

Interpretation of Kuratowski's Theorem in Graph Theory as both a Topological Abstraction and a Chemical Reality

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Although Kuratowski's theorem is probably the most quoted theorem in graph theory, its underlying *raison d'être* in topology has not been clarified from an intuitive perspective. This paper gives (1) an explanation why the graphs K_5 and $K_{3,3}$ are of particular importance from a geometrical perspective; (2) the theoretically simplest chemical molecules that could be formed having these particular structures, as well as a reexamination of the Moebius strip as an "example" of $K_{3,3}$; (3) techniques that might produce a chemically realizable molecule that "reduces" (using traditional graph theory methods) to K_5 ; and (4) the logical extension of the above to give description of the chemical counterparts of other, even more, esoteric figures, including a molecular Klein bottle and Escher-inspired constructs, that are chemically viable—despite the fact that the mental pictures that we have of them make such molecules appear to be unattainable.

It has been nearly 60 years since Kazimir Kuratowski proved that the deciding factor as to whether a graph could be drawn in a plane without two edges crossing was its correlation to two "primitive" graphs¹—the complete five-vertex graph, K_5 , and the complete bipartite graph, $K_{3,3}$. Any graph containing a subgraph (including itself) that is reducible (by pruning of vertices of degree 1 and suppression of vertices of degree 2) to either of these two graphs is precluded from being embeddable in a plane, whereas any graph that contains no subgraphs that can be reduced to either of these two graphs can be manipulated so as to have a planar form.

We believe that the reason why these two particular graphs are fundamental to the determination of the geometrical property of planarity is related to the observation that K_5 is the simplest way that one can project the 4-simplex onto a plane,² while $K_{3,3}$ represents the simplest nonorientable figure in 3-space. In other words, the realization of planarity in a graph is *conjectured* to be isomorphic to some particular projection of a three-dimensional orientable figure onto a plane, whereas nonplanarity is isomorphic to those extensions of mathematical abstraction that a synthetic geometry uses to model "figures" that cannot be embedded in a space that is both three-dimensional and orientable. (The word *conjectured*, in this context, maintains the heuristic idea of "to draw an inference from slight evidence",³ in contradistinction to the more mathematical ideal of having a finite progression of operations to be carried out that will yield the desired demonstration of isomorphism.)

At this point it should be noted that the technique for synthesizing figures in an n -dimensional Euclidean space involves the union of "faces"—which are "segments" of dimension $n - 1$. Each of these faces, in turn, is the union of segments of dimension $n - 2$, etc. In other words, in ordinary (three-dimensional) geometry we have three different sets of elements (faces, edges, and vertices) to use in describing the heuristic concept that we call figure. In such a characterization, however, observe that with each step down in complexity (from figure to set of faces, from set of faces to set of edges, from set of edges to set of vertices) we pay a price in how much information is stored. If we had been interested in the metric properties of an object, this could be a major sacrifice; however, since our main interest is in incidence relationships, the price is relatively small. For this reason the use of graph theory, in which we have limited our attention to only two of these sets—vertices and edges—is of great utility.

By the judicious use of graph theory, we gain not only a tool for organization purposes but also the apparent ability to

formulate both four-dimensional and nonorientable (three-dimensional) molecules in chemistry. Although the use of the exotic (four-dimensional and nonorientable figures) may seem to be a deviation from reality, we must remember that, in actuality, we are not describing a molecule, but rather a model that, we hope, mirrors most of the important attributes of the molecule; consequently, any mental construct is viable. The existence of any paradoxes that may arise can be traced to the use of inconsistent definitions and descriptions for the geometrical model as well as for the physical phenomenon that is being modeled.

In this vein we should remember that in chemistry the model that is relevant for most (aliphatic) compounds is the embedding of one-dimensional modules in a three-dimensional space⁴ rather than the traditional geometry in which the dimension of a figure is exactly one dimension higher than the dimension of its boundary. Despite this, the description that is usually chosen for aliphatic compounds involves one-dimensional molecules in a two-dimensional embedding space, thereby allowing for the direct use of graph theory without regard to topological properties of the figures involved.

Next, let us further limit our attention not only to a three-dimensional space but also to those "simple" figures for which there is a one-to-one and onto isomorphism between a boundary-defined figure and the corresponding content-defined figure. In most instances this is a negligible limitation; however, in the mathematical models used for a few selected chemical moieties, this one-to-one isomorphism between boundary-defined and content-defined figure is not valid. Such is the case for geometrical figures that are either nonorientable or intrinsically disconnected, such as the Moebius strip and interdigitating rings, respectively. For such figures we lose information about the chemical moiety we are modeling through the indiscriminate use of graph theory.⁵ To see this, let us turn our attention to the chemical molecule that is often referred to as Moebiane. We shall see below that "linear Moebiane" would be a more accurate name.

It is interesting to note that one useful picture of the Moebius strip is that of a one-dimensional geometrical figure which requires a three-dimensional embedding space for its intrinsic existence. In such an embedding space the imputed isomorphism between boundary-defined and content-defined figures is not valid. Thus, we envision two topologically different chemical Moebius strips: In terms of *strictly* a one-edged figure the $C_{42}H_{72}O_{18}$ crown ether created by Walba⁶ meets all of the requirements of the Moebius strip. Furthermore, assuming the traditional methods of reduction to the mathematical minimum size of C_6H_6 ,⁷ such a molecule

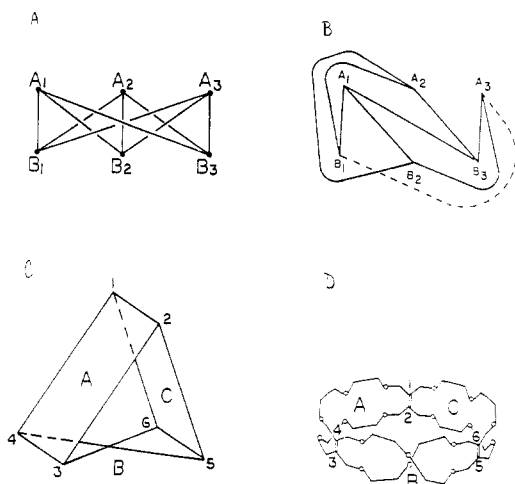


Figure 1.

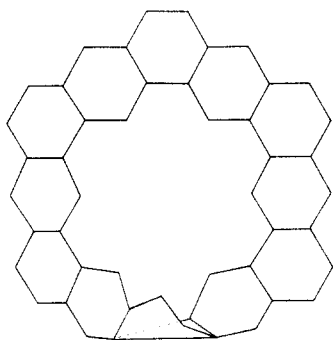


Figure 2.

is adequately represented by the graph $K_{3,3}$. This is shown in Figure 1: Part A is the traditional graph theory representation for $K_{3,3}$; part B illustrates the successive joining of edges in a plane that demonstrates the need for a noncoplanar line; part C is the geometrically simplest model that meets this ideal—which we may think of as a “squared-off” Moebius strip; and part D illustrates the chemical molecule which Walba synthesized that we referred to above as Moebiane.

But what about the more traditional geometrical model in which the one-sided attribute of the model is considered of paramount significance? To examine this perspective, let us envision building a molecule by using planar-defined modules such as, say, benzene modules, instead of linear (alkoxy) chains in a crown ether. This would be viable only so long as the twist in the individual modules was not sufficient to lose the aromatic character of each module. Laarhoven's synthesis of a double helicene,⁸ with its inherent distortions in the rings, as well as Martin's measurement of an interplanar angle of 58.5° between the two terminal rings of hexahelicene⁹ shows that this is not a problem. Consequently, we can envision forming a theoretical model that meets all of the requirements for “planar Moebiane” by starting with an “elongated coronene” of, say, 12 or 18 modules, and having each module contain a twist of, say, 15° or 10° out of the plane. Note that these measurements are consistent with Laarhoven's and Martin's studies. The end rings would then be able to be joined together so that the more traditional picture of planar Moebiane is created. This is illustrated for 12 benzene modules in Figure 2.

Returning now to consideration of K_5 , the seeds for a molecule represented by K_5 also exist in chemistry; however, since molecules having all vertices with valency of 4 are rare (excluding the theoretical limits of the polymantanes),¹⁰ a compound with this property has not as yet been isolated. The prototype, however, is available in the propellanes.¹¹ To actually form a K_5 graph, all that is theoretically necessary is

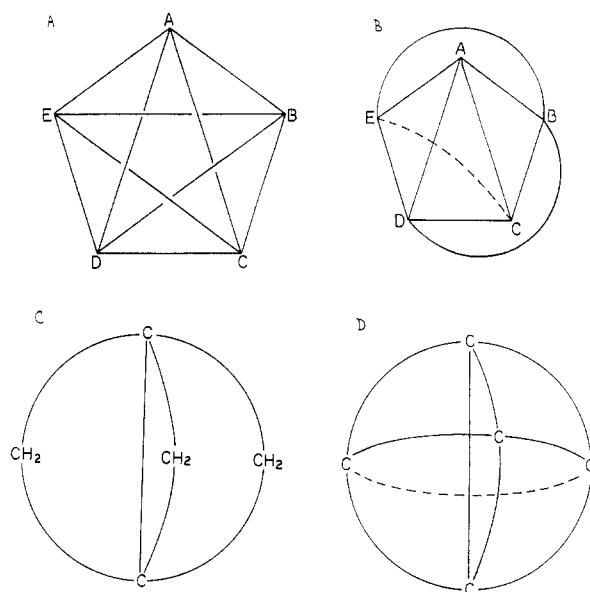


Figure 3.

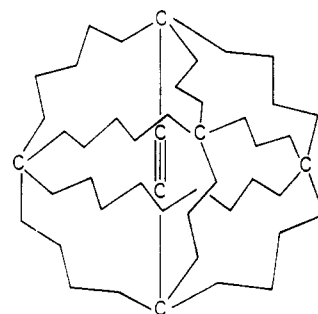


Figure 4.

to create a tribridged propellane, where a single atom on each “propeller blade” is chosen as a new bridge to be joined to the other two blades. Note that all five “bridgehead” atoms have incidence of 4, while the remaining atoms each have incidence of 2 and thus may be ignored in the reduced graph. In Figure 3 we have shown (A) the traditional graph theory representation for K_5 , (B) the successive joining of edges in a plane that demonstrates the need for a noncoplanar line, (C) the geometrically simplest starting material that we use, namely, [1,1,1]propellane, and (D) the modifications that were needed—the bonds to be added and the concurrent elimination of the hydrogen atoms.

The above description is not to be interpreted as implying that a small K_5 molecule is a pragmatic reality any more than the C_6H_6 version of $K_{3,3}$ was.⁷ Like the “chemical Moebius strip”, which was created by lengthening the “edges” from a single bond to a chain of carbon and oxygen atoms, the corresponding replacement of single bonds by, say, methylene (or alkoxy) chains may be a viable possibility. Figure 4 is an extended model of Figure 3D having single bonds replaced by methylene chains. In such a case these five carbon atoms are the bridgehead atoms of a larger system. The remaining atoms, which each have incidence of 2, may be ignored in the reduced graph. Note that in this picture we chose to replace nine of the single bonds by methylene chains and one by an extended alkyne linkage. From an energy or entropy perspective there is no reason not to keep the 10th bond (between the two bridgehead carbon atoms) as is and thus truly have a propellane; however, for illustration purposes, we have elongated this chain by including an alkyne chain—which maintains the mental picture of a propellane, while, in reality, presenting the picture of a paddlane.

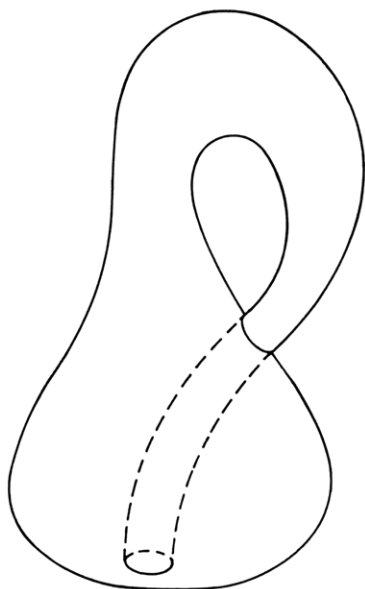


Figure 5.

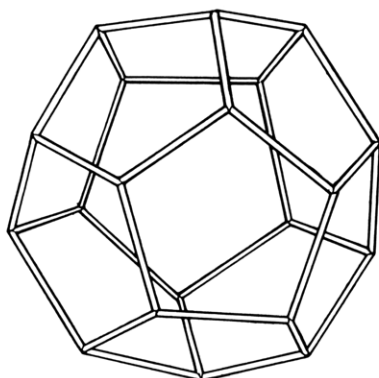


Figure 6.

It is interesting to note at this point that, in a similar manner, the logical extension to even more "esoteric" figures may be readily pursued. For example, ideally, one may envision the Klein bottle as a figure in a Euclidean 4-space, which has a three-dimensional representation formed by allowing the figure to intersect itself. This intersection, however, is not to be viewed as the delineated point set that problems of representation in a planar picture caused us to portray as in Figure 5, but rather as a rotaxane¹² with a "movable collar" around the "self-intersecting tube", in just the same way as the Moebius strip in Figure 1C should not be viewed as having exactly one of the three faces twisted and the other two strictly coplanar. With this interpretation in mind, and recognizing a chemical model in terms of the union of linear modules in 3-space, formulation of a molecular Klein bottle is a realizable goal. A blueprint for forming such a molecule is given in Appendix A, while a typical Escher¹³-inspired molecule that is chemically viable is described in Appendix B.

APPENDIX A: A BLUEPRINT FOR FORMING A MOLECULAR KLEIN BOTTLE

Because dodecahedrane¹⁴ has already been synthesized, it forms a good starting material. Remember that the carbon skeleton of dodecahedrane is the union of 30 bonds (Figure 6)—which coincidentally form themselves into 12 pentagonal rings. There is no concept of "surface" for any of these "pentagons" in the same sense that would exist for a benzenoid compound.⁴ This is equivalent to saying that so long as the 30-edge set is intact, the faces are fictitious and no volume is enclosed.

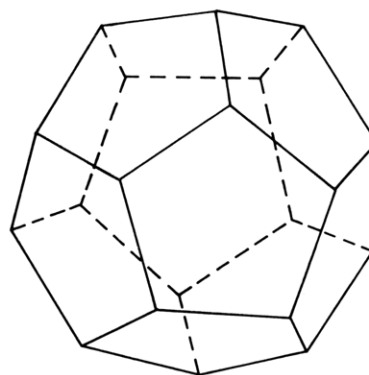


Figure 7.

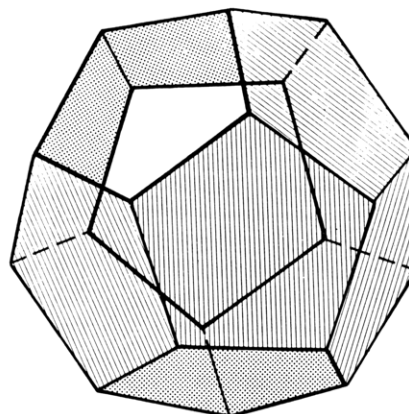


Figure 8.

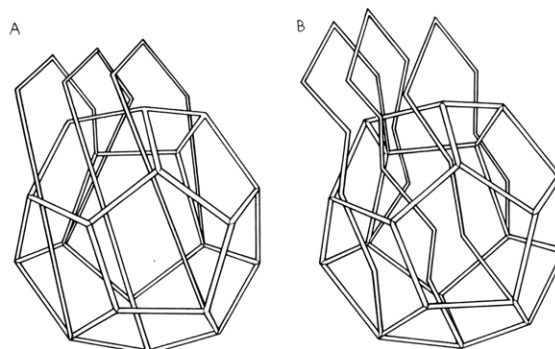


Figure 9.

An interesting observation that may be seen by focusing on the fictitious planar boundary-defined dodecahedron (Figure 7) is that this model is structurally sound¹⁵ despite the removal of three nonconnected "panels" (Figure 8). Additionally, note that no edges have been removed by the elimination of these specified panels; however, had two of the panels been connected, at least one edge would have been deleted. In other words, the edge set is not affected by the removal of the specified panels, and, therefore, it would be immaterial whether the modules used had been linear (aliphatic) or planar (aromatic). The foundation for creating a Klein bottle is now provided by running a "tubing" section "internally" from one such section "out" a second and back "into" the third removed panel area to join up with the perimeter of this panel. This is shown in Figure 9A with linear tubing, such as polyynes, and in Figure 9B with methylene chains.

At this point there are two perspectives to examine: (1) the most efficient set chemically and (2) the minimum set mathematically that can be used to form such a compound. In doing this, a comparison with Walba's Moebius-type compound⁶ is in order. Note that Walba's compound is $C_{42}H_{72}O_{18}$,

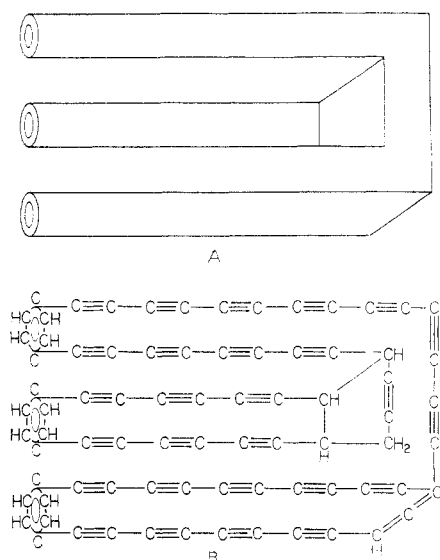


Figure 10.

whereas the minimum set mathematically is C_6H_6 .⁷ In other words, the physical model actually created for linear Moebiane has a full order of magnitude more skeletal atoms (and even more hydrogen atoms) than the minimum set mathematically.

In the formation of the proposed Klein bottle, on the other hand, to create the interior tubing it is anticipated that the first attainable molecule will be only slightly larger than the minimum set inasmuch as the strain factors in creating a triangular cylindrical tubing will be of far less problem than the steric interference of "threading" a "large"-diameter tube through the removed panels. Similarly, the length of this tubing (especially that "interior" to the dodecahedral structure) is relatively small and may be selected to accommodate the unstrained bond angles of sp , sp^2 , or sp^3 orbitals. Such an interior structure appears, in a crude model, to be approximately two atoms long if we may assume linearity in the form of a polyyne structure (Figure 9A) and slightly longer if bonding is at the more prevalent tetrahedral or trigonal angles before emerging through the removed panel. Once exterior to the dodecahedral structure, tetrahedrally bonded chains of approximately three atoms long appear to be adequate to complete the tubing. This model has a 38 carbon atom structure with 51 bonds. Actually, some of the edges of the dodecahedral cage can be dispensed with, and instead of two or more fused pentagonal rings, a single octagonal ring, etc., will suffice.

An observation on the above paragraph is that this is more accurately a linear Klein bottle. Furthermore, analogous to the Moebius strip, the Klein bottle may be viewed as "a two-dimensional figure in a four-dimensional space"; consequently the use of planar modules for the boundary-defined Klein bottle or solid modules for the content-defined Klein bottle might seem to be more apropos.

One further comment on the formation of a molecular Klein bottle is that in the event that the internal steric problems cannot be overcome, it might be possible to use a much larger "superstructure"—such as the Archimedean solid formed with 12 pentagons and 20 hexagons. Unlike the theoretical structure described by Haymet, which he referred to as "footballene",¹⁶ at least three of the hexagons of the superstructure would have to be saturated in order that connecting bonds to form the tubing would be available. One advantage to such a figure is that there would be no interfering hydrogen atoms; however, such a superstructure would be built around 90 edges for the "cage" (by use of only the pentagonal and

hexagonal faces) plus those needed to form the tubing. Actually less would suffice since complete pentagons and hexagons are not necessary. Additionally, the tubing might well have numerous acetylenic or allenic linkages to create the needed tube length. Walton et al.^{17,18} have created the necessary shape molecules to serve as the tubing with the production of polyynes. Similarly, the new class of "fullerenes"^{19,20} provides many usable superstructures through which this tubing may be run.

APPENDIX B: A BLUEPRINT FOR MOLECULES WITH ESCHER-INSPIRED GEOMETRY

One of the common optical illusions, which on one end looks like three parallel cylindrical tubes and on the other a square cross-section rectangular parallelepiped with two right angle bends (Figure 10A), is easily modeled by a hydrocarbon of approximately $C_{80}H_{20}$ (Figure 10B). In fact, by use of polyynes of the type created by Walton,^{17,18} the necessary combination of contiguous acetylenic linkages would not be an insurmountable synthesis problem.

In a similar manner, any other combinations that can be drawn can also theoretically be a chemical "molecule" since the requirements inherent in a linear taxonomy model are not influenced by projective distortion of the type made famous by Escher. This is equivalent to saying that the global picture is immaterial so long as no excessive local distortions exist.

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