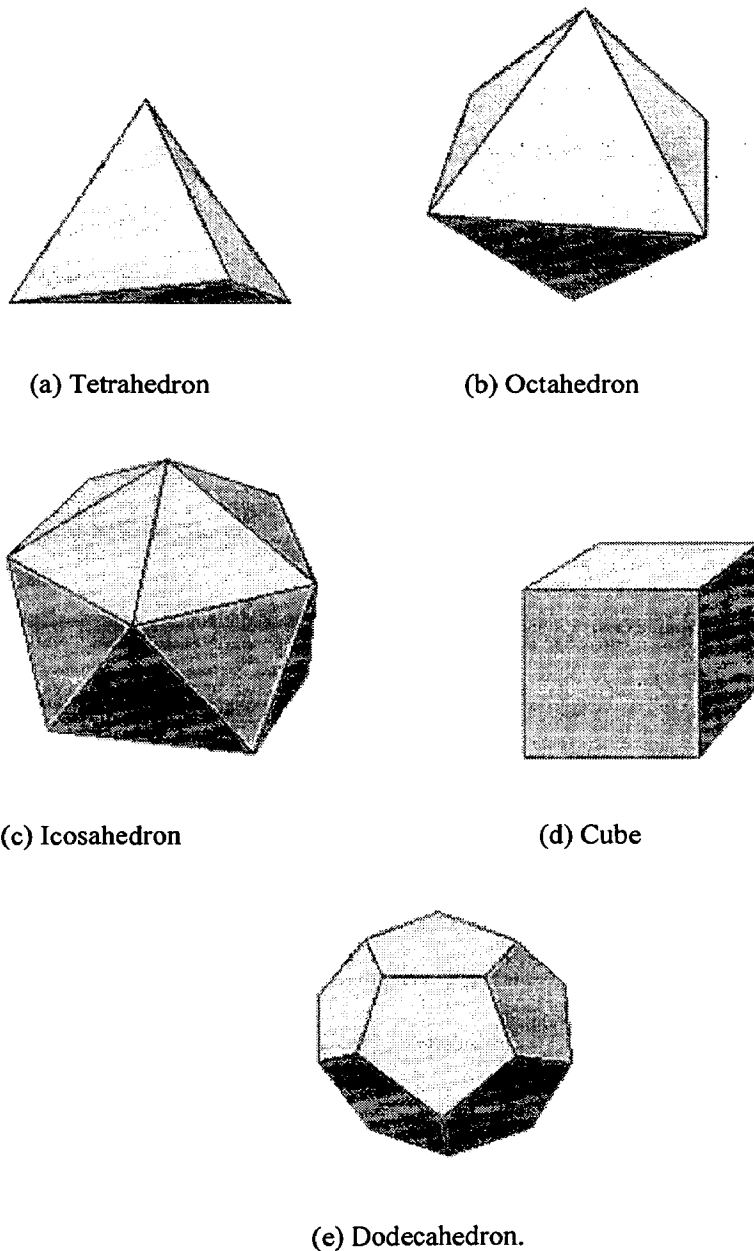
### 1.3) Geometrical aspects of Fullerenes

#### 1.3.1 Platonic Solids:

Regular solids (regular polyhedra, or Platonic solids after their description by Plato) are solid geometric figures, with identical regular polygons as their faces, and with the same number of faces meeting at every corner (vertex).

The equilateral triangle is the simplest regular polygon. Three equilateral triangles meet at a vertex (total angle of  $180^\circ$ ) of the tetrahedron (4 faces, 4

vertices). With four equilateral triangles meeting at each vertex (total angle of  $240^\circ$ ) we get an octahedron (8 faces, 6 vertices). When we try five equilateral triangles at each vertex ( $300^\circ$ ) we end up with an icosahedron (20 faces, 12 vertices). A sixth equilateral triangle meeting at a vertex will tile the plane ( $360^\circ$ ).



**Fig 1: The Platonic Solids**

The next simplest regular polygon is the regular pentagon. Three pentagons meeting at vertex produce a dodecahedron (12 faces, 20 vertices).

Three regular hexagons meeting at each vertex will tile the plane. And there is no room, at a vertex, for more complicated polygons. Hence the set of regular solids is limited to these five forms.

The relation between number of faces, vertices and edges is given by Euler's formula, which is given by:

$$V+F-E=2$$

**Table 1: Faces, Vertices and Edges of Regular solids**

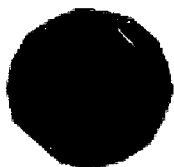
S.No	Solid	Faces	Vertices	Edges
1	Tetrahedron	4	4	6
2	Octahedron	8	6	12
3	Cube	6	8	12
4	Icosahedron	20	12	30
5	Dodecahedron	12	20	30

From the table it is clear that no of faces in octahedron is equal to no of vertices in cube and vice versa. This property is termed as "duality". So, Octahedron and Cube are dual to each other. Similarly icosahedron and dodecahedron are dual to each other. Tetrahedron is dual to itself. Polyhedra dual to one another have the same symmetry elements and belong to the same point group. Thus the cube and octahedron have octahedral symmetry ( $O_h$ ), where as the icosahedron and dodecahedron have icosahedral symmetry ( $I_h$ ).

### 1.3.2 Archimedean Solids:

In geometry an **Archimedean solid** is a highly symmetric, semi-regular convex polyhedron composed of two or more types of regular polygons meeting in identical vertices. They are distinct from the Platonic solids, which are composed of only one type of polygon meeting in identical vertices, and from the Johnson solids, whose regular polygonal faces do not meet in identical vertices.

The symmetry of the Archimedean solids excludes the members of the dihedral group, the prisms and antiprisms.  $C_{60}$  fullerene is a truncated icosahedron. (Fig 2)



**Fig 2: Truncated icosahedron**

#### 1.4) Fullerene Structures:

The requirement for certain numbers of polygons  $m_k$  of  $k$  sides to form a closed structure is given by

$$\sum_k (6 - k)m_k = 12$$

This constraint, when applied to rings having only 5 or 6 members, gives

$$12 = m_5 + 0 m_6$$

This relation can be used to define the family of fullerene structures.[1] It implies that any such closed structure must have 12 five sided elements, but any number (0, 1, 2...) of hexagons are possible. As a result, a fullerene having the chemical formula  $C_n$  must have 12 pentagonal faces and  $(n-20)/2$  hexagons. Hence the lowest number of the fullerene family must have twelve pentagonal faces ( $C_{20}$ ) alone. Similarly  $C_{60}$  must have 12 pentagonal and 20 hexagonal faces.

#### 1.5) Discovery of the fullerene $C_{60}$ :

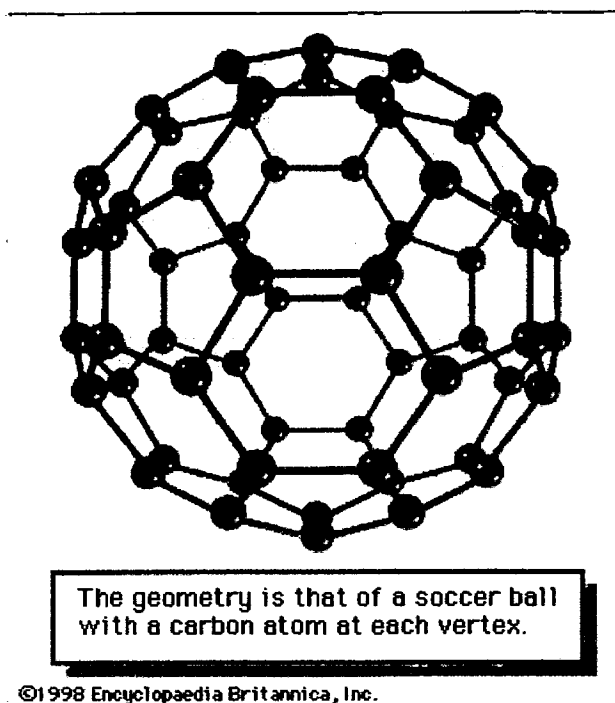
The discovery of fullerene came about during an investigation into a problem of interest to astronomers. Kroto was interested in radio astronomy. In order to determine whether carbon containing molecules present in interstellar clouds were responsible for some of the signals, he began making and characterizing new carbon species in the laboratory, using microwave spectroscopy as his main tool. Interstellar clouds cyanopolynes were discovered by Kroto and coworkers through a synergistic combination of laboratory

microwave spectroscopy experiments, theoretical analysis and observational radio astronomy. Curl, a fellow spectroscopist on the other side of the Atlantic, suggested that collaboration with Smalley would be beneficial. Smalley was interested in cluster chemistry. He had designed and built a special laser-supersonic cluster beam apparatus which could vaporize almost any known material into plasma of atoms and lead to precise information about the pattern and distribution of the clusters. In an action packed fortnight in September 1985, Curl, Kroto and Smalley along with graduate students JR Heath and SC O'Brein began to carry out some experiments on laser vaporization of carbon.

Generally vaporized carbon is obtained by directing an intense beam of laser onto graphite or any other carbon surface. The carbon atoms produced in this way in an inert atmosphere combine to form a series of clusters where the size varies from a few atoms to many more hundreds. These experiments were aimed at synthesizing long chain carbon molecules, since the conditions might reproduce those existing in red giant stars, which give off large amounts of carbon. This would then provide good evidence to show how such molecules originate in the interstellar medium.

During the course of the experiments which probed the behavior of the pure carbon clusters, a striking observation was made. Under some clustering conditions the peak corresponding to 720 mass units appeared extremely strong. The intensity of this peak relative to adjacent peaks varied dramatically under different clustering conditions. Under a particular condition, the mass spectrum was totally dominated by the 720 peak, corresponding to sixty carbon atoms.

The next difficult task was to assign a structure for the 720 mass peak which could explain its unique stability, Kroto, Smalley and Curl came up with a brilliant resolution to the problem. Using handmade models, they found that the planar graphite sheet structure curls up on the introduction of a few pentagons. For a 60 atom cluster with 12 pentagons, the structure closes in on itself, forming a beautiful cage (*Fig 3*).



**Fig 3: Structure of  $C_{60}$  (Courtesy: Britannica Encyclopedia)**

The shape is identical to that of a soccer ball. But the inspiration for the remarkable proposal of  $C_{60}$  having a spheroidal cage structure came from the geodesic domes designed by the renowned architect R. Buckminster Fuller. The whole family of hollow cage carbon clusters is now called fullerenes. The most important member of this family, apart from  $C_{60}$  is  $C_{70}$ . It is usually a major contaminant in the production of  $C_{60}$ .

## **1.6) Structures and Physical Properties of Some Higher Fullerenes**

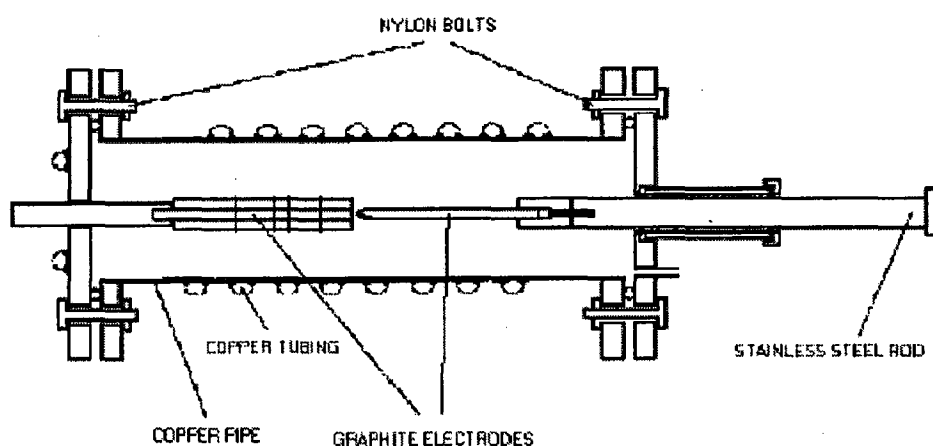
The fullerene  $C_{60}$  has 20 hexagonal and 12 pentagonal rings as the basis of a closed cage structure icosahedral symmetry. Each carbon atom is bonded to three others and is  $sp^2$  hybridised. The  $C_{60}$  molecule has two distinct bond lengths - the 6:6 ring bonds can be considered "double bonds" and are shorter than the 6:5 bonds.  $C_{60}$  is not "superaromatic" as it tends to avoid double bonds in the pentagonal rings, resulting in poor electron delocalisation. As a result,  $C_{60}$  behaves like an electron deficient alkene, and reacts readily with electron rich



species. The geodesic and electronic bonding factors in the structure account for the stability of the molecule. In theory, an infinite number of fullerenes can exist, their structure based on pentagonal and hexagonal rings.

### 1.7) Production of Fullerenes

The first method of production of fullerenes used laser vaporization of carbon in an inert atmosphere, but this produced microscopic amounts of fullerenes. In 1990, a new type of apparatus using an arc to vaporize graphite was developed in Germany by Kratschmer and Huffman.



**Fig 4: Kratschmer-Huffman apparatus as used at Widener University**

In their method the system is pumped down and Helium gas is introduced into the chamber and this process is repeated. Finally the bell-jar is filled with about 100 Torr of Helium. The welding kit power supply is connected and the on / off switch on the supply is turned to the on position for 10 to 15 seconds. Afterwards there should be plenty of black soot like material produced inside the bell-jar. After a 5-10 min cool down period the bell-jar is filled to atmospheric pressure taken off and the glass surfaces scraped clean. Nearly 10 % of the soot is usually made up of C<sub>60</sub>. The fullerenes in the soot are then extracted by solvation in a small amount of toluene.

After extraction, the solvent (toluene) is evaporated off, leaving behind a solid mixture of mostly  $C_{60}$  with small amounts of larger fullerenes. Pure  $C_{60}$  is obtained by liquid chromatography. The mixture is dissolved in toluene and pumped through a column of activated charcoal mixed with silica gel. The magenta  $C_{60}$  comes off first, followed by the red  $C_{70}$ . The differently coloured solutions are collected separately and the toluene removed using the rotary evaporator.

### 1.8) Lower Fullerenes:

The experimental and theoretical study of carbon clusters has a long history, much of this history, as well as the more recent developments have been revolved around the  $C_{60}$  species. Extensive work has been done related to  $C_{60}$  and other higher fullerenes. However, clusters in the intermediate range  $n=20-50$  have been studied in considerably less detail in the literature and have not been subjected to comparable levels of experimental and theoretical examination. This is due to their low relative stability. Among fullerene cages,  $C_{60}$  has the icosahedral cage structure with each pentagon surrounded by five hexagons and is highly stable. In contrast,  $C_{20}$  fullerene cage consists of solely 12 pentagonal rings that form a dodecahedron with no hexagons incorporated, resulting in extreme curvature. Another carbon cluster which is important in understanding the relative stabilities of different fundamental structural units is  $C_{24}$ . Two cage structures have been proposed, one of them containing four membered rings too and the other having six membered rings and few calculations are in existence.

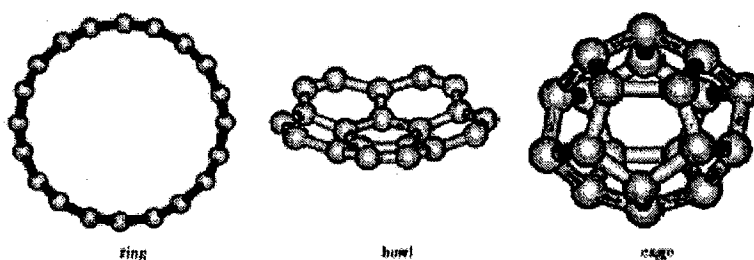
### 1.9) $C_{20}$ :

Over the past decade, considerable attention has been paid in searching for the ground-state  $C_{20}$  isomer from either theoretical calculations or experimental measurements. These studies can be traced back to the discovery of the fullerene structure  $C_{60}$  and thereafter, of their novel properties such as high temperature superconductivity. [2]

$C_{20}$  cage is the smallest and the most strained fullerene structure. Investigations into this and other small fullerenes were critically evaluated in the paper by Chen et al. [3].

### 1.9.1) Isomers of $C_{20}$ :

It is fairly well established [4] that among numerous stable isomers of the carbon cluster  $C_{20}$  – which include chains, rings, bowls, plates, cages and combinations of these – the lowest in energy are the ring, bowl and cage, illustrated in Fig 5.



**Fig 5: Isomers of  $C_{20}$**

For these three, however, the available theoretical methods give a variety of differing predictions for the relative energies. For over a decade that the issue of relative stability of  $C_{20}$  isomers remains controversial.

$C_{20}$  fullerene cage consists of solely 12 pentagonal rings that form a dodecahedron with no hexagons incorporated. The bowl isomer is an open structure that has one central graphitic pentagon surrounded by five hexagonal rings. These three geometrically different  $C_{20}$  isomers are close in energy and could be potentially used as building blocks to the  $C_{60}$  fullerene formation.

### 1.9.2) Experimental evidence for the existence isomers of $C_{20}$ :

As discussed earlier, the smallest possible fullerene is  $C_{20}$ , which consists solely of pentagons. But the extreme curvature and reactivity of this structure have led to doubts about its existence and stability. The question has been asked in the literature to “whether the cage  $C_{20}$  exists only in computers” [5]. Although

theoretical calculations have identified, besides this cage, a bowl and a monocyclic ring isomer as low-energy members of the  $C_{20}$  carbon cluster family, only ring isomers of  $C_{20}$  have been observed experimentally till a few years ago.

In the work of Prinzbach et al [6] the cage structured fullerene is produced from its perhydrogenated form (dodecahedrane  $C_{20}H_{20}$ ) by replacing the hydrogen atoms with relatively weakly bound bromine atoms, followed by gas phase debromination. For comparison the bowl isomer of  $C_{20}$  using the same procedure. Then the generated clusters are characterized using mass-selective anion photoelectron spectroscopy.

### 1.10) $C_{24}$ :

$C_{24}$  is the first cluster which contains a stable planar graphite like fragment. It is thus clearly important in comparing fullerene like cluster growth with that of graphite-like growth. However, neither fullerene-like nor graphite-like isomers were observed for  $C_{24}$  experimentally. Studies by von Helden et al [5] have shown clearly that the dominant isomer of  $C_{24}$  is a monocyclic ring. The various predicted isomers of  $C_{24}$  are depicted below in Fig 6.

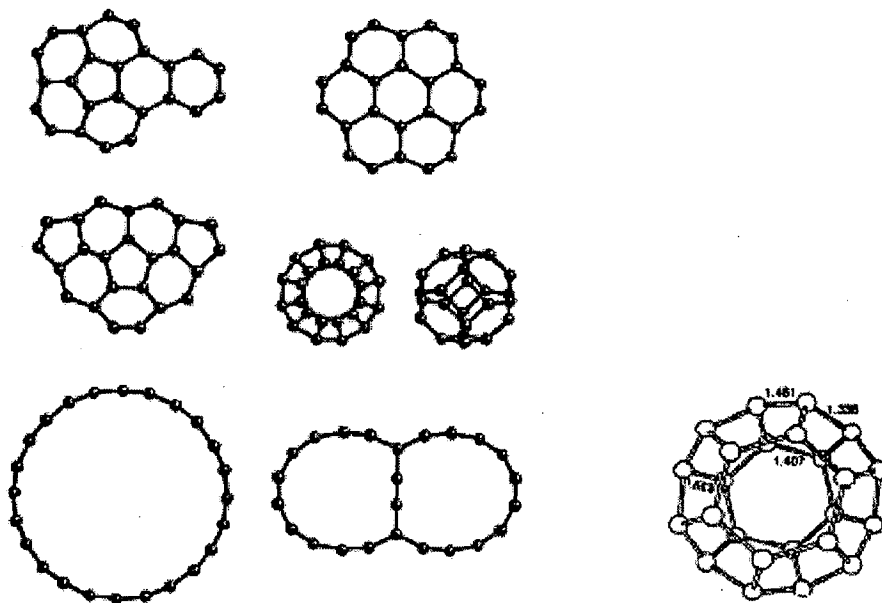


Fig 6: Overview of different structures of  $C_{24}$

### **1.11) Potential uses of fullerenes:**

Since the discovery of fullerenes in 1985, scientists have discussed a myriad of possible uses for these unusual molecules. Just some of these possibilities are described here.

#### **Chemical sponges**

Medical researchers believe that fullerenes could be put to work as tiny chemical sponges, mopping up dangerous chemicals from injured brain tissue. Excess production of free radicals (eg, peroxide) in the brain following a head injury or a stroke destroys nerve cells. Buckyballs, made soluble in water, appear able to 'swallow' and hold free radicals, thereby reducing the damage to tissue.

#### **Nanotubes in microscopes**

Smalley and colleagues have used nanotubes as chemical probes in a scanning-force microscope. The microscope relies on a tiny tip that detects and skims the surface of target molecules. The tube springs back into its original shape when bent.

#### **Buckyballs in miniature circuits**

A supercomputer the size of a paperback is the ambition of European researchers who have managed to attach a single buckyball to a sheet of copper. The scientists compressed the buckyball by 15 per cent, improving electrical conductivity by more than 100 times compared to the undisturbed molecule. A tiny electronic component like this could make miniature circuits feasible.

#### **Lubricants, catalysts and superconductors**

Other exciting potential uses of fullerenes include buckyballs behaving as 'molecular ball bearings' allowing surfaces to glide over one another. Fullerenes with metal atoms attached to them might function as catalysts, increasing the rate

of important chemical reactions. Scientists know that buckyball compounds with added potassium act as superconductors at very low temperatures.

### **Molecular sieves**

Because of the way they stack, buckyballs could act as molecular sieves, trapping particles of particular sizes while leaving others unaffected. Scientists talk of designing sieve-like membranes from buckyballs that allow biological materials to pass through, but not larger particles such as viruses. This would be useful for handling transplant organs, for example.

### **Buckycopiers**

In the United States, Xerox owns patents for using buckyballs to improve resolution of photocopies. They are 1000 times smaller than the particles used in conventional photocopier toner.

## **REVIEW OF LITERATURE ON THEORETICAL STUDIES:**

The earliest calculations on the relative stability of  $C_{20}$  isomers were made using semi-empirical methods. Newton and Stanton [7] performed calculations at MNDO level. Slanina and Adamowicz [8] used the AM1 method and concluded that the ring structure was the stablest. However the approximations inherent in these models make the validity of their conclusions questionable. Several calculations at the *ab-initio* level have also been made and we discuss these in the following.

Parasuk and Almlöf [9] have studied the structure of 20-atom carbon clusters using correlated *ab-initio* calculations with large contracted basis sets. They showed that a regular dodecahedral structure ( $I_h$  point group) would have partially filled degenerate orbitals, giving rise to the electronic states  $^1A_g$ ,  $^3T_{1g}$ ,  $^3T_{2g}$ ,  $^1G_g$  and  $^1H_g$ , of which the triplet states would be stablest in accordance with Hund's rule. As these states are spatially degenerate a Jahn-Teller distortion of the molecular geometry leading to the  $C_{20}$  cage having lower symmetry than  $I_h$  was predicted. They obtained a  $D_{5d}$  structure at SCF level from which no further lowering of symmetry by Jahn-Teller effect was anticipated

by them. At this geometry they performed MP2 calculations to include correlation effects. Calculations on the ring structure were also performed. On the basis of SCF calculations, they predicted a monocyclic, polyacetylene structure to be the most stable form. In contrast, a fullerene type cage structure was shown to be the ground state conformer at the correlated level.

Feyereisen et al [1] examined the relative stabilities of closed fullerene, cummulene and polyacetylene carbon structures, as well as cohesive energies for clusters of size  $n=18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 50$  and  $60$  using *ab-initio* self-consistent-field and second order Moller-Plesset perturbation theory and analytical derivative geometry optimization methods. They concluded that fullerene structures are stablest for  $n \geq 32$ , but hypothesized that with larger basis sets, clusters with  $n < 32$  may also favour the fullerene structure.

Raghavachari et al [10] used density functional techniques including gradient corrections to investigate the energies of the ring, bowl and cage isomers of  $C_{20}$  using 6-31G\* basis set. They showed that the local density approximation yielded the cage as the most stable isomer with the bowl and ring forms being significantly higher in energy. They found that in contrast to the work of Parasuk and Almölf [9], where a  $D_{5d}$  structure of cage was found, distortion along a 3-fold axis leading to a  $D_{3d}$  structure was energetically better. These authors also preferred vibrational frequency calculations on these structures and observed one imaginary frequency. Hence they lowered the symmetry further and obtained a  $C_2$  structure for the cage which is a true local minimum at the Hartree-Fock level with 6-31G\* basis set. They also found that the  $D_{10h}$  ring has three imaginary frequencies whereas the  $C_{5v}$  bowl structure is a local minimum. However the inclusion of gradient corrections completely reversed the energy ordering of the isomers. The gradient correction altered the relative energy between ring and cage isomers by more than 7 eV and yielded the ring as the most stable form.

In a later paper, Raghavachari and co-workers [11] used density functional techniques to investigate the relative energies of seven different isomers of  $C_{24}$ . The seven isomers predicted are a monocyclic ring, a bicyclic ring, a graphite like isomer, two bowl like isomers having different symmetries and two different cage isomers having different symmetries. The traditional local density approximation yields the fullerene like

isomer to the most stable. The gradient corrected B-LYP method yielded the monocyclic ring and graphite like isomer to be almost isoenergetic (most stable) while the bicyclic ring, fullerene like and bowl like isomers are progressively higher in energy.

Contrary to the experimental evidence suggesting that the monocyclic ring is the most stable 20-atom carbon species, Taylor et al [12], predicted that the smallest fullerene, dodecahedral C<sub>20</sub>, has lowest energy using coupled cluster calculations, which included higher percentage of correlation energy. They also showed that a related corannulene like bowl is nearly degenerate in energy to the fullerene and would be stabler at higher temperatures. However, they have not performed vibration frequency calculations to verify if their structures are true minima.

Jensen and Koch [13] have calculated the energy difference between the ring and fullerene forms of C<sub>24</sub> by means of *ab-initio* methods and compared to density functional methods. Their calculations strongly suggest that the fullerene form is favored by ~80 kcal/mol over a monocyclic ring structure, which is at variance with experimental findings. The monocyclic ring had an ideal symmetry of D<sub>24h</sub>, however at the HF level an acetylenic structure with D<sub>12h</sub> symmetry was lower in energy. The fullerene has ideal D<sub>6d</sub> symmetry, but a Jahn-Teller distortion reduced the symmetry to D<sub>6</sub>.

Martin et al [14] have studied several structures of C<sub>24</sub> using different density functional methods. Their best calculations indicated that a dodecahydrocoronene planar sheet and a fullerene cage are comparable in energy, followed by a poly acetylenic ring and a bowl structure. At high temperatures they predicted ring structure to prevail due to vibrational entropy from many low-lying vibrations. The ring structure was found to have C<sub>12h</sub> symmetry, rather than D<sub>12h</sub> symmetry. The bowl like sheet is found to be flat and to be a local minimum in D<sub>6h</sub> symmetry. There were two cage isomers predicted. One had D<sub>6</sub> symmetry and the other had O<sub>h</sub> symmetry.

Sokolova et al [4] determined the energetics of the ring, bowl and cage isomers of C<sub>20</sub> in all electron fixed-node quantum Monte Carlo calculations. In good agreement with results from Moller Plesset calculations, they predicted bowl isomer to be the lowest energy isomer. The energies of cage and ring, relative to the bowl, are 1.1±0.5 and 2.1±0.5 eV, respectively. These authors have also made a detailed comparison of earlier results on the stability of these isomers.



Chen et al [3] have investigated the smaller fullerenes  $C_{20}$ ,  $C_{24}$ ,  $C_{32}$ ,  $C_{36}$ ,  $C_{40}$  and  $C_{50}$  and their hydrogenation products systematically at the **B3LYP/6-31G\*** density functional level of theory. They have also showed that owing to Jahn-Teller distortion, the singlet ground state of  $C_{20}$  has  $C_2$  symmetry instead of  $I_h$  symmetry and complete hydrogenation of  $C_{20}$  leads to dodecahedron ( $C_{20}H_{20}$ ) which represents a normal saturated hydrocarbon with C-C bond length of 1.557 Å. The structure of  $C_{24}$  was considered as a trannulene capped with two benzene rings at both sides. Apart from the unique C-C bond length of six- membered rings, the central trannulene ring has localized C-C bond lengths of 1.365 and 1.463 Å, while the C-C bond lengths between six membered rings and the trannulene ring is 1.531 Å. With partially hydrogenated  $C_{24}H_{12}$ , the compensation effect was assessed by the difference between hydrogenation of the trannulene subunit and the two six membered rings.

An et al [2] have carried out high-level *ab-initio* and density functional calculations to examine relative stability of bowl, cage and ring isomers of  $C_{20}$  and  $C_{20}^+$ . The total electronic energies of the three isomers showed different orderings, strongly depending on the hybrid functionals selected. Both CCSD (T) and MP4 calculations indicated that the bowl isomer is most likely the global minimum of neutral  $C_{20}$  isomers, followed by the fullerene cage and ring.

In the present work we investigate the stability of various structures of  $C_{20}$  at Hartree-Fock and Moller Plesset levels as well as by the DFT methods using B3LYP functionals using several basis sets. Hydrogenation of  $C_{20}$  is also investigated. A beginning is made to the study of  $C_{24}$  cage structure also. All our calculations are made using the GAUSSIAN 98W [15] suite of programs.

***METHODS OF THEORETICAL  
CALCULATIONS***

## Methods of theoretical calculations

### 2.1 Molecular Orbital Theory:

The task of predicting molecular structures begins with the separation of electronic and nuclear motion using the Born-Oppenheimer approximation

In a molecular system if we assume nucleus and electrons to be point masses and neglect spin orbit and other relativistic interactions, then the molecular Hamiltonian is

$$H = -\frac{\hbar}{2} \sum_{\alpha} \frac{1}{M_{\alpha}} \nabla_{\alpha}^2 - \frac{\hbar}{2M_e} \sum_i \nabla_i^2 + \sum_{\alpha} \sum_{\beta > \alpha} \frac{Z_{\alpha} Z_{\beta} e'^2}{\gamma_{\alpha\beta}} - \sum_{\alpha} \sum_i \frac{Z_{\alpha} e'^2}{r_{i\alpha}} + \sum_j \sum_{i < j} \frac{e'^2}{r_{ij}} \dots(2.1.1)$$

where,  $\alpha, \beta$  refers to nuclei and  $i, j$  refers to electron .

We have to solve the equation

$$H\psi = E\psi \dots\dots\dots(2.1.2)$$

Or 
$$H\psi(q_i, q_{\alpha}) = E\psi(q_i, q_{\alpha}) \dots\dots\dots(2.1.3)$$

Where,  $q_i$  and  $q_{\alpha}$  symbolize the electronic and nuclear coordinates respectively. Since nuclei are much heavier than electrons, the electrons move much faster than the nuclei and to a good approximations as far as the electrons are concerned we can assume nuclei as a fixed. While the electrons carry out their motion or in other words the change in nuclear configuration is negligible. Thus considering the nuclei as fixed we omit the nuclear kinetic energy terms. This is the Born-Oppenheimer approximations. It is the approximation of separating electronic and nuclear motions. Within the Born-Oppenheimer approximation the true molecular wave function is adequately approximated as

$$\Psi = \Psi_e \Psi_n \dots\dots\dots(2.1.4)$$

So the purely electronic Hamiltonian  $H_{el}$  is:

$$H_{el} = \frac{-\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_{\alpha} \sum_i \frac{Z_{\alpha} e'^2}{r_{i\alpha}} + \sum_j \sum_{i > j} \frac{e'^2}{r_{ij}} \dots\dots\dots(2.1.5)$$

The electronic wave function satisfies

$$H_{el}\psi_e(1,2,3\dots N) = E_{el}\psi_e(1,2,3\dots N) \dots\dots\dots(2.1.6)$$

The electronic energy  $E_{el}$  in the above equation depends parametrically on the nuclear coordinates and becomes potential energy term for the nuclear motions:

$$(T_N + E_{el}(R)) \Psi_n = E \Psi_n$$

Where,  $T_N$  represents the nuclear kinetic energy operator.

As electrons are fermions, the N-electron wave function  $\Psi_{el}(1, 2, \dots, n)$  needs to satisfy the antisymmetry requirement i.e., it has to change sign when the coordinates of a pair of electrons is interchanged.

$$\Psi_{el}(1, 2, \dots, n) = -\Psi_{el}(2, 1, \dots, n) \dots\dots\dots(2.1.7)$$

The simplest function built of one electron functions or orbitals (including spin)  $\mu_k$  is of the form

$$D = \frac{1}{\sqrt{n!}} \begin{vmatrix} \mu_1(1) & \mu_2(1) & \mu_3(1) & \dots & \dots & \dots & \dots & \dots & \mu_n(1) \\ \mu_1(2) & \mu_2(2) & \mu_3(2) & \dots & \dots & \dots & \dots & \dots & \mu_n(2) \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \mu_1(n) & \mu_2(n) & \mu_3(n) & \dots & \dots & \dots & \dots & \dots & \mu_n(n) \end{vmatrix} \dots(2.1.8)$$

Where,  $\frac{1}{\sqrt{n!}}$  the factor accounts for normalization. Such a function is called Slater determinant. In general the molecular electronic wave function can be expressed as a linear combination of Slater determinants. The simplest theoretically acceptable electronic wave function consists of a simple Slater determinant. The orbitals  $\mu_k$  used in its construction are chosen to minimize the expectation value of energy using the Hartree-Fock method. In practice they are expressed as a linear combination of basis functions and the coefficients involved are determined so as to satisfy the normalization and orthogonality conditions among the orbitals.

$$\langle \mu_i(1) | \mu_j(1) \rangle = \delta_{ij} \dots\dots\dots(2.1.9)$$

Where the Kronecker delta function  $\delta_{ij}$  defined as

$$\delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases}$$

## 2.2 Hartree-Fock Method

The molecular Hartree-Fock wave function is written as an anti symmetrized product spin orbitals i.e. products of a spatial function  $\phi_i$  and a spin function.

The expression for Hartree-Fock molecular electronic energy  $E_{HF}$  is given by the variation theorem as

$$E_{HF} = \langle D | \hat{H}_{el} + V_{NN} | D \rangle \dots\dots\dots(2.2.1)$$

Where  $D$  is the Slater determinant Hartree-Fock wave function and  $\hat{H}_{el}$  and  $V_{NN}$  are given by

$$\hat{H}_{el} = \frac{-\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_\alpha \sum_i \frac{Z_\alpha e^2}{r_{i\alpha}} + \sum_j \sum_{i>j} \frac{e^2}{r_{ij}} \dots\dots\dots(2.2.2)$$

$$V_{NN} = \sum_\alpha \sum_{\beta>\alpha} \frac{Z_\alpha Z_\beta e^2}{r_{\alpha\beta}} \dots\dots\dots(2.2.3)$$

Since  $V_{NN}$  does not involve electronic coordinates and  $D$  is normalized, we have

$$\langle D | V_{NN} | D \rangle = V_{NN} \langle D | D \rangle = V_{NN} \dots\dots\dots(2.2.4)$$

The operator  $\hat{H}_{el}$  is the sum of one electron operator  $h_i$  and two electron operator

$g_{ij}$  Using atomic units (where  $e=1$ ,  $\hbar=1$ ,  $m_e=1$ ) we may write

$$\hat{H}_{el} = \sum_i \hat{h}_i + \sum_j \sum_{i>j} \hat{g}_{ij} \dots\dots\dots(2.2.5)$$

Where

$$\hat{h}_i = -\frac{1}{2} \nabla_i^2 - \sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} \dots\dots\dots(2.2.6)$$

$$\hat{g}_{ij} = \frac{1}{r_{ij}} \dots\dots\dots(2.2.7)$$

The Hamiltonian  $\hat{H}_{el}$  is the same as the Hamiltonian  $\hat{H}$  for an atom except that

$$\sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} \text{ Replaces } \frac{Z}{r_{ij}} \text{ in } h_i$$

For closed shell systems where each spatial orbital is doubly occupied, we get

$$E = \langle D | \hat{H} | D \rangle = 2 \sum_{i=1}^{n/2} \langle \phi_i(1) | \hat{h}_i | \phi_i(1) \rangle + \sum_{j=1}^{n/2} \sum_{i=1}^{n/2} (2J_{ij} - K_{ij}) \dots\dots\dots(2.2.8)$$

Therefore, the Hartree-Fock energy of molecule with only closed sub-shells is

$$E_{HF} = 2 \sum_{i=1}^{n/2} H_{ii}^{core} + \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} (2J_{ij} - K_{ij}) + V_{NN} \quad \dots\dots\dots(2.2.9)$$

Where,

$$H_{ii}^{core} = \langle \phi_i(1) | H_{ii}^{core} | \phi_i(1) \rangle = \langle \phi_i(1) | -\frac{1}{2} \nabla_1^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{1\alpha}} | \phi_i(1) \rangle \quad \dots\dots\dots(2.2.10)$$

$$J_{ij} = \langle \phi_i(1) \phi_j(2) | \frac{1}{r_{12}} | \phi_i(1) \phi_j(2) \rangle \quad \dots\dots\dots(2.2.11)$$

$$K_{ij} = \langle \phi_i(1) \phi_j(2) | \frac{1}{r_{12}} | \phi_j(1) \phi_i(2) \rangle \quad \dots\dots\dots(2.3.12)$$

Where, the one electron operator symbol was changed from  $h_i$  to  $\hat{H}_{(i)}^{core}$ . The one electron core Hamiltonian  $\hat{H}_{(i)}^{core}$  omits the interaction of electron  $i$  with the other electrons.

The closed sub-shell orthogonal Hartree-Fock MO's satisfy

$$\hat{F}(1)\phi_i(1) = \varepsilon_i \phi_i(1) \quad \dots\dots\dots(2.2.13)$$

Where  $\varepsilon_i$  is the orbital energy and where the Hartree Fock operator  $\hat{F}$  is

$$\hat{F}(1) = \hat{H}_{(1)}^{core} + \sum_{j=1}^{n/2} [2J_j(1) - K_j(1)] \quad \dots\dots\dots(2.2.14)$$

$$\hat{H}_{(1)}^{core} = -\frac{1}{2} \nabla_1^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{1\alpha}} \quad \dots\dots\dots(2.2.15)$$

Where, coulomb operator  $J_j$  and exchange operator  $K_j$  are

$$J_j(1)u(1) = u(1) \int |\phi_j(2)|^2 \frac{1}{r_{12}} d\mathbf{r}_2 \quad \dots\dots\dots(2.2.16)$$

$$K_j(1)u(1) = \phi_j(1) \int \frac{\phi_j(2)u(2)}{r_{12}} d\mathbf{r}_2 \quad \dots\dots\dots(2.2.17)$$

Where,  $u$  is an arbitrary function and the integrals are definite integrals over all space

To obtain the expression for the orbital energies  $\epsilon_i$ , we multiply (2.2.13) by  $\phi_i^*(1)$  and integrate over all space we obtain

$$\epsilon_i = \int \phi_i^*(1) F(1) \hat{\phi}_i(1) dv_1 \dots\dots\dots(2.2.18)$$

$$\epsilon_i = H_{ii}^{core} + \sum_{j=1}^{n/2} (2J_{ij} - K_{ij}) \dots\dots\dots(2.2.19)$$

Summation of (3.3.19) over  $n/2$  occupied orbital gives

$$\sum_{i=1}^{n/2} \epsilon_i = \sum_{i=1}^{n/2} H_{ii}^{core} + \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} (2J_{ij} - K_{ij}) \dots\dots\dots(2.2.20)$$

Solving the equation for  $\sum_i H_{ii}^{core}$  and substituting results into (2.2.1) we obtain

The expression for the Hartree-Fock energy is

$$E_{HF} = 2 \sum_{i=1}^{n/2} \epsilon_i - \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} (2J_{ij} - K_{ij}) + V_{NN} \dots\dots\dots(2.2.21)$$

Expanding the spatial orbitals in terms of basis functions  $\{u_s\}$ , we write

$$\phi_i = \sum_{s=1}^b C_{si} u_s \dots\dots\dots(2.2.22)$$

Where,  $b$  is the number of basis functions.

Substituting the expression into the Hartree-Fock equation gives the Roothan Hartree-Fock equations

$$\mathbf{F} \mathbf{C} = \mathbf{S} \mathbf{C} \boldsymbol{\epsilon} \dots\dots\dots(2.2.23)$$

Where,  $\mathbf{F} = (F_{rs})$ , is the Fock matrix of molecular expansion coefficients. As  $\mathbf{F}$  is a function of  $\mathbf{C}$ , the solution of this is an iterative process, where an initial  $\mathbf{C}$  is approximated suitably. One method is to choose it to satisfy

$$\mathbf{H}^{core} \mathbf{C} = \mathbf{S} \mathbf{C} \boldsymbol{\epsilon} \dots\dots\dots(2.2.24)$$

Where,  $\mathbf{H}^{core}$  is the core Hamiltonian matrix. The solution of Roothan-Hartree-Fock equations proceeds iteratively once a starting  $\mathbf{C}$  is found and is terminated when the input  $\mathbf{C}$  to a cycle is sufficiently close to the output  $\mathbf{C}$  (the self-consistency criterion)

### 2.3 Basis functions:

Early calculations used a basis constituting of Slater type orbitals (STO). An STO centered on atom  $a$  has the form

$$R_n(r, a) = \frac{[2\xi/a_0]^{\frac{n+1}{2}}}{[(2n)!]^{\frac{1}{2}}} r_a^{n-1} e^{-\xi r_a} Y_l^m(\theta_a, \phi_a) \dots\dots\dots(2.3.1)$$

The real form of the STO is:

$$R_n(r, a) = \frac{[2\xi/a_0]^{\frac{n+1}{2}}}{[(2n)!]^{\frac{1}{2}}} r_a^{n-1} e^{-\xi r_a} (Y_l^{m*} \pm Y_l^m) / 2^{1/2} \dots\dots\dots(2.3.2)$$

In calculations on polyatomic molecules we use STO's centered on each of the atoms. The presence of more than two atoms causes difficulty in evaluating the needed integrals. One must deal with 4 centered, 3 centered, 2 centered and 1 centered integrals. For accurate SCF molecular calculation on small to medium size molecules, one might use from 20 to 200 basis functions producing 20000 to  $2 \times 10^8$  electron repulsion integrals. Evaluation of three and four centered integrals over STO basis function is very time consuming. This problem is alleviated by the use of Gaussian type functions, since the product of two Gaussians centered on two centers is expressible as a multiple of a Gaussian centered at a point intermediate to them.

#### 2.3.1 Gaussian type functions (GTF):

A Cartesian Gaussian centered on atom  $a$  is defined as

$$g_{ijk}(XYZ\alpha) = NX_a^i Y_a^j Z_a^k e^{-\alpha r_a^2} \dots\dots\dots(2.3.4)$$

Where  $N$  is the normalized atom constant  $i, j, k$  are nonnegative integers and  $\alpha$  is the positive orbital exponent

When  $i+j+k=0$  the GTF is called  $s$  type Gaussian.

When  $i+j+k=1$  the GTF is called  $p$  type Gaussian.

When  $i+j+k=2$  the GTF is called  $d$  type Gaussian.



In general, linear combination of Cartesian Gaussian can be formed to have the form

$$Nr_a^l e^{-\alpha r_a^2} (Y_l^m \pm Y_l^m) / 2^{1/2} \dots\dots\dots(2.3.5)$$

Even though Gaussians are better suited for integral evaluation, they have poor cusp behavior near the nuclei. Thus 1s-type Gaussian has zero slope at r=0 whereas the STO has a non-zero slope. This makes it necessary to use a larger number of Gaussians in a basis set for comparable accuracy.

**2.3.2 Minimal basis set:**

A minimal basis set consists of one STO for each inner shell and valence shell AO of each atom. For example, for C<sub>2</sub>H<sub>2</sub> a minimal basis set consist of 1s, 2s, 2p<sub>x</sub>, 2p<sub>y</sub> and 2p<sub>z</sub> AO's on each carbon and 1s STO on each hydrogen (total 12 basis functions).

**2.3.3 Double Zeta basis set:**

Double Zeta basis set is obtained by replacing each STO of a minimal basis set by with two STOs that differ in their orbital exponents ζ(zeta).

**2.3.4 Split Valence basis set:**

Split Valence basis set uses two STOs for each valence AO but only one STO for each inner shell AO. This basis set is minimal for the inner shell AOs and Double Zeta for the valence AOs.

**2.3.5 Contracted Gaussian functions:**

Instead of using individual Gaussian functions, we may use a smaller basis, with each function expressed as linear combination of a small number of Gaussian, according to

$$\chi_r = \sum_u d_{ur} g_u(\alpha_u) \dots\dots\dots(2.3.5)$$

Where g<sub>u</sub> are Cartesian Gaussian centered on same atom and having the same i, j, k values as one another, but the different α's. The coefficients d<sub>ur</sub> are constants that are held fixed during the calculation. χ<sub>r</sub> is called a contracted Gaussian type function and g<sub>u</sub> are called primitive Gaussians.

To obtain gaussian sets one starts with a minimal basis set of one STO per AO, with the STO orbital exponent fixed at a value found to work well in calculations on small molecules. Each STO then approximated as a linear combination of N Gaussian functions eg. STO-3G.

Another way to form contracted Gaussian is to start with atomic GTF SCF calculations. The 3-21G and 4-31G and 6-31G are commonly used CGTFs.

6-31G\* or 6-31G (d) basis set is a Split Valence set with some polarization function added. It uses a linear combination of six primitives in each inner shell AO and adds a single set of 6 d-type Cartesian Gaussian polarization function for each non hydrogen atom

6-31G\*\* or 6-31G (d,p) set adds to the 6-31G\* set a set of p-type Gaussian polarization function on each hydrogen atom.

D95V basis set [16] is a double zeta quality contracted Gaussian basis. D95V basis is a related split valence set.

## 2.4 Determination of equilibrium geometry

The equilibrium geometry of a molecule is that for which the electronic energy (including nuclear repulsion energy) has a minimum. Since  $E_e(q_x)$  is the potential energy for nuclear motions (vibrations and rotations of the molecule), a local minimum is also characterized by positive force constants in all vibrational modes. Other stationary points on the potential energy surface may correspond to saddle points, which correspond to minima along several vibrational modes with a maxima along one (or few) vibrational modes. These correspond to transition structures.

The stationary points on the potential energy surface correspond to zeros of the gradient of the potential energy. These are located using suitable optimization methods. The default optimization method used in the Gaussian 98 system is due to Schlegel [17]. Once a stationary point is found, calculation of vibrational frequencies enables one to characterize the stationary point as a true minima or a transition structure.

## 2.5 Moller Plesset Perturbation theory

The Hartree-Fock method does not include correlation between the motions of electrons of dissimilar spins and hence the Hartree-Fock energy is higher than true non-relativistic energy. The difference is called correlation energy. One of the methods available to include correlation energy is to use perturbation theory. In Many body perturbation theory (MBPT) as formulated by Moller and Plesset, [18] the unperturbed

Hamiltonian  $H_0$  is written as the sum of the Fock operators and the difference between the true Hamiltonian and  $H_0$  is treated as the perturbation  $H'$

$$H_0 = \sum_{i=1}^n F_i \dots\dots\dots(2.5.1)$$

$$H' = \sum_{i,j>i} \frac{1}{r_{ij}} - \sum_i \sum_j [J_j(i) - K_j(i)] \dots\dots\dots(2.5.2)$$

The unperturbed energy in this case corresponds to the sum of occupied orbital energies and the first order perturbation correction gives the Hartree-Fock energy. The second order corrections are commonly used and inclusion of these gives MP2 energy. Higher order calculations are feasible only for very small systems.

## 2.6 Density functional theory

Density functional methods owe their origin to a result by Hohenberg and Kohn [19] which states that the ground state energy of a many electron system is a functional of the one-electron density  $\rho(r)$ . In practice, the exact form of functional is not known and approximate functionals for exchange and correlation energies are in use. For molecular systems the densities are obtained from one-electron functions  $\chi(r)$

$$\rho(r) = \sum_i^{occ} \chi_i^*(r) \chi_i(r) \dots\dots\dots(2.6.1)$$

Which are determined from a solution of Kohn-Sham equation [20].

The currently most popular DFT scheme uses the B3LP functional which incorporates Becke's [21] three parameter exchange functional with Lee-Yang and Parr's [22] correlation functional.

***RESULTS***  
***AND***  
***DISCUSSION***

## Results and Discussion

The structures of isomers of  $C_{20}$  were optimized at RHF, MP2 and B3LYP levels using D95V(d,) and cc-pVDZ basis sets. The former basis set is a split valence type basis set including polarization functions due to Dunning [16] that has been found in our laboratory [23] to yield better energies than the more popular 6-31G(d,p) basis sets at comparable costs in terms of computational time. Since no hydrogen atoms are present in the molecules being studied, the basis set is equivalent to D95V (d), but since in the study of hydrogenated systems D95V(d,p) basis is used for uniformity; the same designation is applied throughout. The cc-pVDZ basis set [24] is a correlation consistent polarized double zeta basis set due to Dunning. A ring structure of  $D_{10d}$  symmetry, a bowl structure of  $C_{5v}$  symmetry and cage structures of  $D_{5d}$  and  $D_{3d}$  symmetries were obtained at each of these levels. The energies are presented in Table 2. At Hartree-Fock and B3LYP levels the vibrational frequencies were also calculated and the number of imaginary frequencies obtained is given in parenthesis following the energy values. At MP2 level the frequency calculations could not be performed since the very large memory requirements in this case could not be met by our computing system.

It is seen that the bowl structure has no imaginary frequencies at all levels and therefore corresponds to a true minimum. The  $D_{5d}$  and  $D_{3d}$  cages and the  $D_{10d}$  ring structures all have imaginary frequencies and so do not correspond to stable structures.

At a late stage in this study we were able to obtain cage structures of  $I_h$  and  $C_2$  symmetries also. The  $I_h$  cage structure has a triplet electronic state, but did not converge fully. A distorted dodecahedral cage of  $C_2$  symmetry was also found and had no imaginary frequencies, which therefore corresponds to a stable structure.

A comparison of the energies of the different structures of  $C_{20}$  (relative to the stablest, form taken as zero) is presented in Table 3. All the compared results are for the D95V(d,p) basis and are expressed in kcal/mole. It is seen that partial inclusion of correlation energy at the MP2 level has stabilized all the cage structures relative to the bowl, so that the  $D_{3d}$  cage now becomes the 'stablest' form. Since frequency calculations at the MP2 level are not available, no comment can be made about whether this structure represents a true local minimum at present. The  $C_2$  cage energy reported is based on a

**Table 2: Energies<sup>a</sup> of different structures of C<sub>20</sub>**

(Number of imaginary frequencies within parenthesis)

Method/Basis set	RING	BOWL	CAGE D <sub>5d</sub>	CAGE D <sub>3d</sub>	CAGE I <sub>h</sub>	CAGE C <sub>2</sub>
B3LYP/cc-pVDZ	-761.5153231 (2)	-761.5432279 (0)	-761.4750451 (2)	-761.3940566 (2)		
B3LYP/D95V(d,p)	-761.3167832 (2)	-761.5528801 (0)	-761.525987 (1)	-761.5220475 (2)		
RHF/cc-pVDZ	-756.6605821	-756.7024386 (0)	-756.5741483 (5)	-756.6143239 (2)		
RHF/D95V(d,p)	-756.6711562 (2)	-756.7380563 (0)	-756.6168389 (5)	-756.2118413 (2)	-756.6602227 <sup>b</sup> (0)	-756.6579235 (0)
MP2/cc-pVDZ	-759.0438415	-759.3170182	-756.3204315	-759.3258671		
MP2/D95V(d,p)	-759.0319399	-759.3291092	-759.3274817	-759.3351973		-759.2914193 <sup>c</sup>

<sup>a</sup> All the energy values are in Hartrees

<sup>b</sup> UHF calculations, Triplet ground state (not fully converged)

<sup>c</sup> MP2 energy at RHF geometry

single point MP2 calculation at RHF geometry and is also not very high. The possibility that on full MP2 optimization this form may turn out to be the stablest cannot be ruled.

**Table 3: Relative stabilities of different structures of C<sub>20</sub> with D95V(d,p) basis set.(Energies are in kcal/mole)**

Method	Ring	Bowl	D <sub>5d</sub>	D <sub>3d</sub>	C <sub>2</sub>
RHF	41.953	0.0	76.015	329.99	50.251
MP2	190.173	3.818	4.838	0.0	27.453*
B3LYP	148.088	0.0	16.865	19.335	-

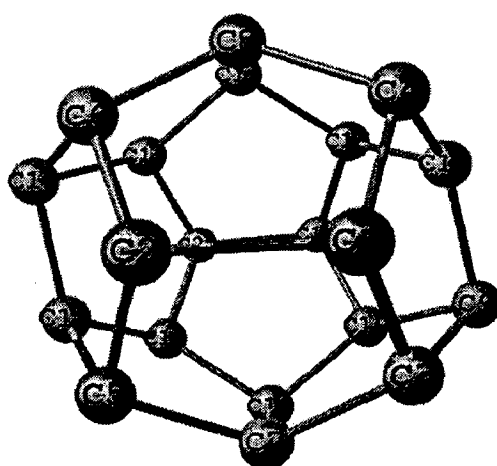
\*MP2 energy at RHF geometry

The numbering of atoms with C<sub>2</sub> structure is given in *Fig 7* and the distance obtained by us with D95V(d) basis are compared in Table 4 with the earlier reports of Raghavachari et al [10] at RHF/6-31G(d) level. We see that the differences are only of the order of 0.001 Å in bond lengths. *Fig 8* gives the numbering of atoms for the D<sub>3d</sub> structure and Table 5 gives the distinct bond lengths obtained at the RHF/D95V(d) level. Table 6 and *Fig 9* give the corresponding data for the D<sub>5d</sub> structure. In the I<sub>h</sub> (triplet) structure all the C-C bond lengths were 1.443 Å and the C-C-C bond angles were 108° as expected.

**Table 4: Bond lengths (Å) of C<sub>2</sub> optimized cage structure**

Parameter <sup>a)</sup>	RHF/D95V(d,p)	RHF/6-31G* (Reported [10])
C <sub>6</sub> -C <sub>12</sub>	1.503	1.504
C <sub>12</sub> -C <sub>11</sub>	1.438	1.437
C <sub>12</sub> -C <sub>18</sub>	1.454	1.451
C <sub>2</sub> -C <sub>6</sub>	1.388	1.385
C <sub>6</sub> -C <sub>8</sub>	1.440	1.437
C <sub>11</sub> -C <sub>17</sub>	1.483	1.481
C <sub>11</sub> -C <sub>5</sub>	1.410	1.406
C <sub>18</sub> -C <sub>14</sub>	1.425	1.423
C <sub>18</sub> -C <sub>20</sub>	1.462	1.460
C <sub>17</sub> -C <sub>20</sub>	1.371	1.367
C <sub>17</sub> -C <sub>13</sub>	1.471	1.469
C <sub>8</sub> -C <sub>14</sub>	1.416	1.413
C <sub>2</sub> -C <sub>5</sub>	1.500	1.444
C <sub>1</sub> -C <sub>2</sub>	1.481	1.479
C <sub>19</sub> -C <sub>20</sub>	1.498	1.497
C <sub>8</sub> -C <sub>4</sub>	1.457	1.455

a) For the numbering system see Fig 7

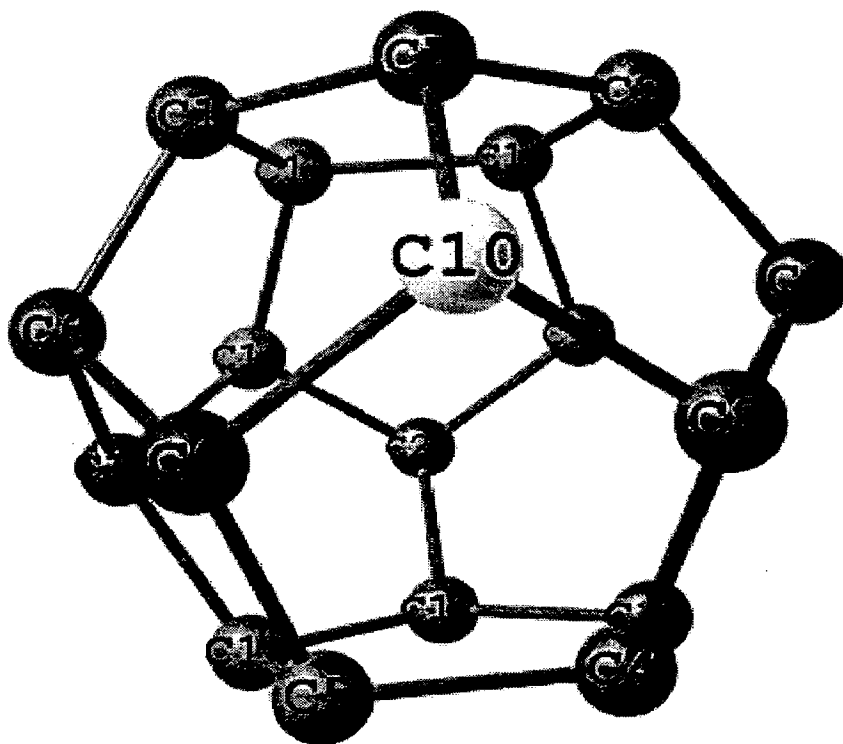
**Fig 7: The cage isomer of C<sub>20</sub> (C<sub>2</sub> symmetry)**



**Table 5: Bond lengths (Å) of  $D_{3d}$  optimized cage structure**

Parameter <sup>b)</sup>	RHF/D95V(d,p)
C <sub>10</sub> -C <sub>9</sub>	1.474
C <sub>9</sub> -C <sub>6</sub>	1.446
C <sub>1</sub> -C <sub>6</sub>	1.419
C <sub>1</sub> C <sub>11</sub>	1.485

b) For the numbering system see Fig 8

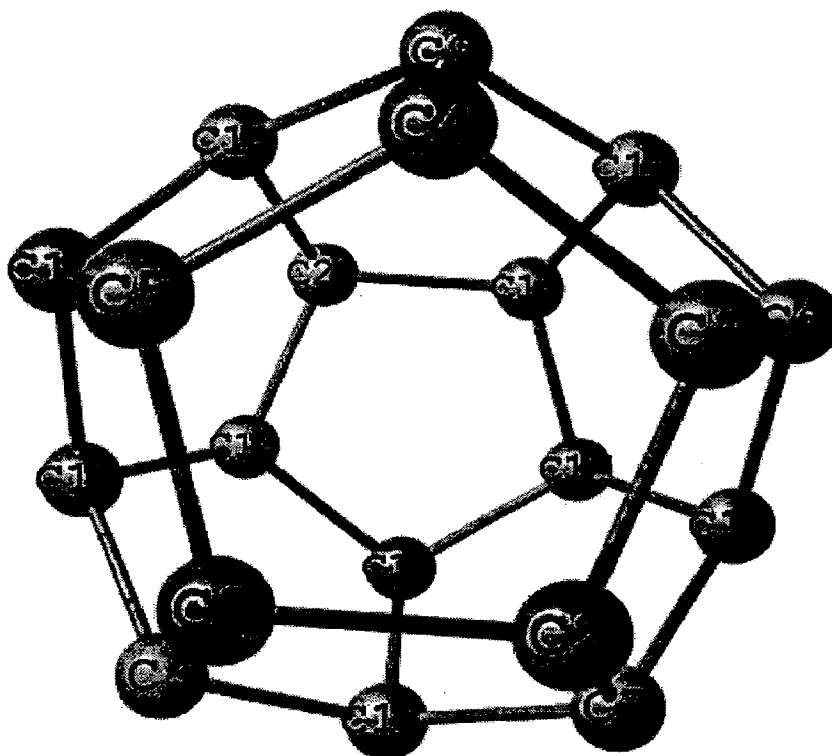


**Fig 8: The cage isomer of  $C_{20}$  ( $D_{3d}$  symmetry)**

**Table 6: Bond lengths ( $\text{\AA}$ ) of  $D_{5d}$  optimized cage structure**

Parameter <sup>c)</sup>	RHF/cc-pVDZ
$C_1-C_2$	1.418
$C_1-C_6$	1.466

c) For the numbering system see Fig 9

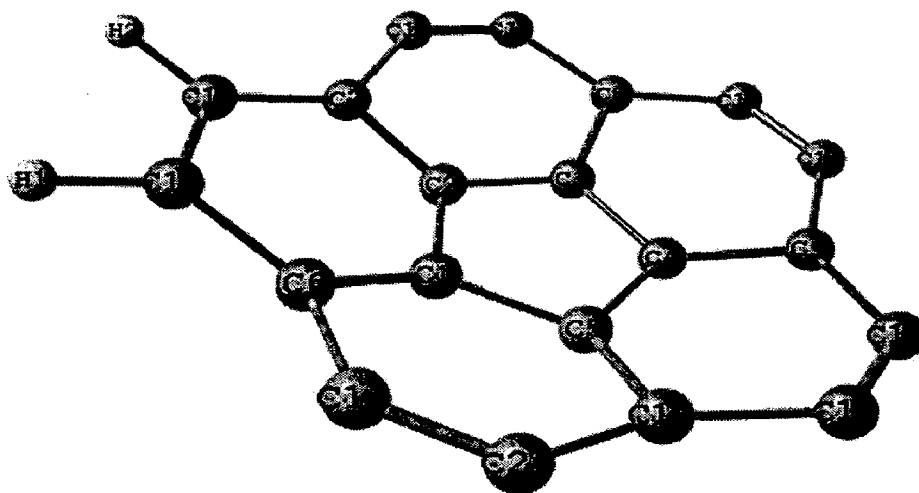


**Fig 9: The cage isomer of  $C_{20}$  ( $D_{5d}$  symmetry)**

The distance values at other levels and basis sets are slightly different from those presented in tables 4 to 6.

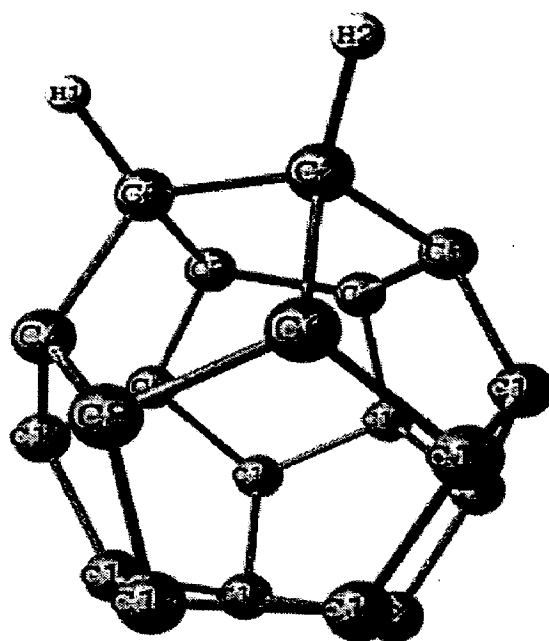
## Hydrogenation of C<sub>20</sub>

The energetics of addition of hydrogen to cage (C<sub>2</sub>) and bowl structures of C<sub>20</sub> was studied at the Hartree-Fock level. In the bowl structure, addition across the shortest C-C bond is expected to be the most favourable. Therefore, the peripheral C-C bond was chosen for the addition of H<sub>2</sub>. The resultant structure of C<sub>20</sub>H<sub>2</sub> was optimized and is shown in *Fig 10*. The peripheral C-C bond lengthens from the value of 1.22 Å to 1.378 Å in the process, as is to be expected.



**Fig 10:** Hydrogenated C<sub>20</sub> bowl structure

The newly formed C-H bond has a length of 1.075 Å which is in the typical range of values for C-H bonds, in the case of the cage structure the stable (in the sense of being a true local energy minimum) C<sub>2</sub> structure was chosen and hydrogen molecule was added across the C-C bond perpendicular to the C<sub>2</sub> axis. The resulting structure of C<sub>20</sub>H<sub>2</sub> is shown in *Fig 11*. In this case after addition the C-C bond lengthens from 1.481 Å to 1.582 Å and the C-H bond formed have a length of 1.079 Å, again within the normal range. Other distances also change marginally.



**Fig 11:**Hydrogenated  $C_{20}$  cage ( $C_2$  symmetry) structure

The energy of the various species involved and the energy changes on hydrogen are presented in Table 7. as expected the addition of  $H_2$  is exoergic and the  $\Delta E$  value is numerically higher for the bowl, consistent with the greater change in bond length.

**Table 7: Hydrogenation of  $C_{20}$  at RHF/D95V(d,p) level**

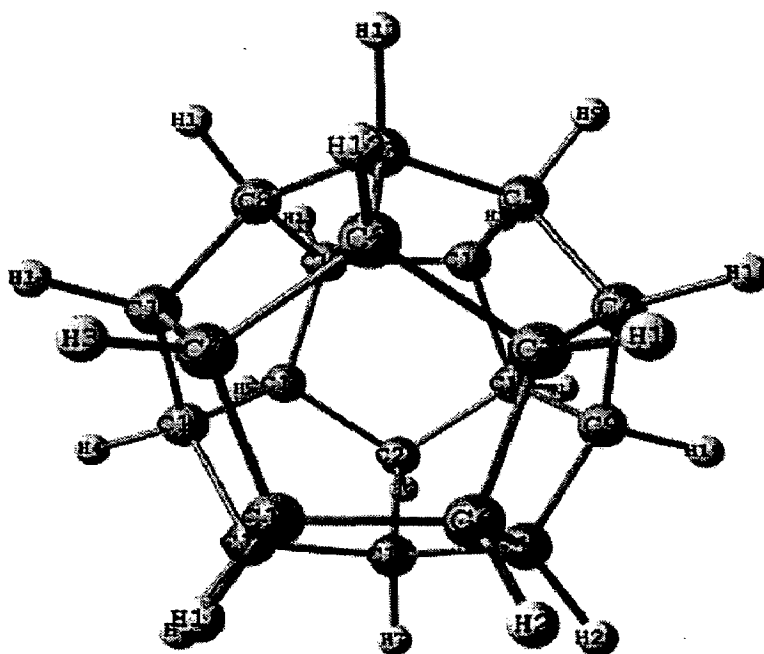
(Number of imaginary frequencies within parenthesis)

Isomer	$H_2$	$C_{20}$	$C_{20}H_2$	$\Delta E$ (Hartree)	$\Delta E$ (kcal/mole)
Cage ( $C_2$ )	-1.1312414	-756.6579235 (0)	-757.950263 (0)	-0.1610981	-101.025
Bowl ( $C_{5v}$ )	-1.1312414	-756.7380563 (0)	-758.0540322 (0)	-0.1847345	-115.847

Complete hydrogenation of the cage to form perhydrofullerene ( $C_{20}H_{20}$ ) was also studied. The resulting structure of  $C_{20}H_{20}$  had icosahedral ( $I_h$ ) symmetry, shown in Fig 12, with C-C bond distance of 1.548 Å and the C-H bond distance of 1.085 Å. The C-C

distance is comparable to the C-C bond length in ethane and is higher than all the C-C bond distances found in the case of  $C_{20}$  symmetry as given in Table 4.

Isomer	:	Cage
Energy of $10H_2$	:	-11.3124140 Hartrees
Energy of $C_{20}$	:	-756.6579235 Hartrees
Energy of $C_{20}H_{20}$	:	-769.1824165 Hartrees
$\Delta E$ (Hartree)	:	-1.212079
$\Delta E$ (kcal/mole)	:	-760.095



**Fig 12:** Perhydrofullerene structure

The above results refer to pure electronic energies at the optimum geometries only and therefore correspond to 0 K results. To include thermal effects contributions from zero point energy, vibrational, rotational and translational motions at 298 K were calculated on the idealized rigid rotor-harmonic oscillator approximation using statistical mechanical methods. The energy (electronic + thermal) enthalpy and free energy values so obtained for the various species and the changes in these for hydrogenation process are presented in the Table 8. The numerical values are consistently higher for bowl structure.

**Table 8:** Energy, Enthalpy and free energy changes  
at 298 K AT RHF/D95V(d,p level)

Species	Energy (Hartree)	Enthalpy (Hartree)	Free Energy (Hartree)
H <sub>2</sub>	-1.118276	-1.117331	-1.132098
C <sub>20</sub> (cage)	-756.527516	-756.526572	-756.568259
C <sub>20</sub> (bowl)	-756.611183	-756.610238	-756.657073
C <sub>20</sub> H <sub>2</sub> (cage)	-757.792863	-757.791919	-757.832834
C <sub>20</sub> H <sub>2</sub> (bowl)	-757.900777	-757.899833	-757.948091
$\Delta E/ \Delta H/ \Delta G$ (cage) (kcal/mole)	-92.33	-92.82	-83.08
$\Delta E/ \Delta H/ \Delta G$ (bowl)(kcal/mole)	-107.43	-108.27	-99.66

With a view to determining the activation energies, the transition structures of C<sub>20</sub>H<sub>2</sub> were also optimized. For the bowl structure the transition structure could be determined only at the RHF/3-21G level, the calculation at RHF/D95V(d,p) level failing to converge. Hence the energies of reactants were also computed at this level for consistency. The transition states obtained had two and seven imaginary frequencies, respectively and so represent saddle points of higher order than desired. Hence the activation energies presented in Table 9 are to be taken as tentative values at present. Because of the differing basis sets used, no serious interpretation can be placed on relative magnitudes of activation energies reported, viz. 65.142 kcal/mole for the cage isomer and 44.189 kcal/mole for the bowl isomer.

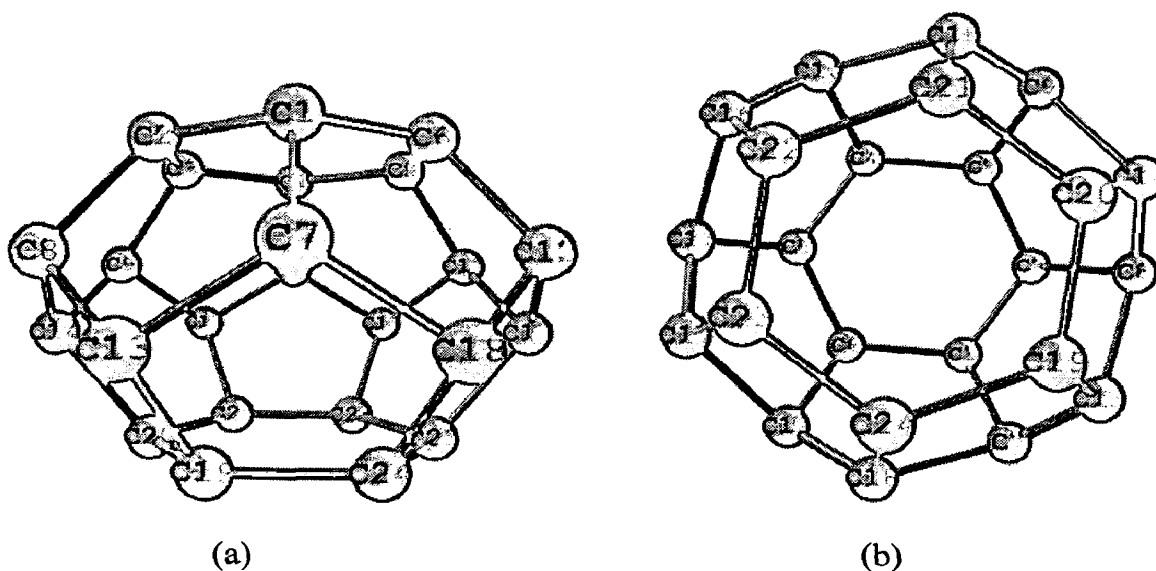
It may be mentioned at this point that to our knowledge present study is the first report on the hydrogenation of C<sub>20</sub> in the literature.

**Table 9:** Activation Energies of  $C_{20}$  structures

Isomer	$H_2$	$C_{20}$	Transition state ( $C_{20}H_2$ )	$\Delta E$ (Hartree)	$\Delta E$ (kcal/mole)
Cage RHF/D95V(d,p)	-1.1312414	-756.5580093	-757.5853730	0.1038777	65.142
Bowl RHF/3-21G	-1.1229598	-752.3829567	-753.4343673	0.0715492	44.189

### Studies on $C_{24}$

A beginning was made on the study of  $C_{24}$  cage structures too. In this case the fullerene has an ideal  $D_{6d}$  symmetry, but a Jahn-Teller distortion is expected to lower the symmetry to  $D_6$  [13]. In our calculations, the  $D_{6d}$  structure had its energy oscillating during the optimization process at the RHF/6-31G(d) level and the lowest energy reached being -907.8968864 Hartree. The  $D_6$  structure also did not converge satisfactorily; the least energy reached being -907.9573647 Hartree at RHF/D95V(d) level. The structures corresponding to these points are shown in *Fig 13*.



**Fig 13:**  $C_{24}$  structures (a)  $D_{6d}$  symmetry (b)  $D_6$  symmetry

Further lowering of symmetry to  $D_3$  appears to be warranted. There is also the possibility that a larger basis possibly with diffuse functions may be necessary and work in these directions is in progress.

### **Concluding Remarks:**

In these studies, the  $C_2$  structure of  $C_{20}$  was optimized at a late stage and therefore we have results on this system only for one basis set and DFT results for comparison are not available at present. It is hoped that further work to fill up these gaps will be taken up shortly in this laboratory. Activation energy calculations and similar studies on hydrogenation of  $C_{24}$  also merit further work. Studies on hydrogenation are the first of its kind to the best of our knowledge. It may also be remarked that most other work in this area, have used the 6-31G or 6-31G (d) basis sets and our results using D95V (d) provide a check on basis set effects in comparison.



## ***REFERENCES***

## References:

1. Feyereisen, M., Gutowski, M., Simons, J., *J. Chem. Phys.* **96** (4) 2926 (1991)
2. An, W., Gao, Y., Bulusu, S., Zeng, X.C. *J. Chem. Phys.* **122** 204109 (2005)
3. Zhongfang, C., Haijun, J., Michael, B., Andreas, H., Walter, T. *Theoretical Chem Acc***106**: 52-363 (2001)
4. Sokolova, S., Luchow, A., Anderson, J.B. *Chem. Phys. Lett.* **323** 229-233 (2000)
5. Helden, G.V., Hsu, M.T., Gotts, N.G., Kemper, P.R., Bowers, M.T. *Chem. Phys. Lett.* **204** 15 (1993)
6. Prinzbach, H., Weiler, A., Landenberger, P., Wahl, E., Worth, J., Scott, L.T., Gelmont, M., Olevano, D., Issendorff, B.V. *Nature* **404** 60 (2000)
7. Newton, M.D., Stanton, R.E., *J. Am. Chem. Soc.*, **108** 2469 (1986)
8. Slanina Z, Adamowicz, L. *Thermochimica Acta* **205** 299 (1992)
9. Parasuk, V., Almlöf, J., *Chem. Phys. Lett.* **184** 1-3 (1991)
10. Raghavachari, K., Strout, D.L., Odom, G.K., Scuseria, S.E., Pople, J.A., Johnson, B.G. and Gill, P.M.W. *Chem. Phys. Lett.* **214** number 3,4 357 (1993)
11. Raghavachari, K., Zhang, B., Pople, J.A., Johnson, B.G. and Gill, P.M.W. *Chem. Phys. Lett.* **220** 385-390 (1994)
12. Taylor, P.R., Bylaska, E., Weare, J.H. and Kawai, R., *Chem. Phys. Lett.* **235** 558 (1995)
13. Jensen, F. and Koch, H., *J. Chem. Phys.* **108** 3213 (1998)
14. Martin, M.L., Yazal, J.E., Francois JP, *Chem. Phys. Lett.* **255** 7-14 (1996)
15. Gaussian 98, Revision A.11.4, M. J. Frisch, G.W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, N. Rega, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen,

- M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian, Inc. Pittsburgh PA, 2002.
16. Dunning, T.H. Jr, Hay, P.J, in *Modern Theoretical Chemistry* Edited by H.F.Schaeffer III, (Plenum, NewYork, 1976) vol 3, 1
  17. Schlegel, H.B., *J Comp. Chem* 3 (2) 214-18 (1982)
  18. Moller, C. Plesset, M.S. *Phys. Rev.* 46 618 (1954)
  19. Hohenberg, P. and Kohn, W. *Phys. Rev.*, 136 B864 (1964)
  20. Kohn, W. and Sham, L.J. *Phys. Rev.* 140 A133 (1965)
  21. Becke, A.D., . *J. Chem. Phys.* 98, 5648 (1993)
  22. Lee, C., Yang, W., Parr, R.G. *Phys. Rev. B*, 37, 785 (1988).
  23. Vibha and Thankachan.P.P., “*Barriers to internal rotation and geometry of hydrazine*”, Presented at National conference on Modern Trends in Chemical Science and Technology, 15-17 October, 2005, Jalandhar (India)
  24. Woon, P.E., Dunning, T.H.Jr. *J. Chem. Phys.* 98 1358 (1993)

