Introduction to Molecular Schläfli Indices

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Abstract-The polygonality, n, and the connectivity, *p*, are topological indices that are rigorously defined for the polyhedra through the Schläfli relation. The ordered pair of numbers (*n, p*) constitute the Schläfli symbol for a polyhedron. It has recently been discovered that the Schläfli indices, although not rigorously defined for extended structures through a Schläfli-type relation, are nonetheless computable for the units of pattern described by extended structures. These indices can be used to define a topology map of the polyhedra and extended structures. Such a topology map is useful in one sense for identifying the location of a structural pattern and its relation to other structures. In the present paper, a methodology is outlined for the computation of Schläfli indices for discrete molecules. An aufbau process is used to create the fullerene and graphene structures from molecular precursors in a continuous fashion, the topology indices of the various intermediate structures to the fullerene icosahedron and the graphene sheet are traced with a quadratic fit and are thus shown to form ordered pairs of a continuous function in *n* and *p* that is internally consistent. Such topological indices of molecules complement those indices that have already been formulated as molecular descriptors in the burgeoning field of molecular graph theory. The role that the Schläfli symbols of discrete molecules might play in the identification of structure-activity relationships is briefly discussed.

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1. Introduction

Euler's relation for the polyhedra, shown as Equation 1 below, marks the origin of the discipline of topology. [1] This relation between the number of vertices, V, edges, E, and faces, F, of convex polyhedra holds for any division of a sphere into polygons.

(1) $$V - E + F = 2$$

Such a topological relation provides an organizing principle for the study of structures, both discrete and extended, as will be discussed below. [2]

The equation can be defined, alternatively, in terms of the relationship between the primary topological indices of the polyhedra; V, E and F, and the secondary topological indices, the polygonality, and the connectivity. The polygonality, n, refers to the weighted average number of sides of the polygonal faces of a polyhedron, and the connectivity, p, refers to the weighted average connectivity of the vertices of a polyhedron. There are two topological identities that establish the connection between the secondary and primary topological indices. We can note that each edge of a polyhedron is shared by two faces, therefore we can write $nF = 2E$. This relation simply states that the product of the averaged polygonality of a polyhedron and the number of faces of the polyhedron is just equal to twice the number of edges. Similarly, we can note that each edge terminates at two vertices of a polyhedron, the corresponding relation therefore can be written as $pV = 2E$. This identity simply states that the product of the averaged connectivity of the vertices of a polyhedron and the number of vertices of the polyhedron is just equal to twice the number of edges. These latter two topological identities can be substituted into Equation 1 to obtain Equation 2, the Schläfli relation for the polyhedra: [3]

(2)
$$\frac{1}{n} - \frac{1}{2} + \frac{1}{p} = \frac{1}{E}$$

The Schläfli relation establishes a rigorous connection between the secondary topological indices, n and p, and the primary topological indices, V, E and F; for the convex polyhedra. One value of this connection lies in the fact that the averaged polygonality, n, and the averaged connectivity, p, can be computed not only for the polyhedra, but such parameters can be computed for fully two-dimensional and three-dimensional patterns, as well, through the identification of the Wells point symbol for the polyhedron or network. [4] A topology map, such as that shown in Figure 1 below, is used to identify the relative positions and identities of the innumerable discrete polyhedra and extended structures to which the Schläfli indices can be applied. [5]

p \ n	3	4	5	6	7	8	...
3	t	o	i	(3,6)	(3,7)	(3,8)	
4	c	(4,4)	(4,5)	(4,6)	(4,7)	(4,8)	
5	d	(5,4)	(5,5)	(5,6)	(5,7)	(5,8)	
6	(6,3)	(6,4)	(6,5)	(6,6)	(6,7)	(6,8)	
7	(7,3)	(7,4)	(7,5)	(7,6)	(7,7)	(7,8)	
8	(8,3)	(8,4)	(8,5)	(8,6)	(8,7)	(8,8)	
⋮							

Figure 1: A topology map of the regular polyhedra and extended structures.

This topology map is written for the identities and locations of only the regular structures and can be magnified and extended indefinitely for inclusion of the semi-regular and irregular structures, as well. Interestingly, there is a

corresponding Euler relation for the cell analogous to the Euler relation for the sphere. [6] A cell is a topological concept, like the sphere, which involves the division of the plane into fused polygons in which some of the edges form a boundary. In the sphere, there are no such bounded edges. The Euler relation for the cell is shown in Equation 3:

(3) $$V - E + F = 1$$

The characteristic for the cell is just 1, where the characteristic for the sphere is 2. This is because the cell, in any of its innumerable manifestations, has one less face; the infinite bounded face, than does the division of a sphere into polygons. A cell can be envisioned, in one sense, as a molecular Schlegel diagram in which a discrete molecule, such as a hydrocarbon, has connections drawn about all the 1-connected atoms and thus is a completely polygonalized structure when including adumbrated polygons that may already exist in the structure. The drawing of connections about the 1-connected atoms is said to be an operation of polygonalizing the discrete molecule, this means dividing up the discrete molecule into polygonal compartments for the purpose of computing a polygonality index.

The present communication extends the concept of the Schläfli symbol for discrete polyhedra and extended structures to the vast area of discrete molecular structures as topological cells. A molecular polygonality index, *n,* is computed by drawing a connection halo about the peripheral atoms of a discrete molecular structure. As described above, the peripheral atoms are given as those atoms whose connectivity is 1. The process polygonalizes the peripheral as well as the core atoms of such a structure. Therefore, in the foregoing process a molecular Schlegel diagram, analogous to the Schlegel diagrams for the polyhedra, is produced. [7]

The polygonality index, *n,* is therefore defined as the weighted average number of sides over the polygons inscribed within the connection halo (Schlegel diagram) of a discrete molecular structure. The connectivity index, *p*, is computed similarly, and in the usual way for the polyhedra and extended structures, by taking a weighted average over the connectivities of the atoms comprising the molecular structure. The artificial and non-chemical edges introduced in the polygonalization procedure are not taken as bonds in the structure and thus play no role in the computation of the molecular connectivity index. The connectivity index is calculated according to the number of atoms bonded to the atom in question according to the most plausible Lewis structure that may be drawn for the molecule based upon elementary chemical valence theory. [8]

2. Aufbau Process for Fullerene

The methodology for computing the polygonality, *n,* and the connectivity, *p*, for discrete molecules can be envisioned in one way in terms of an "aufbau" process through which, in one particularly illustrative example of this, the icosahedral fullerene molecule is built up sequentially from 1,3-cyclopentadiene, C_5H_6, to the corannulane moiety, $C_{20}H_{10}$, onto an annelated corannulane molecule, $C_{40}H_{10}$, and finally onto the complete fullerene molecule, C_{60}, with its full icosahedral topology. The icosahedral fullerene molecule has 12 pentagonal faces and 20 hexagonal faces connected through trigonal vertices and thus has the topology of $(5^{5/8}, 3)$. [5]

All along this aufbau pathway, which is a heuristic device used to show the rigorous applicability of the Schläfli symbols to molecular structures as shown in Figure 2; the topological parameters of molecular polygonality, *n,* and molecular connectivity, *p*, can be traced.
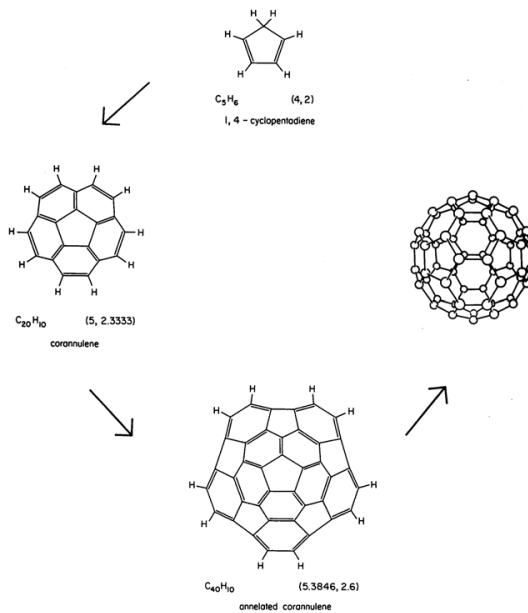
Figure 2: Aufbau molecular structures for icosahedral fullerene.

In Figure 3 is shown the relevant molecules with the corresponding connection halos drawn around each one. The polygonality, *n,* can easily be computed in each case by summing over the various polygons in the structure, and dividing by the number of discrete polygons inscribed within the connection halo.
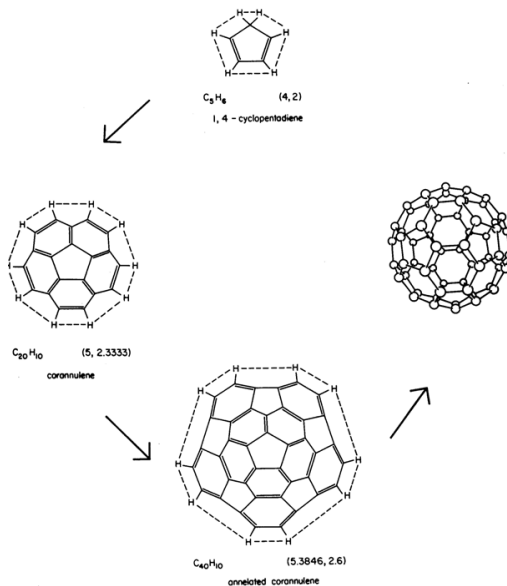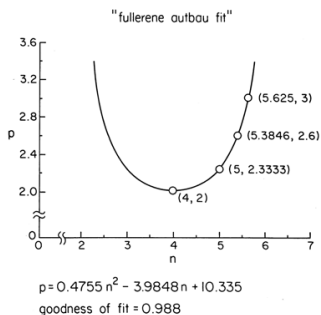
Figure 3: Aufbau molecular structures for icosahedral fullerene with connection halos drawn around each member

In the original 1,3-cyclopentadiene molecule we have a collection of five 4-gons traced as C-C-H-H rings, a single C-H-H 3-gon and a single C-C-C-C-C 5-gon. The latter pentagon is termed the adumbrated polygon in the molecular structure as it is evident before the full molecular Schlegal diagram is realized; the remaining polygons which present themselves for counting upon polygonalization of the molecule, are termed the dumbrated polygons. Therefore the 7 polygons enumerated above, which are distributed over the skeleton of the 1,3-cyclopentadiene molecular Schlegel diagram, lead to a polygonality, n, of 4. Similarly, the connectivity index, p, can be computed for 1,3-cyclopentadiene by

summing each of the connected atoms with their respective connectivities; six 1-connected H atoms, one 4-connected C atom and four 3-connected C atoms; and dividing by the number of atoms in the molecule. This leads to a molecular Schläfli index of (4, 2) for the 1,3-cyclopentadiene molecule.

Similarly, the molecular Schläfli index for the annelated 1,3-cyclopentadiene molecule, called corannulane, $C_{20}H_{10}$ [9], is computed to be (5, 2.3333). And the annelated corannulene molecule, $C_{40}H_{10}$, is computed as (5.3846, 2.6). By tracing these topological parameters as the shell of the evergrowing discrete fullerene molecule is realized, one may see that indeed these parameters of "n" and "p", which for the fullerene molecule are given as ($5^{5/8}$, 3), are converged upon gradually in the aufbau process. One can separately plot the topological parameters in a Schläfli space and show the convergence process graphically. This plot simply places polygonality, n, on the ordinate axis and connectivity, p, on the absicca axis. Such a topology graph is shown in Figure 4. Note that the points on the curve correspond to a continuous function of the form shown in Equation 4 below:

"fullerene aufbau fit"

(5.625, 3)
(5.3846, 2.6)
(5, 2.3333)
(4, 2)

$p = 0.4755\, n^2 - 3.9848\, n + 10.335$

goodness of fit = 0.988

Figure 4: Topology graph in Schläfli space of fullerene aufbau data fit to a quadratic function in "n", the polygonality.

**(4)** $\qquad p = 0.4755n^2 - 3.9848n + 10.3350$

Because this quadratic fit to the Schläfli data for the aufbau process of icosahedral fullerene is a continuous function, it is suggested here that such indices are rigorous descriptors of the topology of the discrete molecules. The convergence of the aufbau process on the topology of the icosahedral fullerene insures that the aufbau process is a valid heuristic for defining the topologies of the intermediate discrete molecular structures, the molecular Schlegel diagrams, using the methodology outlined here.

3. Aufbau Process for the Graphene Sheet

The graphene sheet is well-known, its topology is (6, 3). The sheet is a honeycomb network composed of the familiar hexagons linked together through trigonal centers. [10] This is shown in Figure 5.
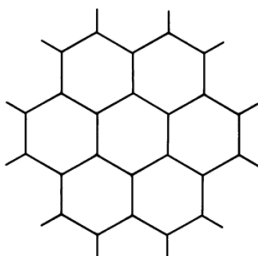

graphene　　　　(6, 3)

Figure 5: Graphene sheet with honeycomb topology.

In a manner entirely analogous to the aufbau process for the icosahedral fullerene molecule, one can envision a building-up pathway for the graphene sheet. The

process begins, naturally, with the benzene moiety and the Schläfli indices are calculated for it as (4.2857, 2) from the same polygonalization prescription already described for 1,3-cyclopentadiene. This is shown in Figure 6.
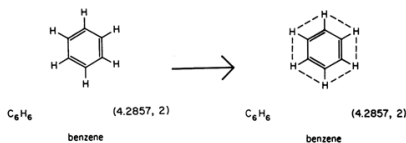
Figure 6: Polygonalization of the benzene moiety.

Annelating benzene means placing a shell of hexagons outside the core benzene molecule to form the coronene moiety. Successive annelations produce the higher poly[m]hexes to coronene as is shown in Figure 7.
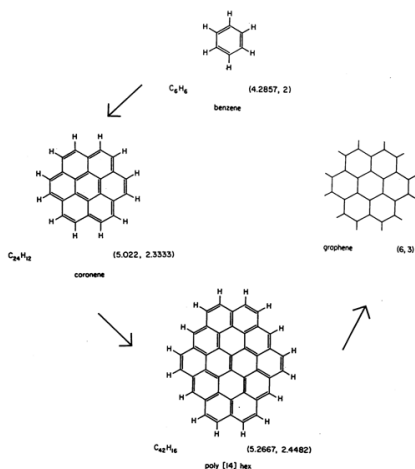
Figure 7: Members of the poly[m]hex family that are molecular building blocks in an aufbau process leading to the graphene sheet.

The index m in the name poly[m]hexes refers to the number of adumbrated hexagons in the discrete molecular structure. The process is by now familiar, and one arrives at a set of Schläfli symbols for the next 2 members of the poly[m]hex family, after beginning with benzene. These are listed in Table 1.

Table 1: Schläfli Indices of Three Precursors of the Graphene Sheet Extended Structure.

name	polygonality, n	connectivity, p
benzene	4.2857	2.0000
coronene	5.0220	2.3333
poly[14]hex	5.2667	2.4482
Graphene	6.0000	3.0000

By graphing these Schläfli indices in a Schläfli space, where one plots polygonality on the ordinate axis, and one plots connectivity on the absicca axis, it is possible to fit a continuous function in n and p to these points as they converge and pass through the ordered pair (6, 3) corresponding to the topology of the graphene sheet. This is shown in Figure 8 below. This is just the process that was used to validate the convergence of the discrete molecular building blocks of fullerene to the icosahedral topology of the full fullerene molecule, as described in the previous Section. As in the case of the icosahedral fullerene molecule, the Schläfli indices for the poly[m]hexes must indeed converge upon the index (6, 3) in the limit of large m, as they structurally converge upon the graphene sheet in this limit.

A perfect quadratic fit to the data, shown as Equation 5 below, insures the internal consistency of the Schläfli indices for the discrete molecules, the poly[m]hexes, through the aufbau process for the complete graphene sheet.

"graphene aufbau fit"

$p = 0.1643 n^2 - 1.1079n + 3.7302$
goodness of fit = 1.000
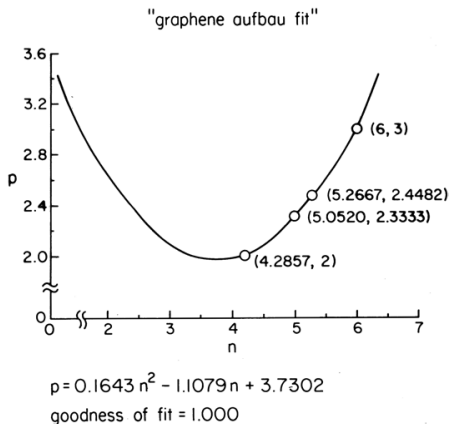
Figure 8: Topology graph in Schläfli space of graphene aufbau data fit to a quadratic function in "n", the polygonality.

(5) $$p = 0.1643n^2 - 1.1079n + 3.7302$$

It is not clear why the aufbau processes for the construction of fullerene and the graphene sheet should lead to quadratic fits to the Schläfli data. At this point it is a mathematical abstraction which will be investigated further for its possible physicality in terms of the topology of the molecular Schlegel diagrams, the molecular cells which obey Euler's relation for the cell.

4. A Modified Topology Map

The topology map shown in Figure 1, applicable to the topology of the polyhedra and 2-dimensional and 3-dimensional extended structures, can be modified for the inclusion of Schläfli indices for the molecular structures, the molecular Schlegel diagrams or cells we have been discussing thus far in this paper. Figure 9 shows just such a modified topology map in which the column headed by the tetrahedron (3, 3) is appended to its left by columns headed by (2, 2) and (1, 1). (2, 2), a cell with a polygonality of 2 and a connectivity of 2, is a seemingly impossible object. (1, 1) would appear to be the Schläfli symbol for a diatomic molecular graph.

n \ p	1	2	3	4	5	6	···
1	(1,1)	(1,2)	(1,3)	(1,4)	(1,5)	(1,6)	
2	(2,1)	(2,2)	(2,3)	(2,4)	(2,5)	(2,6)	
3	(3,1)	(3,2)	(3,3)	(3,4)	(3,5)	(3,6)	
4	(4,1)	(4,2)	(4,3)	(4,4)	(4,5)	(4,6)	
5	(5,1)	(5,2)	(5,3)	(5,4)	(5,5)	(5,6)	
6	(6,1)	(6,2)	(6,3)	(6,4)	(6,5)	(6,6)	
⋮							

Figure 9: A modified topology map for inclusion of the Schläfli symbols for the discrete molecular graphs, or the molecular Schlegel diagrams.

To insure that one is getting what one would hope for in such a topology map, there are also the more familiar entries like (4, 2), the entry for the topology of the 1,4-cyclopentadiene molecule, as was discussed above. It is clear at this juncture that there will be redundancies in this map and in the Schläfli symbols that represent the topology of these molecular cells. For example, the molecules formaldehyde, H_2CO, and phosgene, Cl_2CO, have the same Schläfli index of (3,

1.5) but have very different physical and chemical properties. They are said to be similar chemical graphs. A way to distinguish between them in this Schläfli indexing methodology is to introduce a weighting scheme for the atoms in the topologically isomeric molecular graphs to distinguish them chemically and physically. Such weighting schemes are commonly employed in the various graph theoretical approaches to molecules. [11]

Therefore, the original topology map of Figure 1, that was the guiding principle for Wells in his enumeration of the various networks numbering over 100 that he worked on in his lifetime, is modified for connectivities lower than the characteristic minimum of 3 required for polyhedra and extended structures. We just have introduced panels starting with (1, 1) and (2, 2) to amend the topology map of Wells for inclusion of the problem of molecular Schlegel diagrams, or molecular cells. Such a modified topology map does indeed specify the identity and location of a molecular Schlegel diagram, or chemical graph, conclusively. It labels the discrete location and relationship of a particular chemical graph to all other chemical graphs as we have already seen in the mappings of the aufbau Schläfli data for the icosahedral fullerene and the graphene sheets in Figures 4 and 8 above. These mappings were done in Schläfli space, that is the space of n and p, in the same manner that the more familiar topology maps are constructed.

Unfortunately, although we have a closed form Euler relation for the cell that describes the topology of the polygonalized molecular graphs, the molecular Schlegel diagrams, shown as Equation 3 above [6]; we do not have a corresponding Schläfli relation for the molecular graphs, in terms of a relation between n and p, on the one hand; and V, E and F, on the other hand. It is just because of this lack of a Schläfli relation for molecular graphs, in a sense, that one can look to the validity of separating the methodologies for computing the connectivity (based upon valence concepts [8]) and the polygonality (based upon

drawing a connection halo around the atoms in the chemical graph). If there were just such a rigorous Schläfli relationship for the molecular graphs, a separation of these methodologies would not be necessary [12].

5. Structure-Activity Relationships

As an extension of the ideas presented in this paper regarding the computation of molecular Schläfli indices, it would be a natural application of such data in the prediction of the physical, chemical and biological properties of molecular graphs through structure-activity relationships. One approach to this, would be to employ the Schläfli space already used in the modeling algorithms above in the construction of the fullerene and graphene structures, and append onto it an axis in fully 3-space that corresponds to a molecular property; be it physical, chemical or biological. A prototype of such a graph is shown in Figure 10. A separate communication will discuss a specific application of the molecular Schläfli indices in modeling molecular phenomena.
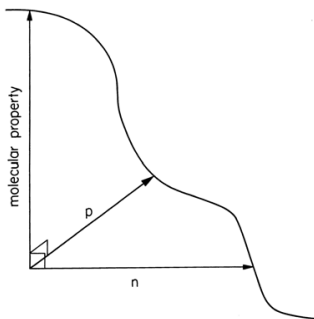
Figure 10: An example of a structure-activity graph between the Schläfli indices and a molecular property in a 3-dimensional space that is an extension of the ordinary Schläfli space of "*p*" versus "*n*" for molecules.

6. Acknowledgement

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12. Although the problem of computing the connectivity, *p*, of molecular graphs is straightforward, the complementary problem of computing a polygonality, *n,* of a molecular graph is, in many instances, complicated by structural considerations and their related polygonalization ambiguities. This paper is the first in what it is hoped will be a pair of papers clarifying the rules by which polygonalities of molecular graphs may be computed. Some rules to be addressed in the next paper include (1) the adjacency principle, which states that in cases of ambiguity, the polygonalization that results in the 1 connected atoms being connected to adjacent 1-connected atoms, for the molecular graph, takes precedence; and with (1) satisfied we have a second rule; (2) the parsimony principle, which states in cases of a polygonalization ambiguity, the polygonalization which minimizes the total number of polygons counted in the polygonalization procedure takes precedence.