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Hybrid Carbon Orbitals and Structures of Carbon Cage Clusters

Arjun Tan*, AlmuatasimAlomari, Marius Schamschula and Vernessa Edwards

Department of Physics, Alabama A & M University, Normal, AL 35762, U. S. A.
**E-Mail: arjun. tan@aamu. edu*

Abstract

The formation of Carbon cage clusters having regular and semi-regular polyhedral structures is studied from orbital hybridization considerations. It is found that only sp_2 hybridized Carbon atoms are capable of forming closed cage structures. Three criteria, viz., bond, bond angle and solid angle criteria are applied. It is found that only one Platonic solid and four Archimedean solids are capable of supporting Carbon cage cluster structures. Specifically, the Dodecahedron, Truncated Octahedron, Great Rhombicuboctahedron, Truncated Icosahedron and Great Rhomicosidodecahedron are able to represent the structures of C_{20}, C_{24}, C_{48}, C_{60} and C_{120} clusters, respectively.

1. INTRODUCTION

Since the discovery of the *Buckyballs* and *Fullerenes*, there has been an explosion of the study of Carbon clusters having cage-like structures [1, 2]. It has been suggested that small Carbon clusters can have linear and ring structures and only the larger clusters can have closed cage structures [3]. The possibility of smaller clusters having cage structures has put forward [4, 5]. It was suggested that the *Platonic solids* and *Archimedean solids* could provide potential structures for Carbon cage clusters [4, 5]. Bond limitations and sphericity were postulated to be the requirements for such possibilities [4, 5]. The present study re-examines this problem from the standpoint of atomic orbitals configurations, bond angles and solid angle considerations.

2. ORBITAL HYBRIDIZATION

The concept of atomic orbital hybridization was advanced by Pauling in order to explain the observed bonding patterns of the Carbon atom [6]. Carbon atoms undergo three types of orbital hybridizations as follows [7].

First, *sp hybridization*, in which one *s* electron in the valence shell hybridizes with one *p* electron (p_x, say) to produce two hybrid *sp orbitals*, as expressed by

$$[s + p_x] + p_y + p_z \rightarrow [sp^1 + sp^2] + p_y + p_z \quad (1)$$

The two hybrid orbitals are co-linear and oppositely directed. Their normalized wave functions are given by

$$\psi_{sp}^1 = \frac{1}{\sqrt{2}}\left[\psi_s + \psi_{px}\right] \quad (2)$$

and

$$\psi_{sp}^2 = \frac{1}{\sqrt{2}}\left[\psi_s - \psi_{px}\right] \quad (3)$$

When this atom undergoes chemical bonding, the two unmixed *p* electrons will form either a triple bond on one side and a single bond on the other, or one double bond on each side [8].

Second, *sp₂ hybridization*, in which one *s* electron in the valence shell hybridizes with two *p* electrons (p_x and p_y, say) to produce three hybrid *sp₂ orbitals*, as expressed by

$$\left[s + p_x + p_y\right] + p_z \rightarrow [sp_2^1 + sp_2^2 + sp_2^3] + p_z \quad (4)$$

The three hybrid orbitals are co-planar in the *x*-*y* plane with the nucleus at the origin and directed at angles of 120° apart. If one hybrid orbital is directed along the *x*-axis, then then normalized wave functions of the three orbitals are given by

$$\psi_{sp2}^1 = \frac{1}{\sqrt{3}}\left[\psi_s + \sqrt{2}\psi_{px}\right] \quad (5)$$

$$\psi_{sp2}^2 = \frac{1}{\sqrt{3}}\left[\psi_s - \frac{1}{\sqrt{2}}\psi_{px} + \sqrt{\frac{3}{2}}\psi_{py}\right] \quad (6)$$

and

$$\psi_{sp2}^3 = \frac{1}{\sqrt{3}}\left[\psi_s - \frac{1}{\sqrt{2}}\psi_{px} - \sqrt{\frac{3}{2}}\psi_{py}\right] \quad (7)$$

When this atom undergoes chemical bonding, the unmixed p_z electron produces one double bond.

Third, *sp₃ hybridization*, in which one *s* electron in the valence shell hybridizes with all three *p* electrons to produce four hybrid *sp₃ orbitals* as expressed by

$$\left[s + p_x + p_y + p_z\right] \rightarrow [sp_3^1 + sp_3^2 + sp_3^3 + sp_3^4] \quad (8)$$

The four hybrid orbitals are directed towards the corners of a regular tetrahedron with the nucleus of the atom at the centroid of the tetrahedron which is at the origin, and separated by angles of $cos^{-1}\left(-\frac{1}{3}\right)$ ≈109. 47°. If one of the hybrid orbitals (sp_3^4, say) is directed along the vertical *z*-axis, the other orbitals lie below the *x*-*y* plane towards the corners of an equilateral triangle. Further, if sp_3^3 lies below the *x*-axis, the normalized wave functions of the hybrid orbitals are given by

$$\psi_{sp3}^1 = \sqrt{\frac{2}{5}}\left[\psi_s + \psi_{px} - \frac{1}{\sqrt{3}}\psi_{py} - \frac{1}{\sqrt{6}}\psi_{pz}\right] \quad (9)$$

$$\psi_{sp3}^2 = \sqrt{\frac{2}{5}}\left[\psi_s - \psi_{px} - \frac{1}{\sqrt{3}}\psi_{py} - \frac{1}{\sqrt{6}}\psi_{pz}\right] \quad (10)$$

$$\psi_{sp3}^3 = \sqrt{\frac{2}{5}}\left[\psi_s + \frac{2}{\sqrt{3}}\psi_{py} - \frac{1}{\sqrt{6}}\psi_{pz}\right] \quad (11)$$

and

$$\psi_{sp3}^{4} = \sqrt{\frac{2}{5}}\left[\psi_s + \sqrt{\frac{3}{2}}\psi_{pz}\right] \quad (12)$$

When this atom undergoes chemical bonding, all four bonds are single [6].

The following facts pertaining to Carbon cage clusters readily follow. Firstly, the *sp hybridized carbon atoms* can only form linear clusters and must therefore be excluded from cage cluster formation [8]. Secondly, each *sp_3 hybridized Carbon atom* must be connected to four other carbon atoms, three of which can be possibly placed on the surface of a sphere. However, the fourth atom will lie perpendicular to that surface (cf. [9]) and the bending required to place the fourth atom on that would be greater than 90º. Covalent bonds formed from orbital overlaps can bend to a certain extent, but not to that degree. Thus, the *sp_3* hybridized carbon atoms must also be ruled out in cage cluster formation. That leaves us with only *sp_2 hybridized Carbon atoms,* which must constitute as building blocks of Carbon cage clusters.

3. CRITERIA FOR CARBON CAGE CLUSTER FORMATION

Three criteria pertaining to the formation of Carbon cage clusters having Platonic and Archimedean solid structures logically follow.

First, *Bond criterion*. Since only *sp_2* hybridized Carbon atoms can assemble a cage cluster, each atom must have three bonds, two of them single and one double. If each vertex of a Platonic or Archimedean solid is connected to four or five edges, that solid cannot accommodate a Carbon cage cluster. All atoms in the cage clusters must be connected to three neighbouring atoms.

Second, *Bond angle criterion*. The Platonic and Archimedean solids are bounded by one to three regular polygons, which include the equilateral triangles, squares, regular pentagons, hexagons, octagons and decagons. The internal angle between two adjacent sides of a regular *n*-sided polygon is$(n-2)\pi/n$. For the triangle, square, pentagon, hexagon, octagon and decagon, this angle is equal to 60º, 90º, 108º, 120º, 135º and 144º, respectively. This angle will be the angle between two adjacent bonds at the boundary of a polygon should a cage cluster be formed. Since the angle between two *sp_2* atoms is 120º, the *angular defect* for the above polygons will be 60º, 30º, 12º, 0º, 15º and 24º, respectively. Knowing that bonds do bend to a certain extent, a tolerance limit of 30º is allowed for the angular defect in this study. This will eliminate only the equilateral triangle amongst the polygons for cage cluster formation.

Third, *Solid angle criterion*. Since the *sp_2* orbitals lie in a plane, the *sp_2* hybridized Carbon atoms most preferentially form *Graphene* sheets, where there is zero strain due to the absence of curvature and the solid angle at each atom is that subtended by an infinite plane or 2π. For the Platonic and Archimedean solids, the solid angle at any vertex is smaller than this value. For such solids to accommodate Carbon cage clusters, it is desirable to have this solid angle as close to the ideal value of 2π as possible. For the Archimedean solids, the values of this solid angle was available in the literature only recently [10].

4. RESULTS

The Platonic and Archimedean solids are regular and semi-regular polyhedra, respectively, made up of one or more kinds of regular polygons, respectively. The formation of Carbon cage structures having Platonic and Archimedean solid geometry has been studied from bond consideration and sphericity [4, 5]. In this study, we examine the same problem from the point of view of bond formation and bond angle considerations and solid angle considerations.

The five Platonic and 13 Archimedean solids are depicted in Fig. 1. Table I specifies the polygons of which the solids are composed. Table I also lists the Carbon clusters these solids can potentially represent. The Carbon atoms would all be sp_2 hybridized and located at the vertices of the solids, their numbers corresponding to the numbers of vertices of the solids.

Table II lists the number of bonds each Platonic and Archimedean solid will prescribe should a Carbon cluster be formed. The number of bonds is the number of edges to which each vertex of the solid is connected. The bond criterion immediately rules out any solid requiring four or five bonds. This is the most stringent criterion for Carbon cage cluster formation and rules out nine of the 18 solids forthwith.

Table III lists the bond angles each Platonic and Archimedean solid will prescribe if a Carbon cage cluster is formed out of the solid. In accordance with the bond angle criterion, only bond angles of 60^o can be ruled out confidently. Quite amazingly, this single exclusion would rule out 12 out of 18, or two-thirds of the solids from Carbon cage cluster formation.

Table IV pertains to the solid angle criterion. The solid angle at a vertex of each Platonic and Archimedean solids is taken from a recent study [10]. Also listed is the solid angle as a fraction of the ideal solid angle (2π). Since the largest Archimedean solid only attains 75% of this ideal solid angle, a cut-off value of one-half of that or 37. 5% is taken as the minimum solid angle at vertex for Carbon cluster formation. This criterion only excludes three smallest Platonic solids and the smallest Archimedean solid from contention.

We now proceed to the results for the individual Platonic and Archimedean solid to decide if they are capable of representing a Carbon cage cluster.

(1) The *Tetrahedron* is the smallest of the 18 solids by all measures. It passes the important bond criterion to potentially represent the C_4 cluster. However, it fails the bond angle criterion and miserably fails the solid angle criterion. Overall, a negative outcome is assessed for Carbon cage cluster formation. A tetrahedral core is actually formed in the synthetically made *Tetrahedral derivatives* [11], but such a core is made of sp_3 hybridized Carbon atoms.

(2) The *Octahedron* is the second smallest of the 18 solids which is a candidate for the C_6 cluster formation. It requires four bonds for each Carbon atom, which is not achievable by sp_2 hybridized atoms. It is therefore ruled out by the most important bond criterion. It also fails the bond angle and solid angle criteria.

(3) The *Hexahedron/Cube* passes the bond criterion and also the bond angle criterion. However, it fails the solid angle criterion. The solid angle at a corner of the cube is that subtended by an octant or $\pi/2$, which is only a quarter of the

ideal solid angle. The outcome for supporting the C_8 Carbon cluster is assessed as highly unlikely. It is interesting to note that the synthetically prepared *Cubane molecule* has a hexahedral structure [11], but that molecule is made of sp_3 hybridized Carbon atoms.

(4) The *Icosahedron* does not pass the bond criterion, requiring five bonds for each Carbon atom. It also fails the bond angle criterion. It however passes the solid angle criterion. Overall, the Icosahedron is incapable of supporting the C_{12} cluster.

(5) The *Dodecahedron* passes all three criteria and is therefore capable of supporting the C_{20} cluster. It is the largest Platonic solid and the only Platonic solid larger than the two smallest Archimedean solids. The Dodecahedron emerges as the only Platonic solid capable of supporting a Carbon cage cluster. It has been referred to as the smallest Fullerene or a Fullerene without any hexagons.

(6) The *Truncated Tetrahedron* is made up of hexagons and equilateral triangles. It passes the bond criterion, but fails the bond angle criterion and the solid angle criterion. It is therefore ruled out as a candidate for the C_6 cluster formation.

(7) The *Cuboctahedron* is made from squares and equilateral triangles. It fails the bond criterion and bond angle criterion, but passes the solid angle criterion. The failure to satisfy the bond criterion categorically rules it out from the contention of the C_{12} cluster formation. In view of the results for the solids (4), (6) and (7), no C_{12} cluster formation by Platonic or Archimedean solids is possible.

(8) The *Truncated Cube* is made from equilateral triangles and octagons. It passes the bond criterion and the solid angle criterion, but fails the bond angle criterion. The possibility of this solid to support C_{24} cluster is assessed as extremely remote.

(9) The *Truncated Octahedron* is made up of hexagons and squares. It passes all three criteria and is therefore able to represent the structure of the C_{24} cluster. The squares are bounded by single bonds, whereas the hexagons are bounded by alternate single and double bonds.

(10) The *Rhombicuboctahedron*, like the Cuboctahedron is made of equilateral triangles and squares. Like the latter, it too fails the bond criterion and the bond angle criterion, but passes the solid angle criterion. Consequently, it is unable to represent the C_{24} cluster.

(11) The *Snub Cube* is yet another solid made from equilateral triangles and squares. It too fails the bond criterion and the bond angle criterion, but passes the solid angle criterion. Consequently, it is unable to represent the C_{24} cluster. Thus, only one Archimedean solid is able support the C_{24} cluster structure.

(12) The *Icosidodecahedron* is made from pentagons and equilateral triangles. It fails the bond criterion and bond angle criterion, passing only the solid angle criterion. It is therefore, unable to represent the C_{30} cluster. Being the lone candidate for C_{30} cluster, this assures that no Archimedean solid can support a C_{30} cage cluster.

(13) The *Great Rhombicuboctahedron* is made up of squares, hexagons and octagons. It passes all three criteria and is therefore eligible to represent the C_{48} cluster. The squares are bounded by single bonds, whereas the hexagons and octagons are bounded by alternate single and double bonds.

(14) The *Truncated Icosahedron* represents the famed C_{60} Buckyball. It is structurally made of pentagons and hexagons like all fullerenes (barring the Dodecahedron). The pentagons are bounded by single bonds, whereas the hexagons are bounded by alternate single and double bonds. The Truncated Icosahedron passes all three criteria comfortably and its bond angles of 108^o and 120^o are the most favourable amongst all solids, which explains why it is formed so readily.

(15) The *Truncated Dodecahedron* is made up of equilateral triangles and decagons. It fails the bond criterion and the bond angle criterion, passing only the solid angle criterion. It is unable to provide an alternative structure of the C_{60} cluster.

(16) The *Rhombicosidodecahedron* is made of equilateral triangles, squares and pentagons. Like the previous candidate, it fails the bond criterion and bond angle criterion, passing only the solid angle criterion. Like the previous candidate, it is unable to provide an alternative structure of the C_{60} cluster.

(17) The *Snub Dodecahedron* is made of equilateral triangles and pentagons. Like the two preceding candidates, it fails the bond criterion and bond angle criterion, passing only the solid angle criterion. Like the two preceding candidates, it is unable to provide an alternative structure of the C_{60} cluster.

(18) The *Great Rhobicosidodecahedron* is made of squares, hexagons and decagons. It is the fifth and final solid which passes all three criteria for Carbon cage cluster formation and represents the giant C_{120} cluster whence formed.

The five solids satisfying all three criteria and therefore able to accommodate Carbon cage clusters are shown in Fig. 2. In that figure, the Carbon atoms occupy the vertices, the solid lines represent double bonds and the broken lines represent single bonds. It is observed that the squares are always bounded by single bonds, whereas the hexagons, octagons and decagons are always bounded by alternate single and double bonds. It can be verified that the total number of bonds in each solid is always divisible by three and single bonds are twice as numerous as the double bonds – a consequence of sp_2 hybridization.

Table I. General Properties of Platonic & Archimedean Solids

Platonic/Archimedean Solid	Polygon 1	Polygon 2	Polygon 3	C cluster if formed
Tetrahedron	Triangle			C_4
Octahedron	Triangle			C_6
Cube	Square			C_8
Icosahedron	Triangle			C_{12}
Dodecahedron	Pentagon			C_{20}
Truncated Tetrahedron	Triangle	Hexagon		C_{12}
Cuboctahedron	Triangle	Square		C_{12}
Truncated Cube	Triangle	Octagon		C_{24}
Truncated Octahedron	Square	Hexagon		C_{24}
Rhombicuboctahedron	Triangle	Square		C_{24}
Snub Cube	Triangle	Square		C_{24}
Icosidodecahedron	Triangle	Pentagon		C_{30}
Great Rhombicuboctahedron	Square	Hexagon	Octagon	C_{48}
Truncated Icosahedron	Pentagon	Hexagon		C_{60}
Truncated Dodecahedron	Triangle	Decagon		C_{60}
Rhombicosidodecahedron	Triangle	Square	Pentagon	C_{60}
Snub Dodecahedron	Triangle	Pentagon		C_{60}
Great Rhombicosidodecahedron	Square	Hexagon	Decagon	C_{120}

Table II. Number of Bonds in Platonic & Archimedean Solids

Platonic/Archimedean Solid	3 Bonds	4 Bonds	5 Bonds	If allowed
Tetrahedron	Yes			Yes
Octahedron		Yes		No
Cube	Yes			Yes
Icosahedron			Yes	No
Dodecahedron	Yes			Yes
Truncated Tetrahedron	Yes			Yes
Cuboctahedron		Yes		No
Truncated Cube	Yes			Yes
Truncated Octahedron	Yes			Yes
Rhombicuboctahedron		Yes		No
Snub Cube			Yes	No
Icosidodecahedron		Yes		No
Great Rhombicuboctahedron	Yes			Yes
Truncated Icosahedron	Yes			Yes
Truncated Dodecahedron			Yes	No
Rhombicosidodecahedron		Yes		No
Snub Dodecahedron			Yes	No
Great Rhombicosidodecahedron	Yes			Yes

Table III. Bond Angles in Platonic & Archimedean Solids

Platonic/Archimedean Solid	Angle 1	Angle 2	Angle 3	If allowed
Tetrahedron	60º			No
Octahedron	60º			No
Cube	90º			Yes
Icosahedron	60º			No
Dodecahedron	108º			Yes
Truncated Tetrahedron	60º	120º		No
Cuboctahedron	60º	90º		No
Truncated Cube	60º	135º		No
Truncated Octahedron	90º	120º		Yes
Rhombicuboctahedron	60º	90º		No
Snub Cube	60º	90º		No
Icosidodecahedron	60º	108º		No
Great Rhombicuboctahedron	90º	120º	135º	Yes
Truncated Icosahedron	108º	120º		Yes
Truncated Dodecahedron	60º	144º		No
Rhombicosidodecahedron	60º	90º	108º	No
Snub Dodecahedron	60º	108º		No
Great Rhombicosidodecahedron	90º	120º	144º	Yes

Table IV. Vertex Solid Angles in Platonic & Archimedean Solids

Platonic/Archimedean Solid	Vertex Solid Angle Ω	Ω/2π	%of ideal	If allowed
Tetrahedron	0. 551	0. 088	8. 8	No
Octahedron	1. 359	0. 216	21. 6	No
Cube	1. 571	0. 250	25. 0	No
Icosahedron	2. 635	0. 419	41. 9	Yes
Dodecahedron	2. 962	0. 471	47. 1	Yes
Truncated Tetrahedron	1. 911	0. 304	30. 4	No
Cuboctahedron	2. 462	0. 392	39. 2	Yes
Truncated Cube	3. 615	0. 575	57. 5	Yes
Truncated Octahedron	3. 142	0. 500	50. 0	Yes
Rhombicuboctahedron	3. 481	0. 554	55. 4	Yes
Snub Cube	3. 590	0. 571	57. 1	Yes
Icosidodecahedron	3. 674	0. 585	58. 5	Yes
Great Rhombicuboctahedron	3. 927	0. 625	62. 5	Yes
Truncated Icosahedron	4. 249	0. 676	67. 6	Yes
Truncated Dodecahedron	3. 871	0. 616	61. 6	Yes
Rhombicosidodecahedron	4. 446	0. 708	70. 8	Yes
Snub Dodecahedron	4. 510	0. 718	71. 8	Yes
Great Rhombicosidodecahedron	4. 712	0. 750	75. 0	Yes

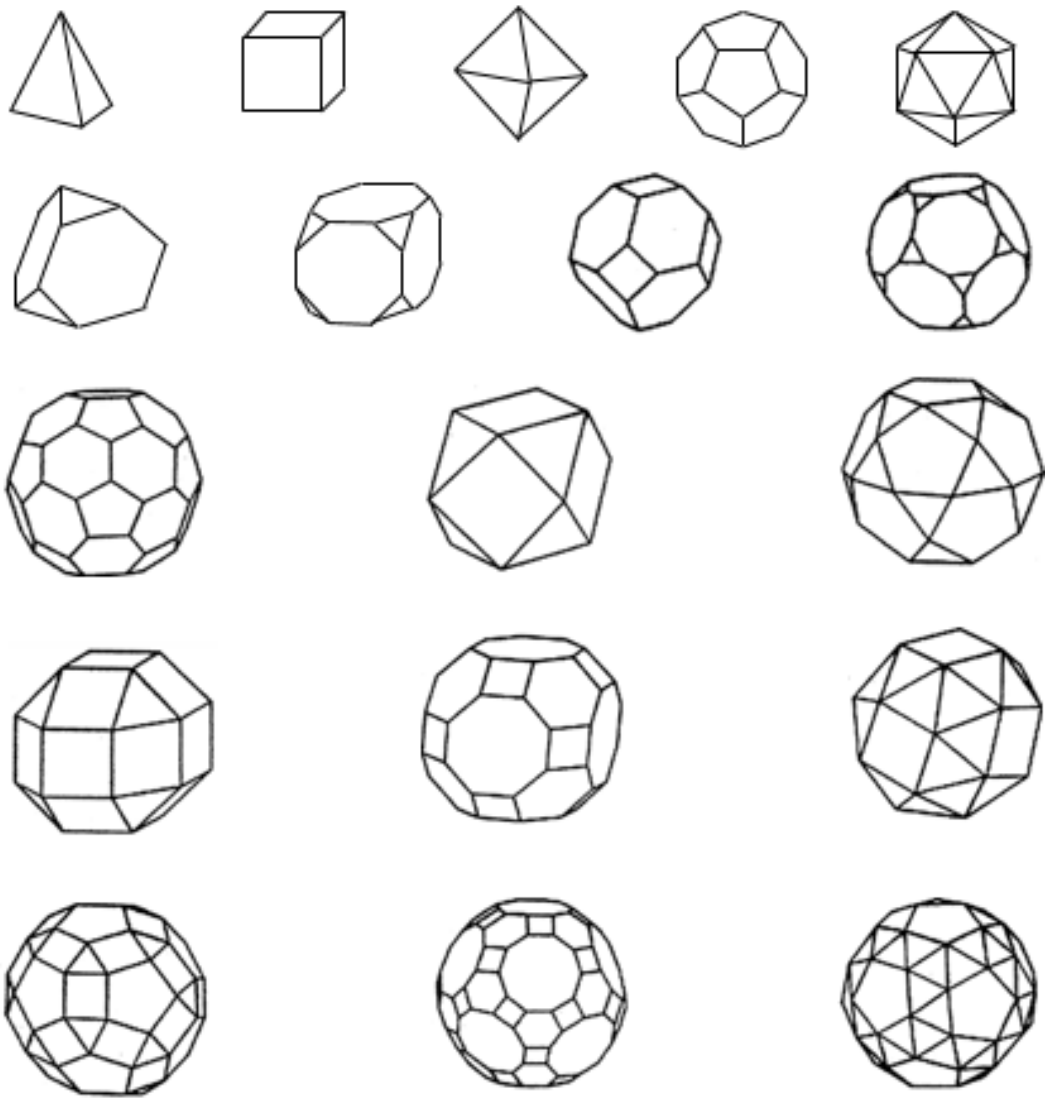

Fig. 1. Platonic and Archimedean solids: Top to bottom, left to right: Tetrahedron, Cube, Octahedron, Dodecahedron and Icosahedron; Truncated Tetrahedron, Truncated Cube, Truncated Octahedron and Truncated Dodecahedron; Truncated Icosahedron, Cuboctahedron and Icosidodecahedron; Rhombicuboctahedron, Great Rhombicuboctahedron and Snub Cube; Rhombicosidodecahedron, Great Rhombicosidodecahedron and Snub Dodecahedron.

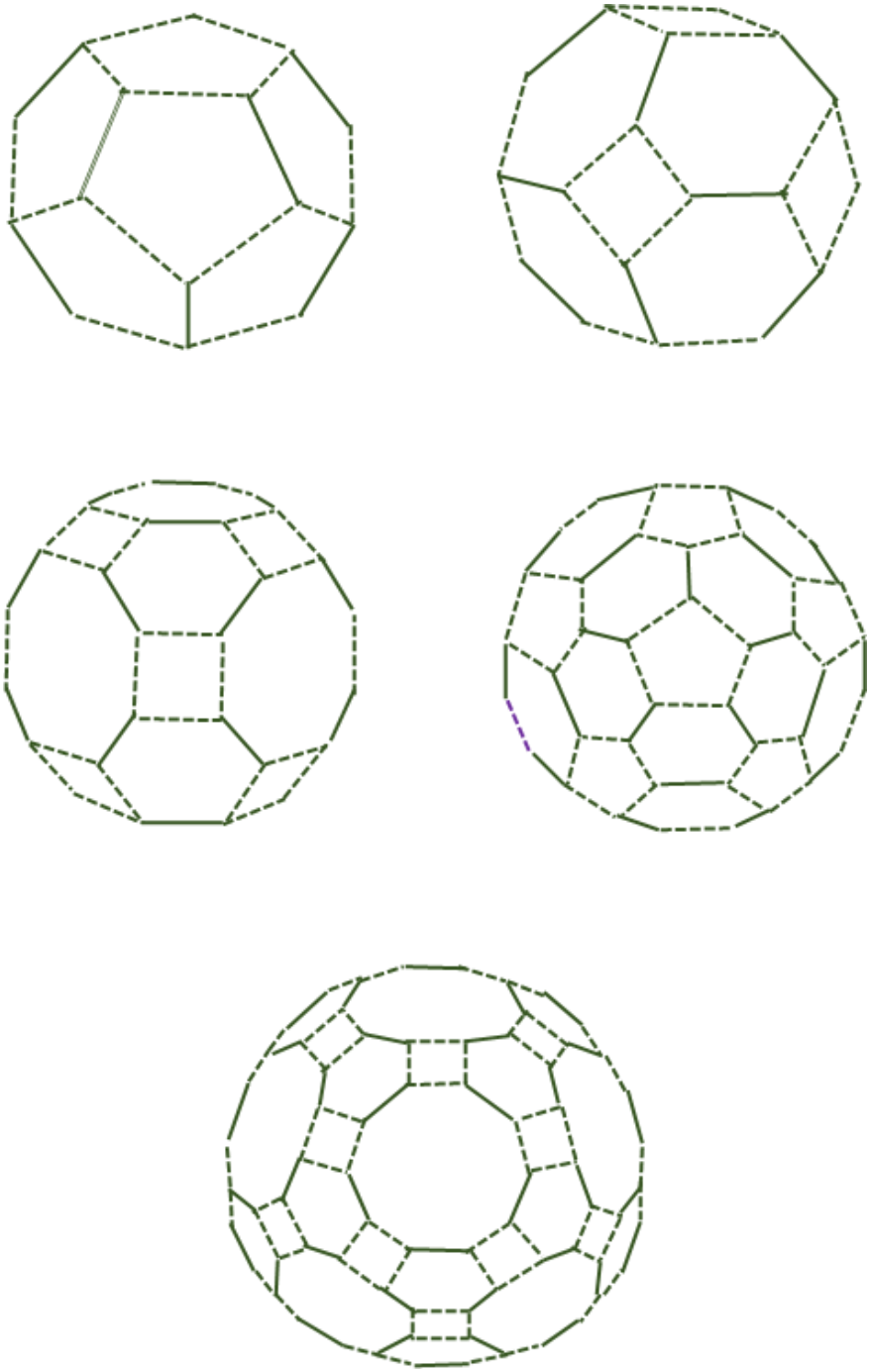

Fig. 2. Platonic and Archimedean solids suitable for cage Carbon cage clusters: Top to bottom, left to right: Dodecahedron, representing C_{20}; Truncated Octahedron, representing C_{24}; Great Rhombicuboctahedron, representing C_{48}; Truncated Icosahedron, representing C_{60}; and Great Rhombicosidodecahedron, representing C_{120}. The solid lines represent double bonds whereas the broken lines represent single bonds.

5. DISCUSSION

The formation of Carbon cage clusters having regular and semi-regular polyhedral structures has been examined. As a result of restrictions imposed by the bonds, bond angle and solid angle criteria, only one Platonic solid and four Archimedean solids are able to support Carbon cage structures. The results differ from our earlier studies [4, 5] in which sp_3 hybridized atoms were allowed to partake in the cage cluster formations. Considering the limitations imposed by hybridized orbital configurations, the result of the present study are deemed more credible.

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