

Topologically Different Models To Be Used as the Basis for Ring Compound Taxonomy

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This paper describes topologically distinct models that can be used for subdividing the class of ring compounds and illustrates why a selected taxonomy is chemically more relevant or efficient for one type of compound than for another. Four topologically disjoint sets—based on point, linear, planar, and solid modules—are described. This taxonomy scheme produces a delineation between alicyclic and aromatic in organic compounds that is based strictly on the intrinsic geometry of the module being used. Furthermore, the extra stability of the compounds being modeled with trigonal bonding to form a planar module and tetrahedral bonding to form a solid module corresponds to the demarcation lines that separate disjoint taxonomy classes.

INTRODUCTION TO TAXONOMY CLASSES FOR USE IN MODELS OF CHEMICAL MOLECULES

One of the functions of a model in science is to replace the actual elements in a given set by an idealized set of mathematical abstractions that approximate these elements. The nearer the approximation, the better the model. In the case of chemical compounds, for example, the assignment of graph theoretical parameters (point or node = atom and line segment or edge = chemical bond) is a convenient first step in building the model. Although actual chemicals contain no parts that are these idealized mathematical building blocks, there being neither zero-dimensional nor one-dimensional components present in the real world, such an approximation is very useful in classifying and naming chemical compounds.

It is the thesis of this paper that a second important step in the process of model building may be found in the inherent topology of the molecules under consideration. This gives rise to lines of delineation that have long been recognized as existent,¹ but partly because topology was not even an organized discipline at the time of their description, the topological origins of this demarcation have not been adequately clarified. It should be noted that the focus of this paper is at the "system", rather than at the "circuit", level. The intended output of this paper is a topologically based explanation of the physically observed difference between aliphatic and aromatic compounds, rather than a "better" algorithm for use in nomenclature.

In this paper, topologically distinct models that can be used for subdividing the class of ring compounds are presented, with emphasis on the reason why a selected taxonomy³ is chemically more relevant or efficient for one type of compound than for another. Four topologically different types of taxonomy class than can exist for a simple solid, such as a cube, are as follows: (1) set of vertexes, i.e., set of eight zero-dimensional elements; (2) set of edges, i.e., set of 12 one-dimensional elements; (3) set of faces, i.e., set of six two-dimensional elements; (4) set of cells, i.e., set of one three-dimensional element—the cube itself. These may be referred to as (1) point, (2) linear, (3) planar, and (4) solid taxonomy classes, respectively. Similarly, the description of compounds limited to a single taxonomy class may be referred to as "point taxonomy", "linear taxonomy", etc.

A unique mathematically consistent set of definitions can be formulated only within a given taxonomy class. Mixed taxonomy classes, such as the set of two diametrically opposed faces and four edges for a cube, are not unique. In this case, any one of three such sets may be selected. Consequently, whenever possible, whichever of the above four (or any other single) taxonomies is selected for the description of a model

for chemical compounds, it is desirable for all components to be of this form.

In certain cases, such as the cyclophanes, it is, at present, pragmatic for there to exist concurrent, but unequal, taxonomies. For these compounds the ability to formulate a comprehensive (expandable, but still simple and internally consistent) nomenclature may be beyond our capabilities—either mathematically⁵ or simply from a practical perspective. This is not to say that, for such a limited class of compounds, better, i.e., more efficient, nomenclature are not attainable and desirable; rather, the mathematical virtues of, say, a nodal nomenclature⁶ may be more than counterbalanced by a chemically illogical taxonomy. The historical development of chemical nomenclature, for example, contains frequent intuitive subdivisions that could not be logically justified, even in the formulator's mind.⁷

Furthermore, the entire perception of when two atoms are actually bonded together has, yet again, recently been brought into focus by Wilberg's formulation of tricyclo[1.1.1.0]pentane,⁹ with the concomitant assertion that the bond order between C-1 and C-3 in this propellane is close to zero. If, in fact, there is no such bond, then the entire concept of incidence in the graph theoretical sense is inapplicable—at least for this one compound.

It is important to remember that although the focus has been placed on geometrical models, the real requirement is the selection of that model having the greatest chemical relevance. For instance, when a molecule contains at least three atoms, description of such a molecule by point taxonomy is inadequate for anything more than listing the composition inasmuch as there is no means of describing the method used in order to join these atoms into an organized structure. In a similar manner, most chemical bonds are described as being localized between exactly two atoms; i.e., a chemical bond is viewed as an electronic pathway between two atoms—rather than being spread out over a plane segment or a portion of three-dimensional space. Thus, a model using linear taxonomy is adequate for describing such bonding. (Notice that both for diffuse and for three-atom bonds, this description, like point taxonomy, is inadequate.)

That the adequacy of a taxonomy is not the same thing as its desirability is illustrated by comparing a model of a geometrical solid with that of a molecule. In the mathematical case, for example, two points uniquely determine a line—of which there is exactly one type. In the case of chemical compounds, on the other hand, it is desirable to distinguish among at least three different types of lines, namely, single, double, and triple bonds, as well as intermediate, including fractional, bonds. Also, in the arena of transition metals, consideration must be given to quadruple bonds.¹⁰



Figure 1.

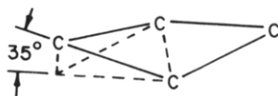


Figure 2.

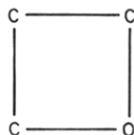


Figure 3.

Because of the different definitions being used for the word "line" when dealing with chemical structure, it is not surprising that a geometry to describe such a structure can be formulated with a variety of postulates linking these elemental building blocks in differing ways. It is, therefore, incumbent upon the formulator of such a system of geometry to seek out natural boundary conditions—assuming such a set exists or, if not, to attain a first approximation to this ideal.

As stated above, one of the simplest, commonly accepted natural boundary conditions used in organic chemistry is the presence of covalent bonds between selected pairs of atoms, with a concomitant electron flow directly between these two atoms. The model normally used for this is a graph theoretical linkage between points representing these atoms. For example, consider a four-member ring, such as in Figure 1. Such a ring is interpreted as having an electronic pathway between A and B, between B and C, between C and D, and between D and A but no electron flow directly either from A to C or from B to D (without going through another atom in the set). Although this description gives rise to convenient geometrical pictures, such a representation is an oversimplification—that is often misleading. Notice that the use of this type of model would mask the differences among the various types of bonding, thereby simplifying the geometrical description and, consequently, the nomenclature that would be applicable.

PLANARITY AS THE BASIS FOR TAXONOMY

A liability of Figure 1 is the implied suggestion that the skeleton of the molecule is coplanar, in contrast to requiring a three-dimensional space.¹¹ The implications of this footnote (see also Figures 2 and 3) are that, although there is a clear dichotomy between planarity in oxetane (as well as certain substituted cyclobutane derivatives) on the one hand and nonplanarity in cyclobutane (and a different set of cyclobutane derivatives) on the other hand, planarity, by itself, is deemed insufficient as a boundary line between chemical classes. To use planarity as a criterion in the naming of chemical compounds would only serve to make such a nomenclature far too dependent on the properties of individual molecules, thereby rendering it unmanageable. Instead, the taxonomical line of demarcation to be used in the description, and consequently the nomenclature, of chemical compounds must have a different fount.

Next note that, although the form of cyclobutane that has minimum potential energy is a skew quadrilateral with a dihedral angle of 35° , there exists an infinite number of other orientations of this molecule—corresponding to other dihedral angles. Furthermore, for each of the different dihedral angles there could exist variable distances between the atoms, etc.



Figure 4.



Figure 5.



Figure 6.

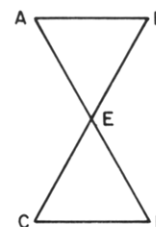


Figure 7.

Each of these different orientations is referred to as a different conformer of a single configuration. It should be noted, however, that for every conformer the atoms are arranged in the same order; all that has varied is the angles and the distances. In other words, there has been set up a "rubber sheet geometry";¹⁶ i.e., if a given geometrical arrangement of atoms were inscribed on a rubber sheet—which could then be stretched or twisted as desired but not torn or overlapped—every conformer that could be formed should be given the same name.¹⁷ Consequently, it is practical to choose the geometrically simplest conformer that exists for a given configuration as the desired picture and to then use this simplified picture as the basis for naming the configuration. For example, the simplest picture for cyclobutane is the planar square shown in Figure 1. This same square may also be used to describe the nomenclature of oxetane (Figure 3) or any other four-membered single ring—regardless of atom type, planarity, bond angles, or bond lengths.

An important geometrical consequence of giving a common name for all conformers is that there exists no distinction between simple vs. multiple closure.¹⁸ The multiply closed quadrilateral illustrated in Figure 5 is chemically identical with the simply closed quadrilateral in Figure 1. Remember that both figures are two-dimensional representations of the electronic pathway of a three-dimensional molecule. From a pragmatic viewpoint, however, Figure 5 should not be used—as it implies the intersection of two electronic pathways at a point other than an atom, which is contrary to the known physics. On the other hand, the three-dimensional representation given in Figure 6 is acceptable. The only difference between the

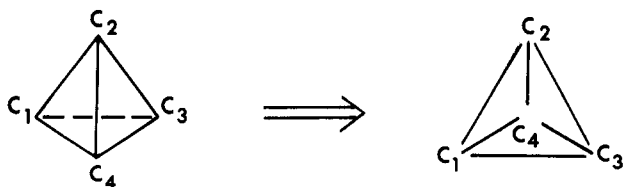


Figure 8.

models shown in Figures 1 and 6 is the position of the observer with respect to the projection of the molecule being viewed. Conversely, Figure 7 is different from Figure 5 inasmuch as point E is a vertex of Figure 7 and thus corresponds to an atom—an atom not present in the molecule represented by Figure 5.

Before progressing further, observe that a common class is given to different nodes having a common edge structure, while structures having identical nodes, but different edges, are assigned to disjoint classes. One reason for this is the pragmatic one of the existence of very many nodes (atoms or groups of atoms) but only a few common types of edges (such as single, double, triple bonds). Furthermore, these different types of edges contain an important common element—the existence of a highly localized (σ) bond between each pair of atoms. For multiple bonds, this is supplemented by π , and sometimes δ , bonds.

In the case of isolated double bonds, cumulenes and alkynes, these π bonds are also localized; however, when the atoms of a compound contain an alternating sequence of double and single bonds, there may exist a delocalization (resonance) energy that tends toward a more stable compound.²⁰ In other words, the presence (or absence) of delocalized π bonding suggests a taxonomical line that was not necessitated by graph theoretical considerations. The presence of localized (orientable) bonding vs. delocalized bonding is a physically more salient property than the geometrical one of planarity alone. This is true despite that the presence of delocalized π bonding usually contains a tendency toward planarity. Chemically observed major differences, such as substitution, rather than addition, to a double bond in a ring system containing such an alternation of bonds led to IUPAC's choice of taxonomy for purposes of nomenclature.²¹ Historically, it had probably been hoped that aromaticity would be the demarcation line between bridged and fused rings. This, however, was not to be since the condition of conjugated unsaturation is usually necessary, but not sufficient, for the increased chemical stability referred to as "aromatic".²²

TAXONOMY BASED ON SKELETAL DIMENSIONALITY

In the characterization of a chemical model, it is convenient to define two important related concepts—dimensionality and minimum embedding space. By "dimensionality" is meant what is the dimension of the module being used in order to construct the model of the named structure. For example, the skeleton of cyclobutane has been formed by the union of line segments. Note that for mixed taxonomies there would not exist a uniquely defined dimensionality.

By minimum embedding space is meant what is the smallest (homoloidal) space in which the skeleton of that molecule is able to exist. In other words, the skeleton of cyclobutane has a dimensionality of one and a minimum embedding space of two but was shown to normally occupy a portion of three-dimensional space.

In order to find the minimum embedding space of a ring compound, first form a reduced graph by eliminating all valency²⁴ = 1 vertexes. This will remove all single atoms, such as hydrogen, as well as all side chains. Now, if every remaining atom has valency = 2, the figure may be inscribed on a plane.

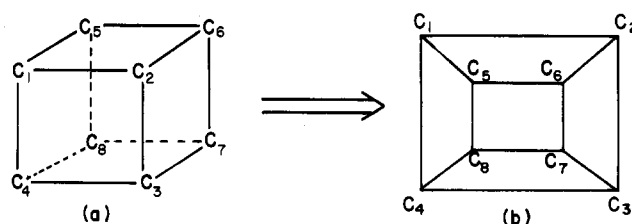


Figure 9.

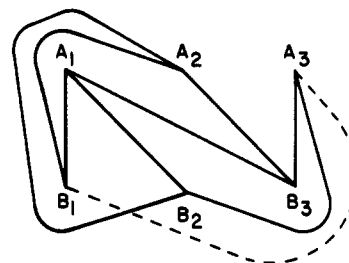


Figure 10.

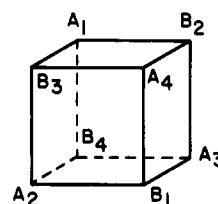


Figure 11.

Similarly, if every remaining atom has valency = 3, the minimum embedding space of the compound is three dimensional, and the graph is called a "cubic graph". Some examples of cubic graphs are tetrahedrane (Figure 8) and cubane (Figure 9).

From Figures 8b and 9b, it may be seen that the graphs of the three-dimensional models shown in Figures 8a and 9a, as well as many other cubic graphs, can be drawn by using only two dimensions; i.e., there was no need for any set of edges to cross each other in the drawing. This illustrates that planarity of the graph is not an indication that the minimum embedding space of the compound is two dimensional. A two-dimension minimum embedding space, on the other hand, will ensure the existence of a planar graph. A cubic graph that is not embeddable in a plane is shown in Figure 10.²⁵

Notice that purely on the basis of mathematics, there is no way to ascertain which taxonomy is chemically applicable. Instead, the laboratory must supply the necessary boundary conditions. Some examples of this follow.

Two Six-Membered Hydrocarbon Rings—Cyclohexane and Benzene. From a chemistry perspective, because there is only one highly unstable conformer of cyclohexane that has a planar skeleton and because there are no important chemical properties of this molecule that take place in the plane, there is negligible chemical benefit in describing cyclohexane in terms of the union of planar segments. Instead, cyclohexane is to be viewed either as the union of line segments (i.e., one dimensional) or as a skew hexagon (a one-dimensional figure in a three-dimensional embedding space)—in which the concept of area is ill defined. Benzene, on the other hand, has both its carbon skeleton and its hydrogen atoms coplanar. Also, the fusion of benzene rings takes place in a plane, whenever possible. Consequently, a description in terms of planar structure is chemically desirable. In fact, the description of benzene as a cyclohexatriene is, at best, pedantic.

For nomenclature purposes, it is useful to consider the projection of cyclohexane onto a plane, despite that structurally there is no justification for so doing. This shall have practical,

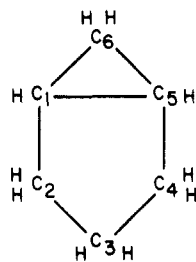


Figure 12.

as well as historical, significance. Such a procedure was originally important because crude sketches could be readily made in the plane that would be extremely laborious in three dimensions. Now, despite sophisticated computer technology that allows three-dimensional representation of any model to be illustrated after being subjected to a wide range of transformations, the unwarranted use of projection still permeates most geometrical reasoning applied to chemical structure. One practical benefit of this is that the distinction between a one-dimensional figure in a two-dimensional embedding space (the ordinary polygon) and a one-dimensional figure in a three-dimensional embedding space (the skew polygon) is unused in any monocyclic or fused bicyclic compound. For these compounds, a desired simplification has been introduced. Unfortunately, however, it also creates frequent oversimplification, i.e., misuse.

Systematic Synthesis of Multiple Rings. (a) The desired model for a molecule of cyclohexane has the same one-, two-, and three-dimensional properties as did cyclobutane. However, although cyclohexane is best described by linear taxonomy, there is no mathematical necessity that compounds formed by adding bonds between existing atoms should also be described by the same taxonomy class. Nevertheless, in the absence of a compelling chemical change—such as the extra stability exhibited in certain ring compounds by conjugating single and double bonds among $4n + 2$ atoms, etc.—this is a reasonable expectation.

Consider now that a single bond replaces one hydrogen atom on each of two nonadjacent carbon atoms of cyclohexane, thereby forming the compound C_6H_{10} shown in Figure 12. The resulting configuration can now be viewed as the union of two sets in the following ways: (i) one six-member ring and one bond, i.e., the closed path $C_1-C_2-C_3-C_4-C_5-C_6-C_1$ and the open path C_1-C_5 ; (ii) one five-member ring and one three-member path, i.e., the closed path $C_1-C_2-C_3-C_4-C_5-C_1$ and the open path $C_1-C_6-C_5$ (or, alternately, the closed path $C_1-C_5-C_6-C_1$ and the open path $C_1-C_2-C_3-C_4-C_5$); (iii) one five-member ring and one three-member ring, i.e., the closed paths $C_1-C_2-C_3-C_4-C_5-C_1$ and $C_1-C_5-C_6-C_1$ (overlapping sets containing a common path). Consideration of this compound in terms of planar segments, i.e., (iv) one content-defined pentagon and one content-defined triangle sharing a common boundary, is possible but serves no useful purpose—either geometrically or for ease of nomenclature. More important, there is no compelling reason for such a description chemically; therefore, no consideration need be given to such a description.

Notice that description i is a Hamiltonian path²⁸ adjoined by open paths to cover all remaining edges, while descriptions ii and iii are Eulerian paths²⁹ that span the network of edges, either without (ii) or with (iii) overlapping. Description i is used in the IUPAC nomenclature for bridged rings,²¹ whereas either description ii or description iii may be used in the Taylor³⁰–Goodson³¹ naming of these compounds. Although further development of this idea could be pursued with cyclohexane as a reference, chemically more important compounds are formed starting from cyclooctane.

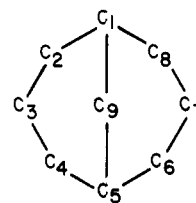


Figure 13.

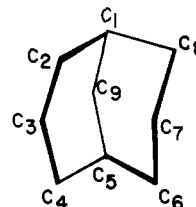


Figure 14.

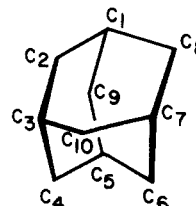


Figure 15.

(b) Add a single bond between two diametrically opposite atoms in the model of a molecule of cyclooctane. Next, replace this added bond (called a "zero-atom bridge") by a one-atom bridge (Figure 13). IUPAC considers this to be a "bicyclic" compound and gives it the name bicyclo[3.3.1]nonane.

Notice that this identical molecular model would have been formed by the fusion of two cyclohexane molecules along two adjacent edges (i.e., three adjacent carbon atoms). Actually, this molecule is a "tricyclic" compound, as the original eight-member ring has not been destroyed. This may further be seen by examining the three-dimensional model shown in Figure 14. Here, the skew octagon is the forward "face" of a "polyhedron", while the two hexagons formed by this bridge are the left-rear and right-rear "faces". In other words, if the term face does not imply a single homoloidal region but rather merely a two-dimensional contiguous region (which may be either curved or else the union of multiple homoloidal sections) such as formed by a soap bubble or a stretched piece of canvas or hide, the seed for a three-dimensional module has been planted.

Although it appears contrary to the underlying foundation of graph theory,³² the main difference between Figures 13 and 14 is the space proximity of two remote vertexes of the octagon (C_3 and C_7). So long as these two nodes are capable of being connected by an edge that seems to be of length comparable to the other lengths of the figure, psychologically we view this configuration as three dimensional. On the other hand, when this length is substantially longer than the other lengths, the idea of projection onto a plane is psychologically more appealing. The actual drawing of a connection between these two nodes reinforces our prejudice toward either a two- or a three-dimensional model—depending on the projection chosen.

That as an important a selection as the fundamental topology of the desired model for a chemical compound should be based on human bias is discomfiting to our sense of logic. Nevertheless, it appears that it cannot be evaded. In practice, planar projection permeates most descriptions of structure and of nomenclature.

Consider next adding a second one-atom bridge between C_3 and C_7 , as shown in Figure 15. This creates a "tri" cyclo-

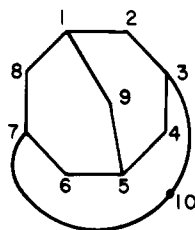


Figure 16.

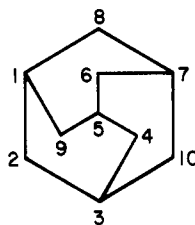


Figure 17.

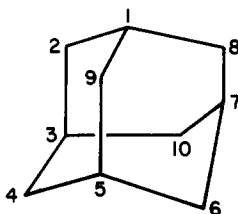


Figure 18.

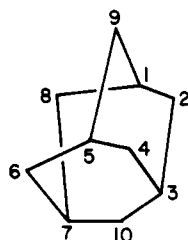


Figure 19.

decane, which has the common name of adamantane. Actually, the addition of this second bridge created not one but two more cyclohexane rings—four in all; also, as well as the original cyclooctane ring, there are two more eight-member rings formed. In other words, there are seven rings in this ten-atom system:

hexagons	octagons
1-2-3-4-5-9	1-2-3-4-5-6-7-8
1-2-3-10-7-8	1-2-3-10-7-6-5-9
1-8-7-6-5-9	1-8-7-10-3-4-5-9
3-4-5-6-7-10	

A distorted picture having the advantage (or disadvantage, depending on the usage intended) of planarity is shown in Figure 16. For drawing purposes, this is usually presented in the more symmetric form of Figure 17. Similarly, the three-dimensional attributes of adamantane are best presented by either Figure 18 or Figure 19—different perspectives emphasizing the modular or the bridging attributes, respectively. Remember that from a chemistry perspective Figure 16 and Figure 17 are, at best, distortions and that the molecule's properties are caused, in large measure, by its three-dimensional geometry.³³

SUMMARY

The intent of this paper has been to suggest a new way to look at an old problem: the bipartite division of polycyclic ring compounds into bridged vs. fused categories. This author

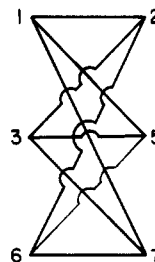


Figure 20.

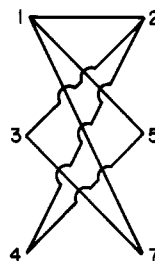


Figure 21.

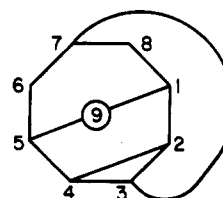


Figure 22.

contends that this division, which is fundamental in nomenclature taxonomy,⁸ is right, but for the wrong reason: namely, it is desired that a linear taxonomy (boundary-defined model) be chemically relevant for the description of alicyclic compounds, while a content-defined model (planar taxonomy) be relevant for aromatic compounds.³⁴

In a similar manner, the generation of a disjoint class of compounds employing solid taxonomy with, say, an adamantane-like module might then be studied as a geometrically distinct class. One of the problems that must be solved in this pursuit is described elsewhere.³⁵

REFERENCES AND NOTES

- (1) Classes B and C in footnote 2.
- (2) Richter, M. M. "Lexikon der Kohlenstoffverbindungen", 3rd Ed.; Verlag Voss: Leipzig, 1903; pp 14-26.
- (3) The term "taxonomy" is used throughout this paper in the general sense of the study of the general principles of scientific classification.⁴
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- (7) "Any distinction between classes B and C must be more or less arbitrary, but the line drawn in these rules conforms fairly closely to actual usage".⁸
- (8) Patterson, A. M. "Proposed International Rules for Numbering Organic Ring Systems". *J. Am. Chem. Soc.* **1925**, *47*, 554.
- (9) Wiberg, K. B.; Walker, F. H. "(1.1.1)-Propellane". *J. Am. Chem. Soc.* **1982**, *104*, 5239-5240.
- (10) Cotton, F. A. "Metal-Metal Bonding in (ReX₈)²⁻ Ions and Other Metal-Atom Clusters". *Inorg. Chem.* **1965**, *4*, 334-336.
- (11) Start with the normal (tetrahedrally oriented) carbon atom. From a purely geometrical perspective, it might have been expected that small rings, such as cyclobutane, would have a coplanar carbon skeleton; i.e., the angles between carbon atoms would be compressed from the unstrained tetrahedral angle of 109° 28.273' to 90°, in order to create ring closure. If this description had been accurate, then Figure 1 would be a fairly representative picture of the skeleton of the cyclobutane molecule. This, however, is not the case. Various studies using electron diffraction, infrared, Raman, and NMR spectra etc. have shown that

cyclobutane has a puckered structure with a dihedral angle of $30 \pm 6^\circ$, Figure 2.¹² In contrast to this, the molecule oxetane has a coplanar skeleton, Figure 3.¹³ In other words, the replacement of a single carbon atom by an oxygen has profoundly altered the geometry of the compound—despite that the skeleton graphs of these two compounds are identical. Furthermore, there exists a complete dichotomy in substituted cyclobutane rings. Crystallographically, either these rings are planar, or else, they have a dihedral angle of $26 \pm 3^\circ$. No such structure has been found with dihedral angles in the range from 1 to 18° . In addition, *trans*-1,3-cyclobutanedicarboxylic acid is planar as the pure crystal but has a dihedral angle of 25° when the sodium salt of this acid is included in the crystalline structure.¹⁴ In other words, crystal packing forces override the preferred nonplanarity of the cyclobutane kernel. Moriarty explains this nonplanarity of the equilibrium structure of cyclobutane as due to the presence of the nonskeleton hydrogen atoms:¹⁵ "The folding of the ring is accomplished by a twisting of carbon-carbon bonds, resulting in directed substituent bonds analogous to the axial and equatorial bonds in cyclohexane....The planar form is destabilized by the eclipsing of the adjacent methylene hydrogen atoms. This is relieved by ring puckering, which increases the torsional angle between the adjacent hydrogens, but also decreases the CCC angles." In other words, there is nothing geometrically illogical or inconsistent with noncoplanar cyclobutane. The oversimplification of considering only the geometry of the carbon skeleton of four atoms, instead of the entire system of 12 atoms, has produced the false expectation of coplanarity.

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- (16) Courant, R.; Robbins, H. "What Is Mathematics?"; Oxford University Press: New York, 1941; p 235.
- (17) Because of the physical constraint of a three-dimensional space in which internally tangent spheres are not transformable to externally tangent ones (Figure 4) despite the obvious homeomorphism, the term "topology" has been avoided in this context.
- (18) A "simple closed curve" is a curve that may be traversed without repeating any point on the curve; i.e., a curve that does not intersect itself.¹⁹
- (19) Courant, R.; Robbins, H. "What Is Mathematics?"; Oxford University Press: New York, 1941; p 224.
- (20) This type of delocalization energy is normally present in noncyclic systems of any size and in cyclic systems that follow Huckel's $4n + 2$ law. Cyclic systems that have $4n$ carbon atoms usually have antibonding orbitals rather than delocalized π -bonding.
- (21) International Union of Pure and Applied Chemistry; "Nomenclature of Organic Chemistry: Section A"; Pergamon Press: Oxford, England, 1979.
- (22) Even such firmly established structural requirements for aromaticity as the presence of a ring have been questioned. Gund²³ has described guanidine as a compound having the same type of stability that has traditionally been referred to as "aromatic".
- (23) Gund, P. "Guanidine, Trimethylenemethane and 'Y-Delocalization'". *J. Chem. Educ.* **1972**, *49*, 100-103.
- (24) The terms "valency", "degree of a vertex", and "incidence of a vertex" are interchangeable and may be applied to either a graph or the skeleton of a molecule.
- (25) Figure 10 is a cubic "complete", "bi-partite" graph. A "complete" graph is a graph in which every vertex of the graph is connected to every other one. Such graphs are represented by the symbol K_n —where n is the total number of vertexes. Examples include the following: K_2 —a line segment, such as the skeleton of ethane; K_3 —three line segments in a triangle, e.g., cyclopropane; K_4 —see Figure 8. A bi-partite graph is one in which the vertexes may be divided into two distinct sets (A and B) such that every vertex is connected only to members of the other set; i.e., A_1 may be joined to B_1, B_2, \dots but not to A_2 etc. A convenient labeling of the vertexes of cubane, which emphasizes the bi-partite nature of the graph is shown in Figure 11. A "complete bi-partite" graph is complete only in the sense that edges permitted by the definition of bi-partite are included. For example, if edges $A_1-B_1, A_2-B_2, A_3-B_3$ and A_4-B_4 were included in Figure 11, then this would be a quartic complete bi-partite graph. $K_{m,n}$ is the symbol used for complete bi-partite graphs, where m and n are the number of vertexes in the two disjoint sets. Kuratowski proved that any graph containing a subgraph K_5 or $K_{3,3}$ cannot be embedded in a plane.²⁶ This could have important consequences for chemical models, as the idea of a rubber sheet geometry would now be inapplicable. The newly created molecule, which has the geometrical configuration of a squared-off Moebius strip,²⁷ is an example of a cubic bi-partite graph, while the reduced graph formed by ignoring all atoms of degree less than three is a cubic complete bi-partite graph, $K_{3,3}$.
- (26) Harary, F. "Graph Theory"; Addison-Wesley: Reading, MA, 1969; p 108.
- (27) Walba, D. M.; Richards, R. M.; Haltiwanger, R. C. "Total Synthesis of the First Molecular Moebius Strip". *J. Am. Chem. Soc.* **1982**, *104*, 3219-3221.
- (28) Harary, F. "Graph Theory"; Addison-Wesley: Reading, MA, 1969; p 65.
- (29) Harary, F. "Graph Theory"; Addison-Wesley: Reading, MA, 1969; p 64.
- (30) Taylor, F. L. "Enumerative Nomenclature for Organic Ring Systems". *Ind. Eng. Chem.* **1948**, *40*, 734-738.
- (31) Goodson, A. L. "Graph-Based Chemical Nomenclature. 2. Incorporation of Graph-Theoretical Principles into Taylor's Nomenclature Proposal". *J. Chem. Inf. Comput. Sci.* **1980**, *20*, 172-176.
- (32) Balaban, A. T. "Chemical Applications of Graph Theory"; Academic Press: London, England, 1976; p i.
- (33) An additional observation to be made about this synthesis process leading up to the formation of adamantane is that adamantane is the last model in this particular progression in which a coplanar representation of this essentially three-dimensional molecule is possible mathematically. Inclusion of yet another bridge between, say, locants 2 and 6 in Figure 16 can not be carried out in the plane. This is seen to reduce to complete bi-partite graphs of the form $K_{3,3}$ (Figure 20) and thus must be noncoplanar.²⁶ Notice that the locant numbering in Figure 20 does not involve those vertexes whose incidence is only two (locants 4 and 8). On the other hand, a bridge between locants 2 and 4 (instead of 2 and 6) is still coplanar, and its reduced graph (Figure 21) is not complete bi-partite. Metric transformations of this graph yield the planar graph shown in Figure 22.
- (34) Notice that the model of planar taxonomy has been applied only to aromatic compounds rather than to the wider class of conjugated compounds; thus, the question of conjugated aromatic vs. antiaromatic compounds is not relevant. Instead, since a content-defined model is not applicable for antiaromatic compounds, by default, the boundary-defined model remains.
- (35) Elk, S. B. "Effects of Taxonomy Class and Spanning Set on Identifying and Counting Rings in a Compound". *J. Chem. Inf. Comput. Sci.* **1985**, *25*, 11-16.