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Santiago Alvarez, Jorge Echeverría

Departament de Química Inorgànica and Institut de Química Teòrica i Computacional,
Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona (Spain). Fax: +34-93-490
7725; e-mail: santiago@qi.ub.es

Abstract

Relevant families of ideal polyhedra (Platonic, Archimedean, prisms Johnson, and Fullerenes) are briefly summarized, and an overview of polyhedral alkanes and alkenes, existing or hypothetical, is presented. The assignment of a polyhedral shape to a specific compound with the help of *continuous shape measures* and derived tools is also briefly discussed, and application of shape analysis to cyclic molecules such as cyclobutane, cyclohexane and cyclooctatetraene is presented to illustrate the usefulness of ideal polyhedra in the stereochemical description of non-polyhedral molecules. Finally, the presence of latent octahedral symmetry in icosahedral polyhedra is used to design new molecules with nested shells of the two supposedly incompatible symmetries, and to explain the cubic crystal structures of icosahedral molecules such as dodecahedrane and Buckminsterfullerene.

Keywords: Continuous shape measures, stereochemistry, polyhedral molecules, polyhedranes, polyhedrenes.

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I filled near full with Pease and Water, the iron Pot and laid on the Pease a leaden cover [...] the Pease dilated [...] and] what they increased in bulk was [...] pressed into the interstices of the Pease, which they adequately filled up, being thereby formed into pretty regular Dodecahedrons.

Stephen Hales, Vegetable Staticks, 1727.

Introduction

While the Platonic tetrahedral coordination around a carbon atom, proposed in 1874 by Jacobus Henricus Van 't Hoff and Joseph Achille Le Bel, represented the cornerstone of a new discipline, stereochemistry, molecules with polyhedral skeletons in which a carbon atom occupies each vertex, are relatively newcomers to the world of synthesized and well characterized molecules. The oldest member of the family of polyhedranes, cubane, was reported in 1964.^[1] A subsequent geometrical analysis of prisms, Platonic and Archimedean polyhedra, pointed to those that could be made of sp^3 -hybridized carbon atoms.^[2] Tetrahedrane had to wait more than a decade to see the light,^[3] and soon after dodecahedrane could be synthesized.^[4] Much more recent is the discovery of buckminsterfullerene, of formula C_{60} , with the shape of a truncated icosahedron.^[5] Besides the Platonic solids, there are other sorts of semiregular polyhedra that can be made as purely organic molecules. These include Archimedean solids, prisms and some of the 92 Johnson polyhedra.^[6]

With the structure of a polyhedral molecule at hand, we must address two relevant stereochemical questions: Which ideal polyhedron represents best its stereochemistry? How similar is the molecular structure to the ideal shape? Avnir and coworkers have proposed that symmetry^[7] and shape^[8] should be treated as continuous properties and defined *continuous symmetry measures* (CSM) and *continuous shape measures* (CShM). These parameters allow us to calibrate the deviation of structures from a given symmetry or shape at the same scale, independent of their size or number of vertices. Later on, we showed that one can define a minimal distortion interconversion path between two polyhedra in terms of continuous shape measures and therefore numerically evaluate not only the deviation of a given structure from a particular polyhedron, but also its deviation from the minimal distortion path between two reference polyhedra.^[9]

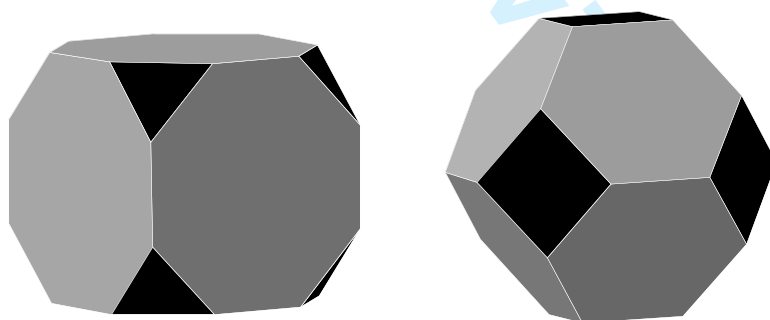
Herein we wish to present an overview of the main polyhedral organic molecules. We will also present examples of minimal distortion paths between a polygon and a polyhedron to organize structural and conformational diversity of cyclohexyl and cyclooctatetraene derivatives. Finally, we will discuss the latency of cubic symmetry in icosahedral and

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4 tetrahedral molecules, and on the implications for crystal packing and for the design of metal-
5 organic frameworks.
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7 8 **Shape and Symmetry of Ideal Polyhedra** 9

10 Although molecular shape and symmetry are intimately associated, it is important to stress
11 here the main differences between these two properties. Let us consider as an example the two
12 Archimedean polyhedra with 24 vertices shown in Figure 1, the truncated cube and the truncated
13 octahedron: they both have octahedral symmetry (i.e., they belong to the O_h symmetry point
14 group), but they differ in their number and type of faces. In other words, they have the same
15 symmetry but different shapes.
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20 In brief, we say that *two objects (molecules) have the same shape if they differ only in size,*
21 *position or orientation in space.* Alternatively, we can say that two objects (molecules) have the
22 same shape if they can be superimposed by combinations of translations, rotations and isotropic
23 scaling.^[10] On the other hand, two objects have the same symmetry if they remain
24 indistinguishable after application of the same set of symmetry operations. It follows that two
25 objects with different shapes may have the same symmetry, and we can therefore conclude that
26 shape is a more stringent criterion than symmetry, as illustrated by the examples in Figure 1.
27 There are, however some cases in which shape and symmetry are equivalent, and these
28 correspond precisely to the Platonic polyhedra, since, e. g., all four vertex polyhedra with
29 tetrahedral symmetry have the same shape, and the same happens for the octahedron, the cube,
30 the dodecahedron and the icosahedron. Among the Archimedean polyhedra, only for the
31 cuboctahedron and the icosidodecahedron are shape and symmetry equivalent.
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51
52 **Figure 1.** Two Archimedean polyhedra with octahedral symmetry and 24 vertices: the truncated
53 cube (left) and the truncated octahedron (right).
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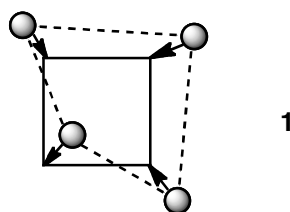
55 The set of Platonic solids (tetrahedron, octahedron, cube, icosahedron and dodecahedron)
56 are the most regular polyhedra, each having all its edges, faces and vertices equivalent. Second
57 to the Platonic solids in regularity come the Archimedean polyhedra, in which all vertices (but
58 not faces or edges) are equivalent. However, these two families provide us with only a limited
59 number of ideal shapes and we should have at hand other sets of less regular polyhedra. For
60

instance, the prisms, whose ideal shapes are conventionally those with all edges of the same length. As a result, all the faces of the ideal prisms are regular polygons. If more reference shapes are needed we can make recourse to the 92 Johnson polyhedra,^[11] defined as those that have as faces only regular polygons with edges of the same length, excluding the Platonic, Archimedean, prismatic and antiprismatic polyhedra. Yet another important family of polyhedra is that of the Fullerenes. Even if the name comes from C₆₀, Buckminsterfullerene, that has the shape of the Archimedean truncated icosahedron, it refers to all those polyhedra with twelve pentagonal and any number of hexagonal faces,^[12] in which all vertices are three-connected.

We note that the Platonic and Archimedean polyhedra belong to one of three high-symmetry point groups, icosahedral (I_h), octahedral (O_h) or tetrahedral (T_d), or to their rotational subgroups. In principle, icosahedral and octahedral symmetries are incompatible,^[13] since the former features five-fold rotational axes, while the latter has four-fold axes instead. However, we have recently shown^[14] that icosahedral polyhedra have latent octahedral symmetry^[15] that can be revealed in chemical structures by an appropriate substitution pattern. We will go back to some chemical implications of this symmetry paradox in a later section.

Continuous Shape and Symmetry Measures

According to the proposal of Avnir and coworkers,^[7, 16] in order to obtain a shape measure for a structure *X* (represented in **1** by the circles joined by dashed lines) we need first to search for the ideal shape *A* (represented in **1** by a square) that is closest to our problem structure. This search requires optimization with respect to size, orientation in space and pairing of vertices of the two structures. Once the reference shape is found, we calculate the distances between the equivalent atomic positions in the two structures, *q_k*, from which we calculate the shape measure according to equation 1, where *N* is a normalization factor that makes the continuous shape measures (CShM) values size independent. To optimize *A*, *S_X(A)* must be minimized with respect to size, orientation and vertex pairing.



$$S_X(A) = \min \frac{\sum_{k=1}^N q_k^2}{N} 100 \quad [1]$$

From the definition of equation 1 it can be shown that the $S_X(A)$ values must lie between 0 and 100. The resulting value is zero if the problem structure X has exactly the desired shape A , and will increase with the degree of distortion. As a rule of thumb we can say that chemically significant distortions should give CShM values higher than about 0.1, while values of the order of 2 or higher indicate important distortions.^[17] Since all CShM values are in the same scale, independently of the reference shape adopted and the number of vertices, we can compare, for instance, the deviation of a given structure from different reference shapes or of different structures with respect to the same ideal shape.

Some Polyhedral Alkanes

Since the fullerenes form a wide family and a huge number of publications have been devoted to them, we concentrate here on the more sparse examples of polyhedral molecules from other families. Some structurally characterized polyhedral alkanes are summarized in Table 1, most of them with Platonic or Archimedean polyhedral shapes. The Johnson and Catalan polyhedra all have vertices with connectivity four or higher, making them poorly adapted for cage alkanes. Nevertheless, if we allow some of the edges of a polyhedron to correspond to non-bonded atoms, accepting some deviation from the ideal polyhedron, we may find a couple of Johnson polyhedranes. One of them is bicyclo(1.1.1)pentane, which resembles a trigonal bipyramid, with structures of its derivatives presenting shape measures relative to such a polyhedron between 1 and 2. Cunneanes (Figure 2), in contrast, deviate significantly from the ideal gyrobifastigium (shape measures of about 8.8), due to the presence of two non-bonded edges. However, the gyrobifastigium is still the polyhedral shape that best describes the structures of cunneanes. Another interesting irregular polyhedron is that showcased by octahedrane (Figure 2), sometimes named "melancholyhedron" because it first appeared in an well known engraving from Albrecht Dürer titled *Melancholy*.^[6]



Figure 2. Structures of the carbon skeletons of bicyclopentane, cunneane and octahedrane, that approximate the geometry of the trigonal bipyramid, the gyrobifastigium, and the melancholyhedron, respectively.

Table 1. Structurally characterized polyhedranes.

Compound	n	Polyhedron	Family	Ref.
Experimental Structures				
Tetrahydrane	4	Tetrahedron	Platonic	[18]
Bicyclo(1.1.1)pentane	5	~ Trigonal Bipyramid	Johnson	[19]
Prismane	6	Trigonal Prism	Prism	[20]
Cubane	8	Cube	Platonic	[21]
Cunneane	8	~ Gyrobifastigium	Johnson	[22]
Pentaprismane	10	Pentagonal Prism	Prism	[23]
Hexaprismane	12	Hexagonal Prism	Prisms	[24]
Octahedrane	12	Melancholyhedron	Irregular	[25]
Dodecahydrane	20	Dodecahedron	Platonic	[26]
Theoretical Structures				
Truncotohydrane	24	Truncated Octahedron	Archimedean	[27]
Fullerane	60	Truncated Icosahedron	Archimedean	[28]

For a polyhedron whose vertices are made of CH groups to be feasible, it must have only three-connected vertices. In the corresponding polyhedrane, the three edges meeting at each vertex correspond to C-C bonds. There are three Platonic and seven Archimedean polyhedra that comply with this requirement, two of which have been reported only as theoretical molecules (Table 1), although they appear scattered in the literature. To have a full gallery of all possible Platonic and Archimedean polyhedranes, we have optimized them via DFT calculations (Figure 3) and found them to correspond to minima in the corresponding potential energy surfaces, with carbon-carbon bond distances characteristic of single bonds. It is customary to relate the energies of polyhedral molecules to the deviation of the carbon atoms from the tetrahedral geometry imposed by the shape of the polyhedron. Thus, a *strain energy* is defined, which is calculated as the total energy divided by the number of CH groups, taking as zero strain energy the value obtained for the most tetrahedral case, which corresponds to dodecahydrane (equation 2). The resulting strain energies show the expected dependence on the H-C-C bond angles, and the most stable polyhedra are those that present average H-C-C bond angles closer to the tetrahedral angle (Table 2).

$$E_s(\text{C}_n\text{H}_n \text{ polyhedrane}) = \frac{E_{\text{total}}(\text{C}_n\text{H}_n \text{ polyhedrane})}{n} - \frac{E_{\text{total}}(\text{C}_{20}\text{H}_{20} \text{ dodecahydrane})}{20} \quad [2]$$

Table 2. Strain energies (E_s , kcal/mol) and bonding parameters for several optimized polyhedranes with general formula C_nH_n . All distances in Å, angles in degrees; experimental values given in parentheses when available.

n	Polyhedron	E_s	C-C (Å)	H-C-C (°)	Σ (°)[a]
120	Trunc. Icosidodecahedron	23.4	1.58-1.61	101.7 96.7	354
60	Truncated Dodecahedron	25.4	1.545 1.534	101.7 97.5	348
60	Truncated Icosahedron	7.4	1.571 1.557	101.6	345
48	Truncated Cuboctahedron	13.0	1.579 1.546	102.8	345
24	Truncated Cube	13.2	1.525 1.513	108.0	330
24	Truncated Octahedron	5.8	1.569 1.533	109.2 107.2	330
20	Dodecahedron	0.0	1.556 (1.545)	110.9 (111)	324
12	Truncated Tetrahedron	6.7	1.522 1.499	116.1 114.2	300
12	Hexagonal prism (hexaprismane)	11.3	1.560 1.566	115.1 122.1	300
10	Pentagonal prism (pentaprismane)	10.7	1.561 (1.55) 1.570 (1.57)	119.4 (119) 123.4 (124)	288
8	Cube	16.7	1.571 (1.551)	125.3 (126)	270
6	Trigonal Prism (prismane)	20.8	1.522 (1.53) 1.558 (1.55)	129.6 (130) 132.7 (132)	240
4	Tetrahedron	31.1	1.479 (1.486)	144.7 (145)	180

[a] Sum of C-C-C bond angles around a carbon atom.

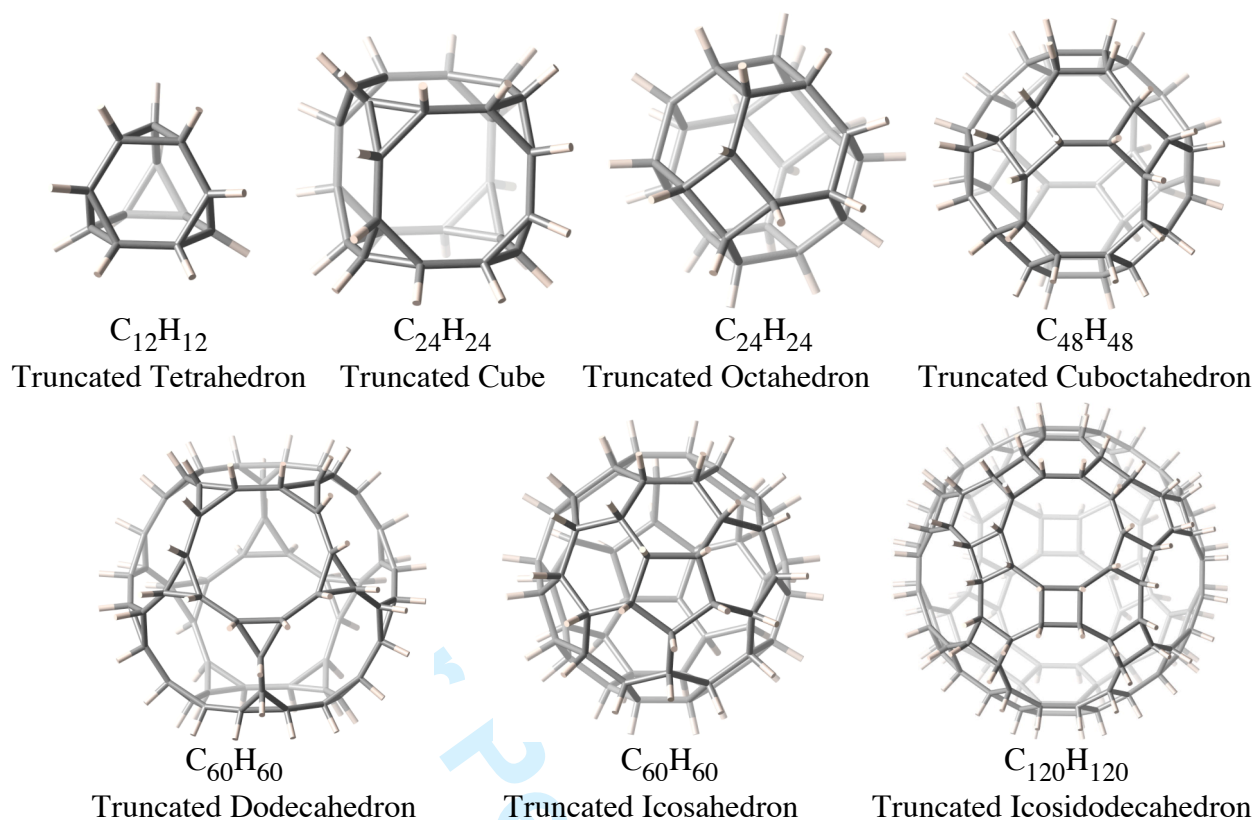


Figure 3. Calculated structures of the Archimedean alkanes.

The geometries of some Archimedean polyhedra are not well suited for fully dehydrogenated C_n molecules, because of the non-planarity of their vertices (measured by the sum of the subtended C-C-C bond angles, Σ , that should be 360° for an ideal sp^2 carbon atom, see Table 2). Nevertheless, small deviations from planarity can be withstood, as in the truncated icosahedron of C_{60} . Theoretically optimized structures of other Archimedean polyhedrenes have been reported in separate studies (Table 3), to which we can add the truncated cube. It must be noted that different delocalization schemes may appear in these molecules, as evidenced for several alternative structures of the Platonic dodecahedrene C_{20} .^[29]

Table 3. Reported theoretical studies of Archimedean and Platonic polyhedrenes with general formula C_n .

n	Polyhedron	Ref.
120	Truncated Icosidodecahedron	[30]
60	Truncated Icosahedron	[31]
48	Truncated Cuboctahedron	[32]
24	Truncated Cube	this work
24	Truncated Octahedron	[33]
12	Truncated Tetrahedron	[34]

Shape Maps and Interconversion Pathways

For the stereochemical analysis of families of compounds we have found it useful to represent scatterplots of their shape measures relative to two alternative ideal polyhedra with the same number of vertices (e.g., *A* and *B*), that we call *shape maps*. In these maps, the lower left limit always corresponds to the interconversion path between the two reference shapes, usually polyhedra or polygons. The shape measures of all structures *i* along the minimal distortion interconversion path between polyhedra *A* and *B*, $S_i(A)$ and $S_i(B)$, must obey the following relationship:^[9]

$$\arcsin \frac{\sqrt{S_i(A)}}{10} + \arcsin \frac{\sqrt{S_i(B)}}{10} = \theta_{AB} \quad [3]$$

where θ_{AB} is a constant for each pair of polyhedra, the *symmetry angle*.^[9] Structures that do not belong to the minimal distortion path do not obey equation 3 and their distance to that path can be calibrated by means of the *path deviation function* defined in equation 4, where *x* refers to an arbitrary structure.

$$\Delta_x(A,B) = \frac{1}{\theta_{AB}} \left[\arcsin \frac{\sqrt{S_x(A)}}{10} + \arcsin \frac{\sqrt{S_x(B)}}{10} \right] - 1 \quad [4]$$

Furthermore, for structures that are along the minimal interconversion pathway we have defined a generalized interconversion coordinate,^[35] that measures the percentage of the path between two polyhedra covered by the problem structure (equation 5).

$$\varphi_{A \rightarrow B} = \frac{100}{\theta_{AB}} \arcsin \left(\frac{\sqrt{S_i(B)}}{10} \right) \quad [5]$$

With such tools we can (a) detect very easily those structures that are intermediate between two ideal shapes, (b) obtain a quantitative description of how close (or how far) a given structure is from a path, (c) obtain molecular models of the shapes that correspond to steps along the interconversion path, and (d) calibrate the distance of the problem structure to the two extremes of the path. According to the proposal that crystal structure data offer clues to reaction pathways,^[36] the analysis of crystal structures from the point of view of minimal distortion paths should be helpful in gaining insight into chemical reactivity aspects.

To illustrate the possible applications of shape maps, we show in Figure 4 the structural data of all non-fused cyclohexyl groups found in the Cambridge Database in two different shape maps. In the first one, the structures are compared with the planar hexagon and the octahedron, since its chair conformation can be seen as an intermediate between those two ideal shapes

(Scheme I). We have found that 97% of the cyclohexyl groups found are aligned along the minimal distortion path between the hexagon and the octahedron, with a deviation of at most 10% (the small portion of molecules that deviate most from that path are not shown in the plot for clarity).

An alternative way of looking at the data plotted in Figure 4 consists in analyzing the frequency of structures found at different steps along the path, shown in the histogram of Figure 5. There we see that the structures are strongly concentrated around a generalized coordinate $\varphi_{OC \rightarrow HP}$ of 74%, suggesting that such a conformation is the most stable one. In effect, a DFT optimization of the molecular structure of cyclohexane in the chair conformation appears at a generalized coordinate $\varphi_{OC \rightarrow HP}$ of 74.8%, exactly on the track from the octahedron to the planar hexagon.

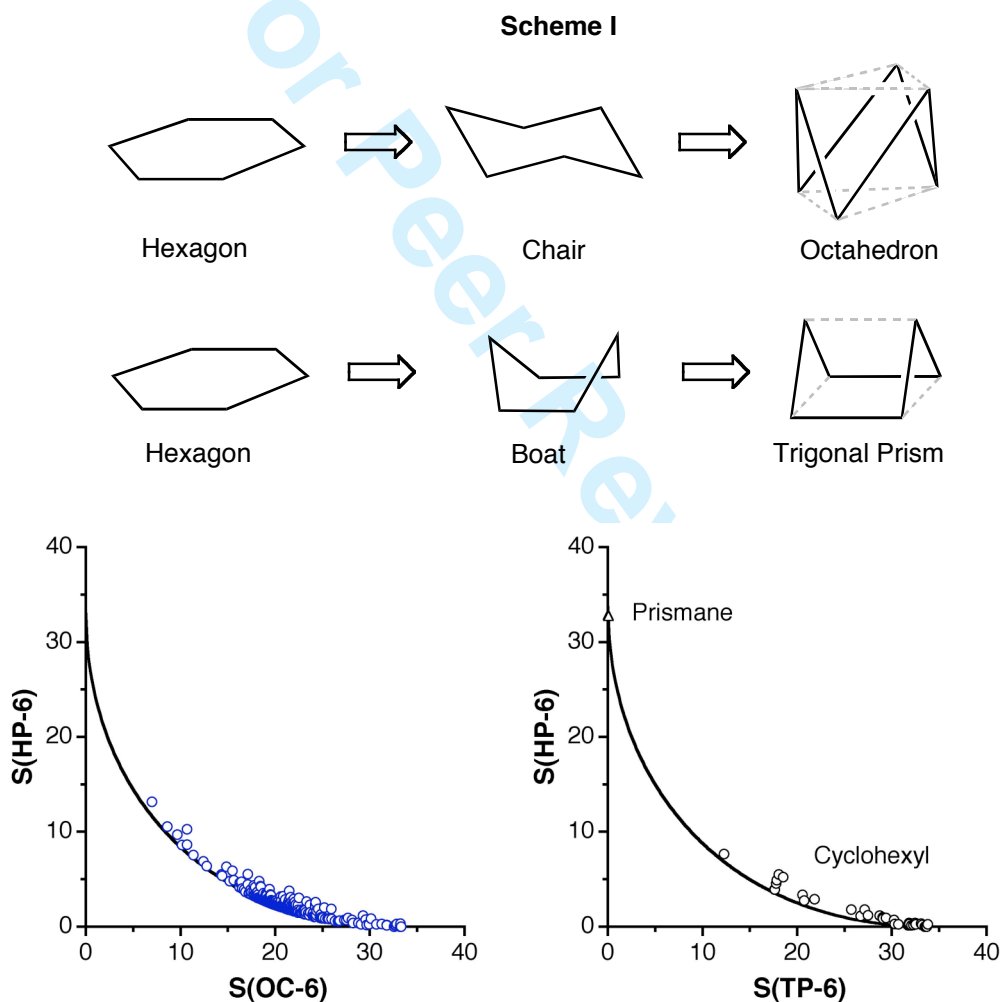


Figure 4. Shape maps for the transformations of a hexagon into an octahedron (left) and into a trigonal prism (right). Structural data for non-fused cyclohexyl groups with deviations from the paths larger than 10% are omitted for clarity. Structures of prismanes also shown in the hexagon-trigonal prism map for comparison.

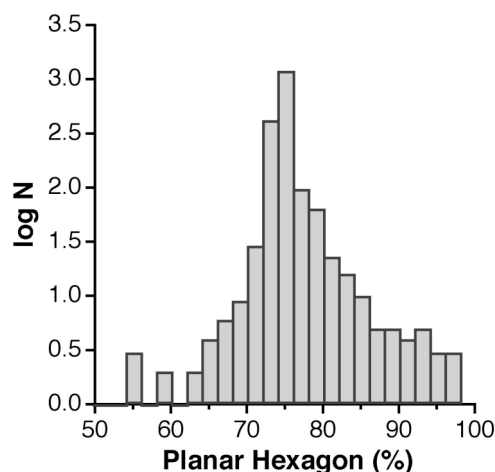


Figure 5. Frequency of cyclohexyl groups as a function of their degree of hexagonality (generalized coordinate for the octahedron-planar hexagon conversion), in a logarithmic scale.

We figured out that the cyclohexyl groups that significantly deviate from this path should probably present a boat conformation. Therefore, we have plotted those structures in a shape map relative to the hexagon and the trigonal prism, since the boat structures are in-between those two ideal shapes. The results (Figure 4, right) clearly discriminate the boat from the chair structures, but also allow us to detect different degrees of each of those two conformations. Of course, it is not possible to ascribe in an unequivocal way a boat or chair conformation to those molecules that are close to the planar hexagon.

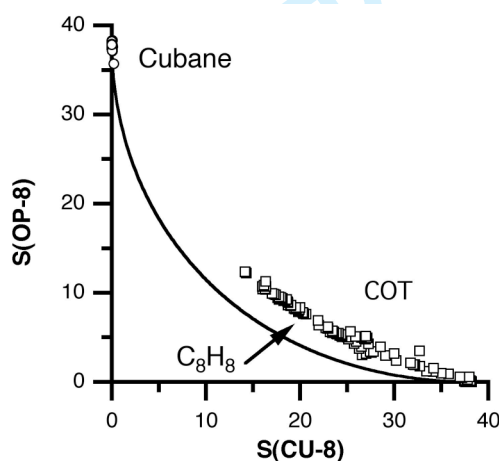
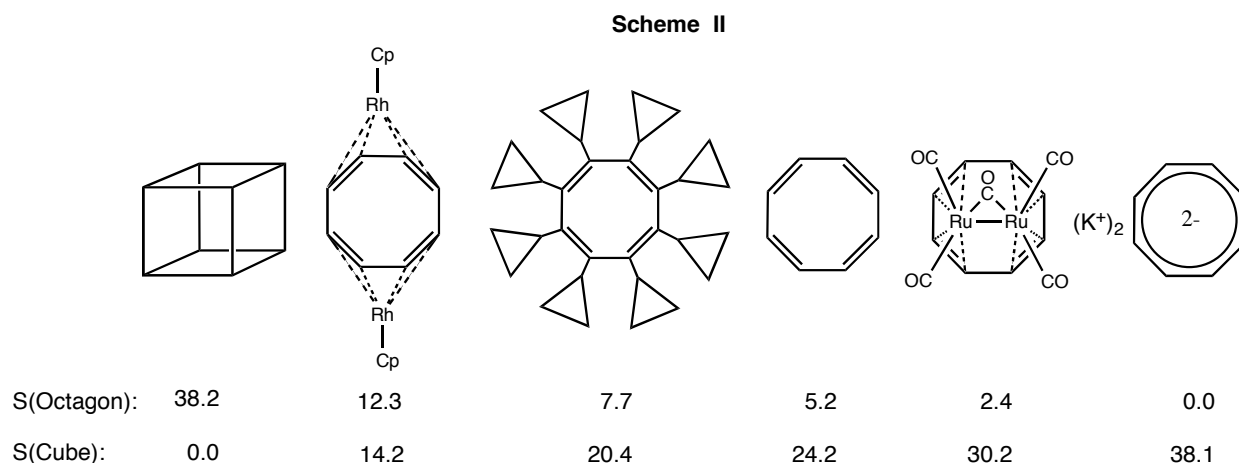
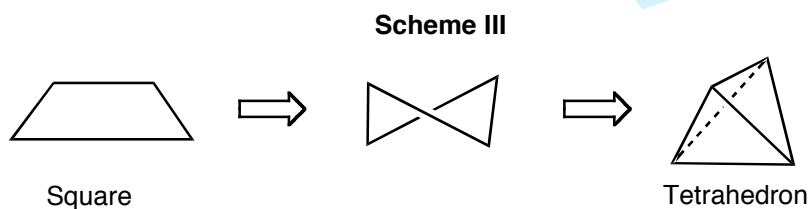


Figure 6. Structural data of cyclooctane, cyclooctatetraene (COT) and cubane derivatives, plotted in a shape map relative to the cube (CU-8) and the planar octagon (OP-8). The line represents the minimum distortion interconversion path between the octagon and the cube.



A second case that we have analyzed is that of the cyclooctatetraene groups (COT). Those skeletons are expected to be in a boat shape (reminiscent of the cube) for the neutral COT, but perfectly octagonal for the aromatic dianion. It is not surprising, therefore, that the structures of all C_8R_8 groups found in the CSD are aligned to a good approximation along the corresponding minimal distortion interconversion path (Figure 6). It is interesting to note that there is no geometric discontinuity between the aromatic dianionic rings and the neutral tetraenes. In addition, the absence of structures in a wide portion of the pathway is suggestive of a high energy barrier for the interconversion of the two isomers, cyclooctatetraene and cubane, through the pathway analyzed here. Let us finally stress that cyclooctatetraene, C_8H_8 , is not among the systems that most deviate from planarity. Some of the compounds that appear along the path are shown in Scheme II, together with their shape measures.

Finally, a look at the structures of cyclobutane derivatives (disregarding those with fused rings) shows also that their conformations can be nicely described as being along the square to tetrahedron pathway (Scheme III). Among 551 crystallographically independent data sets found, all cyclobutane skeletons deviate less than 5% from that path with only two exceptions, covering the range from strictly planar to 28% bending toward the tetrahedron.



Symmetry Paradox

We have recently shown that octahedral symmetry is latent in polyhedra of icosahedral symmetry,^[14] even if the corresponding symmetry point groups are incompatible. A consequence of such a relationship is the capability of molecules with icosahedral symmetry to form a network of intermolecular interactions with octahedral symmetry that results quite often

in cubic crystal structures of icosahedrally symmetric molecules. In Table 4 we present some examples of organic polyhedral molecules that form cubic crystals.

Table 4. Cubic crystal structures of molecules with icosahedrally symmetric carbon polyhedra.

Compd.	Packing ^[a]	Polyhedron	Ref.
$C_{20}H_{20}$ (dodecahedrane)	fcc	Dodecahedron	[37]
C_{60} (fullerene)	fcc	Truncated Icosahedron	[38]
$C_{60}\cdot H_2C=CH_2$	fcc	Truncated Icosahedron	[39]
$K_3Ba_3C_{60}$	bcc	Truncated Icosahedron	[40]
$C_{60}\cdot O_2$	fcc	Truncated Icosahedron	[41]

[a] fcc = face-centered cubic; bcc = body-centered cubic.

We think that octahedrally-arranged atoms or functional groups can also be attached to icosahedral molecules. We have noticed, for instance, that buckminsterfullerene can be considered as formed by six fulvalene units whose centers are arranged in an octahedral way. Alternatively, it can also be described as an assembly of six naphthalene units, whose centers occupy the vertices of an octahedron (Figure 7). Chemical substitutions that occupy the centers of those bonds would result in an octahedron circumscribed around the C_{60} truncated icosahedron. As an example, we have computationally optimized the structure of a hexa-epoxidized fullerene, in which the six oxygen atoms are seen to form a perfect octahedron (Figure 8). In a related experimental structure,^[42] the same positions are occupied by cyclopropane rings, whose carbon atoms also form a perfect octahedron. In both cases, the six substituents directly attached to the fullerene have octahedral shape measures smaller than 0.01, while the fullerene core deviates very little from its truncated icosahedral shape (shape measures of 0.03 and 0.06 for the epoxidized and cyclopropanated derivatives, respectively).

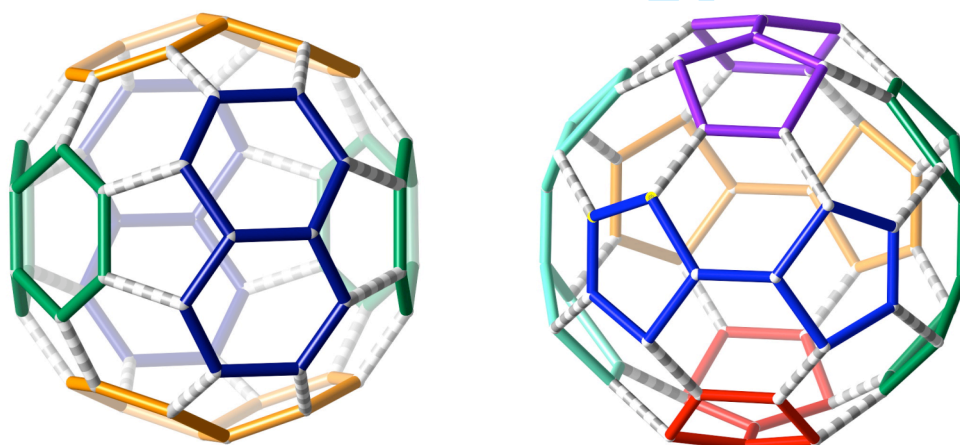


Figure 7. Buckminsterfullerene C_{60} as an assembly of six naphthalene units (left) or six fulvalene units (right).

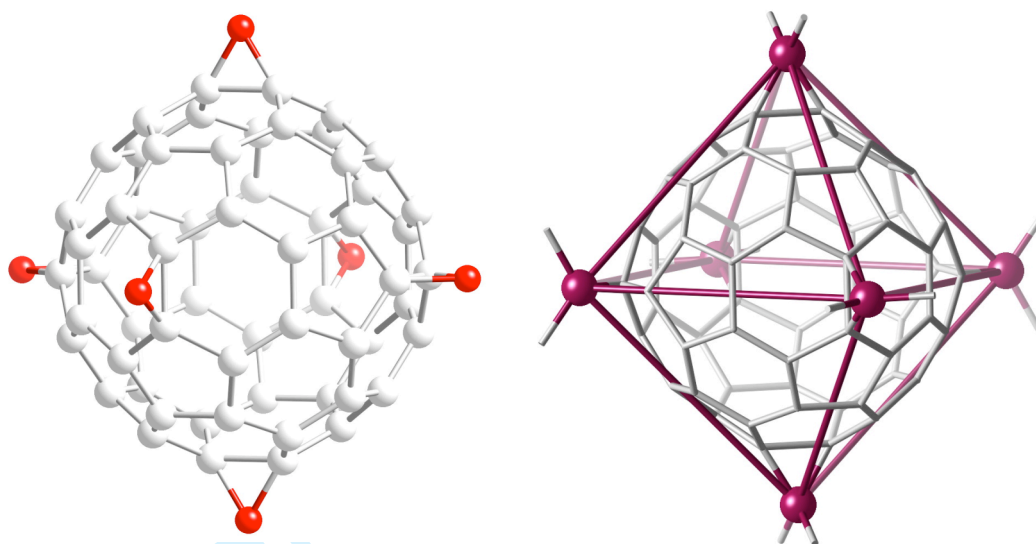


Figure 8. *Left:* Epoxidized fullerene whose six oxygen atoms form a perfect octahedron, templated by the C_{60} truncated icosahedron (computational DFT results). *Right:* Analogous octahedron formed by six cyclopropane fused rings in an experimentally reported compound.^[42]

Another computational example of a molecule that combines the icosahedral symmetry of a dodecahedrane skeleton with the cubic symmetry of eight substituents is that of $C_{20}H_{12}Br_8$, shown in Figure 9.

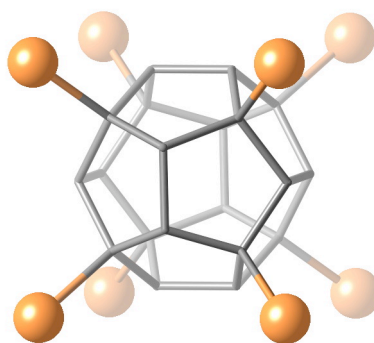


Figure 9. Optimized structure of an octabrominated dodecahedrane $C_{20}H_{12}Br_8$ with a substitution pattern that displays a cubic set of bromine atoms (hydrogen atoms not shown for clarity) circumscribed around the dodecahedron of carbon atoms.

Although adamantane is not usually perceived as a polyhedral molecule, it can be described as a composite of a tetrahedron of tertiary carbon atoms (**2**) bridged by secondary carbon atoms that form a circumscribed octahedron.^[6] Omar Yaghi and coworkers^[43] have taken advantage of the tetrahedron implicit in adamantane to design a network of a porous metal organic framework (MOF) reminiscent of the PtS structure but with larger voids. The tetrahedral adamantane unit is provided with four carboxylate groups that have the same spatial connectivity than a sulfide ion. Those carboxylates are coordinated to a pair of copper(II) ions

forming a square four-connected unit (**3**), that plays the same role of the Pt^{II} ion in PtS. The analogous construction principle of the two structures can be appreciated in Figure 10.

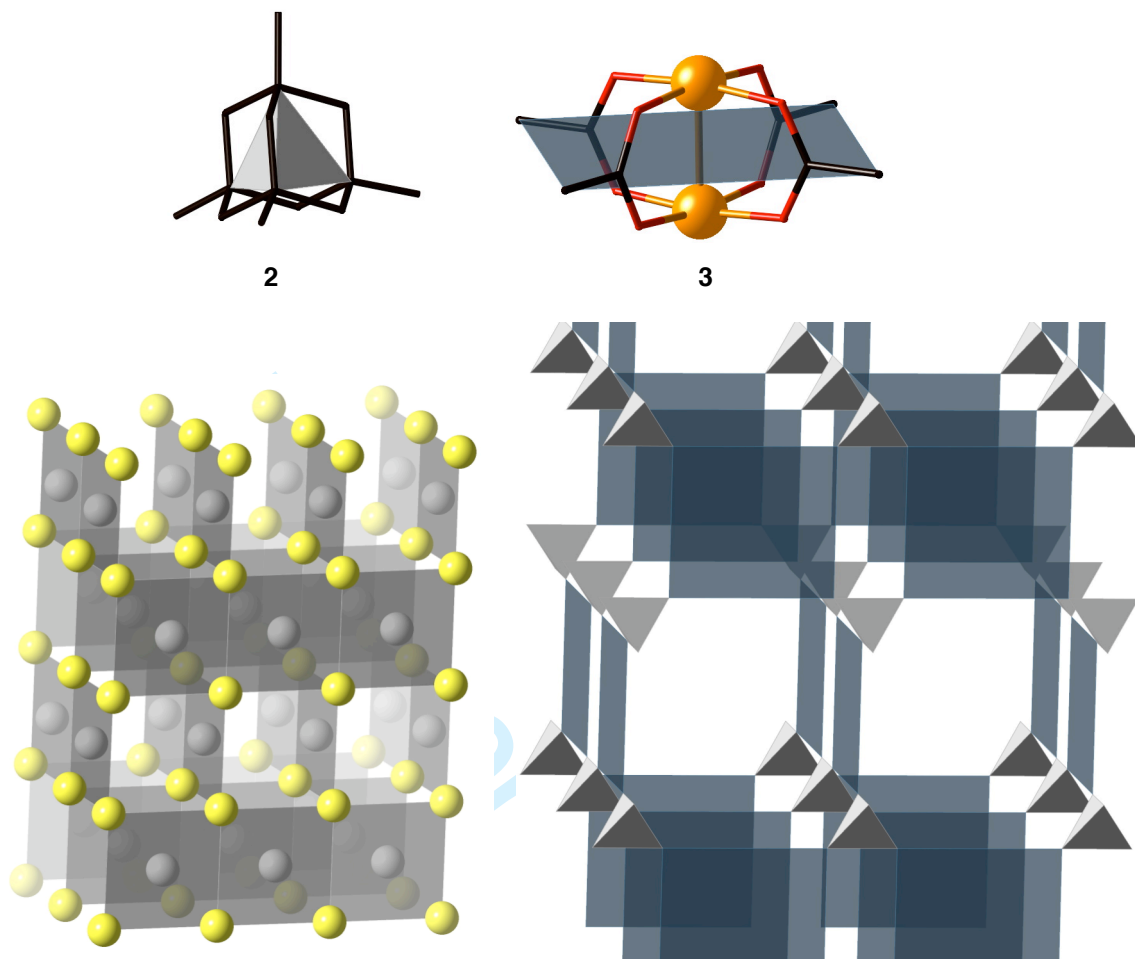


Figure 10. Formal replacement of the tetrahedral sulfide ions in PtS by adamantane units (**2**) and of the square planar Pt^{II} ions by $\text{Cu}_2(\text{carboxylate})_4$ building blocks (**3**).

Concluding Remarks

An assortment of beautifully symmetrical polyhedra can be expressed as organic molecules, and several examples have been obtained in the bench or in the computer. We have shown here also that thinking in terms of polyhedral shapes may be helpful to analyze the stereochemistry of non polyhedral molecules. The implicit polyhedra found in adamantane, for instance, has been used by Yagi and coworkers to design and build up porous extended frameworks. The latent cubic symmetry present in molecules with icosahedral symmetry is important in establishing the directions of intermolecular interactions that often result in crystals with cubic packings, as in dodecahedrane and buckminsterfullerene.

Computational Details

DFT calculations were carried out with Gaussian03,^[44] using the B3LYP hybrid functional and a 6-31G** Gaussian basis set.^[45] All calculated structures reported were characterized as true minima through vibrational analysis. Structural searches were carried out in the CSD,^[46] version 5.30 with three updates, and the atomic coordinates transferred to the SHAPE code^[47] to calculate continuous shape measures, path deviation functions and generalized coordinates.^[48]

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