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TOPICITY OF VERTICES AND EDGES IN THE MÖBIUS LADDERS: A TOPOLOGICAL RESULT WITH CHEMICAL IMPLICATIONS

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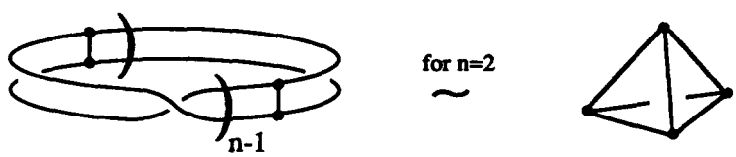
Summary: It is shown that for uncolored Möbius ladders with n rungs, if n=3 all vertices and edges are constitutionally equivalent, while if n>3 all vertices are equivalent but two heterotopic classes of edges appear. Possible chemical consequences of these facts are discussed.

As part of our effort in topological stereochemistry,[2] we have recently synthesized the first organic molecules possessing molecular graphs homeomorphic to the three and four-rung Möbius ladders[3] as defined by Harary and Guy.[4] While for our molecules the "rungs" of the graph are chemically distinct from the other edges (equivalent to a colored graph where the rungs have a different color than the other edges) we began exploring the properties of these graphs in detail, and have calculated all possible automorphisms of the graphs, assuming all edges (including the rungs) are equivalent—a first step towards understanding the more complex topology occurring when the graphs are then embedded in 3-space. For the Möbius ladders, an interesting result occurs at the point where one passes from three rungs to four rungs. For certain easily conceivable molecules, these results have interesting chemical implications.

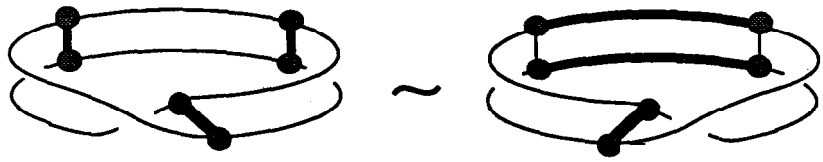
A necessary step in determining topicity of atoms in a molecule is determining if they are constitutionally equivalent, that is, whether or not there exists an automorphism of the molecular graph taking one to the other. We shall use the chemically familiar terms "constitutionally equivalent" vs. "heterotopic" to describe vertices (or edges) of an abstract graph. In application, the vertices of the graph represent atoms, while the edges of the graph represent either bonds between atoms or chains of atoms; in the latter case, topicity of edges largely determines topicity of the atoms that lie along them. Graph theorists use the term p* to denote the number of heterotopic classes of vertices, and q* to denote the number of heterotopic classes of edges.[5]

Consider the Möbius ladders M_n in a standard presentation **1**, where no coloring is used to distinguish edges.[6] In this presentation it is clear that certain edges of the graph may be denoted "rungs" of the Möbius ladder, where n is the number of rungs. If n=2, the graph is not really a Möbius ladder at all, but simply the tetrahedral graph **2**, with p*=1, and q*=1 (the tilde (~) means "topologically equivalent").



1 **2**

If n=3 (the three-rung Möbius ladder), intuition would suggest that the rungs are now heterotopic from the other edges of the Möbius ladder. However, the graph M_3 possesses so much symmetry,[7] that in fact p*=1, and q*=1. That is, topologically the rungs are constitutionally equivalent to the other edges. This at first surprising result is illustrated by the deformation of presentation **3** into **4**, where two rungs of ladder **3** become "other edges" when the ladder is deformed into its mirror image **4** (the reader is encouraged to show that this deformation is indeed possible).



3 **4**

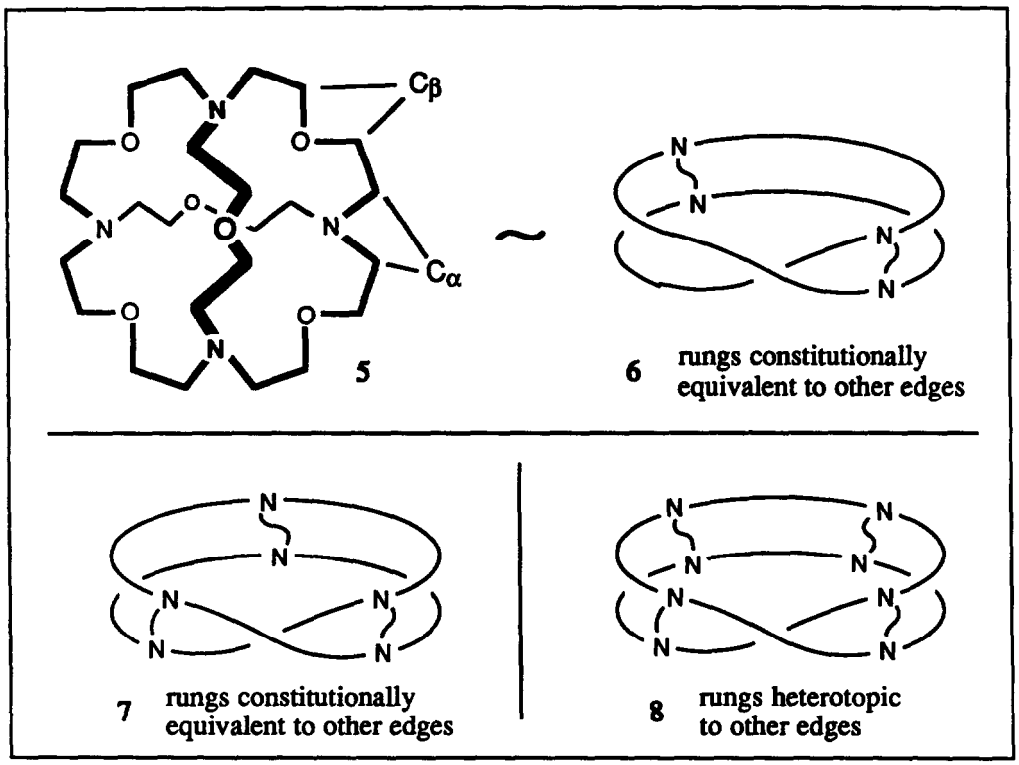
Given the above result, it is interesting to note that when n=4 (the four-rung ladder) the rungs in effect color themselves. That is, p*=1 but q*=2. Thus, the rungs are heterotopic compared with the other edges, but constitutionally equivalent to each other in the four-rung ladder. In fact, for all M_n, n>3, p*=1 and q*=2.[8]

These topological results could actually have real chemical consequences, since the topicity of the vertices and edges of the graphs would correspond to the topicity of atoms in molecular realizations of the graphs (yet to be accomplished in the lab). To illustrate the point, consider the beautiful class of polycyclic cryptands represented by the graphs **1** where the vertices are nitrogen atoms and the edges are $-CH_2CH_2OCH_2CH_2-$ units. The simplest member of this class, structure **5** (where n=2) has, in fact, been synthesized by Lehn and Graf.[9] The topology of the compound in the context of this paper is nicely captured by the graphical representation **6**.

Consider the two chemical classes of carbon atoms C_α and C_β. Since for the tetrahedral graph all edges are constitutionally equivalent, all of the C_α carbons are constitutionally equivalent assuming the actual molecule can realize the topological symmetries possible. In this case only one ^{13}C resonance should be observed for these carbons. The same holds true for the C_β carbons, and indeed compound **5** shows two peaks in the ^{13}C spectrum.[9]

Now suppose that a homologous molecule were synthesized with n=3 (a three rung Möbius ladder), as represented by graph **7** (remember <u>all</u> of the edges of this graph are $-CH_2CH_2OCH_2CH_2-$ units). In this graph q*=1, that is topologically the rungs and other edges of the ladder are constitutionally equivalent. Examination of models suggests that the actual molecule is flexible enough to achieve all of the topologically allowed symmetries on the NMR time scale, and therefore all of the $C\alpha$ carbons are constitutionally equivalent and all of the $C\beta$ carbons are constitutionally equivalent. Thus again only two peaks are expected in the ^{13}C NMR spectrum.

In the case of the four-rung homologue **8**, however, q*=2, and therefore the $C\alpha$ carbons in the rungs are heterotopic with the $C\alpha$ carbons in the edges! The same holds true for the $C\beta$ carbons. Thus, at a high enough field four carbon peaks would be observed for compound **8**: one for the C_α carbons in the rungs; one for the C_α carbons in the other edges; one for the $C\beta$ carbons in the rungs; and one for the $C\beta$ carbons in the other edges. This would be true even if the molecule were infinitely flexible!



How would this prediction normally be accomplished? Having synthesized compounds **7** and **8**, a chemist would start working with models to discover the possible permutations (rigid or otherwise) of the atoms in the molecules. With enough work, the chemist would discover the deformation indicated by **3** ⟶ **4**, or its equivalent, and would know to expect a single carbon peak for the C_α carbons of compound **7**. But, similar "experiments" with models of compound **8** would show a negative result. That is, no motion of the model would take the C_α carbons of the rungs to the C_α carbons of the other edges. Under these circumstances, a negative result with physical models is hardly rigorous, and seems somehow unsatisfying. Calculation of the automorphisms of the abstract graphs, however, gives an unequivocal answer in a simple and straightforward way.

The more complex topological consequences of embedding these graphs in 3-space will be discussed in a later publication.

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References and Notes.

1 Department of Mathematics, University of Iowa, Iowa City, IA 52242.

2 (a) Walba, D.M. "Stereochemical Topology" in "Chemical Applications of Topology and Graph Theory"; R.B. King, ed.; Elsevier: Amsterdam, The Netherlands, 1983; pp17-32. (b) Walba, D.M. Tetrahedron **1985**, 41, 3161-3212. (c) Walba, D.M. "Topological Stereochemistry: Knot Theory of Molecular Graphs," in "Studies in Physical and Theoretical Chemistry"; R.B. King, ed.; Elsevier: Amsterdam, The Netherlands, 1987; in press.

3 (a) Synthesis of the first organic three-rung Möbius ladder: Walba, D.M.; Richards, R.M.; Haltiwanger, R.C. J. Am. Chem. Soc. **1982**, 104, 3219-3221 (Note that vitamin B12, including the cobalt, possesses a three-rung Möbius ladder graph). (b) Synthesis of the first four-rung Möbius ladder: Walba, D.M.; Armstrong, J.D., III; Perry, A.E.; Richards, R.M.; Homan, T.C.; Haltiwanger, R.C. Tetrahedron **1986**, 42, 1883-1894.

4 Guy, R.K.; Harary, F. Can. Math. Bull. **1967**, 10, 493.

5 Harary, F. "Graph Theory"; Addison-Wesley: Reading, 1969.

6 Ignoring the embedding of the graphs in 3-space, the normalization of the crossings, i.e.,which line goes "over" and which goes "under", is meaningless. Crossings are shown to make the graphs easier to visualize.

7 The three-rung Möbius ladder M_3 is the complete bipartite graph $K_{3,3}$ having 72 automorphisms while the four-rung ladder M_4 has only 16 automorphisms. Complete listings of all possible automorphisms for these graphs may be obtained from DMW or JS.

8 Simon, J. Topology **1986**, 25, 229-235.

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