Intrinsic chirality of triple-layered naphthalenophane and related graphs

Erica Flapan [a] and Brian Forcum [b,*]

[a] Department of Mathematics, Pomona College, Claremont, CA 91711, USA
[b] Andersen Consulting LLP, 2101 Rosecrans Ave, El Segundo, CA 90245, USA

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We prove that the graph of triple-layered naphthalenophane and an infinite class of related graphs are all intrinsically chiral. We also give examples to illustrate that not all graphs which are contractible to a Möbius ladder with three rungs are necessarily intrinsically chiral.

1. Introduction

As more and more topologically complex molecules are being synthesized, topological techniques become increasingly important in understanding molecular structure. In particular, topology can be a powerful tool in the study of molecular chirality. While chemical chirality is determined on the basis of experimental evidence, we can define a molecular graph to be *topologically achiral* if it can be deformed to its mirror image, and *topologically chiral* otherwise. It follows from this definition that if a molecular graph is topologically chiral then the molecule that it represents must be chemically chiral. On the other hand, there exist many chiral molecules whose graphs are topologically achiral, because the deformation which takes the graph to its mirror image cannot be achieved on a chemical level.

While the above definition gives us a good intuitive grasp of what is meant by topological achirality, for constructing formal proofs it is often more convenient to use the following equivalent definition.

Definition. Let G be a graph which is embedded in $\mathbb{R}^3$. Then G is said to be *topologically achiral* if there is an orientation reversing homeomorphism $h:\mathbb{R}^3 \to \mathbb{R}^3$ such that $h(G) = G$, and h takes vertices to vertices and edges to edges.

If we think of an orientation reversing homeomorphism as the composition of a mirror reflection and a deformation, then we can see the equivalence of these two definitions of topological achirality.

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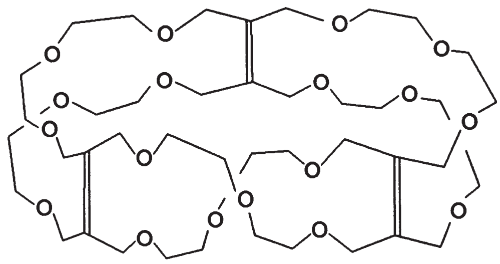

Figure 1. The 3-rung molecular Möbius ladder.

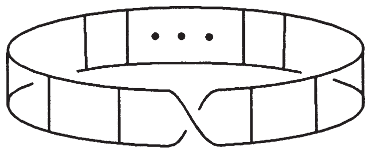

Figure 2. A standard embedding of a Möbius ladder with n rungs.

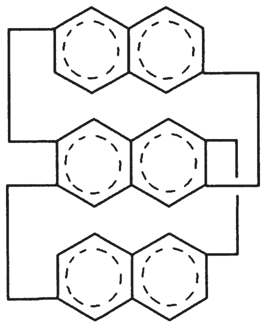

Figure 3. Triple-layered naphthalenophane.

Many molecular graphs have been shown to be topologically chiral (see [5] for a discussion of such molecules). An important example of a topologically chiral molecule is the 3-rung molecular Möbius ladder synthesized by Walba et al. [8], which is illustrated in figure 1. Simon used techniques from knot theory to prove that if M_n is the abstract graph of a Möbius ladder with $n \geqslant 3$ rungs and M_n is embedded in $\mathbb{R}^3$ as is illustrated in figure 2, then there is no orientation reversing homeomorphism $h: \mathbb{R}^3 \to \mathbb{R}^3$ such that $h(M_n) = M_n$ which takes rungs to rungs and sides to sides [6]. In other words, if we think of M_n as a colored graph, where the sides are colored differently than the rungs, then this embedding of M_n is topologically chiral.

Observe that an arbitrary embedding of M_n consists of a circuit (representing the sides of the ladder) together with edges (representing the rungs) connecting points which are halfway around the circuit. Elsewhere, we proved that, no matter how the graph M_n is embedded in 3-space, if $n \geqslant 3$ and n is odd, then there is no orientation reversing homeomorphism $h:\mathbb{R}^3 \to \mathbb{R}^3$ such that $h(M_n) = M_n$ and h takes rungs to rungs and sides to sites [1]. Thus the topological chirality of the colored Möbius ladder M_n, for odd $n \geqslant 3$, depends only on the intrinsic structure of the graph rather than the extrinsic structure of the embedding of the graph in 3-space. We coined the term *intrinsically chiral* to describe any abstract graph (colored or not) which has the property that every embedding of the graph in 3-space is topologically chiral.

While the 3-rung Möbius ladder was the first molecular graph which was shown to be intrinsically chiral, a number of other intrinsically chiral molecular graphs have since been discovered (see [2] and [4]). Here we would like to focus on the graph of the molecule triple-layered naphthalenophane, which is illustrated in figure 3.

Liang and Mislow have asserted that this graph is intrinsically chiral because it is "contractible to M_3", the Möbius ladder with three rungs [4]. What they mean by "contractible to M_3" is that, if we replace the top naphthalene by a single edge and if we replace the bottom naphthalene by a single edge, then we will have a graph which is homeomorphic to the three-rung Möbius ladder. In this paper we begin by presenting a graph which is contractible to M_3 in the above sense, but which is not intrinsically chiral. Thus the fact that a graph is contractible to M_3 does not necessarily imply that the graph is intrinsically chiral. After this example, we shall prove that the graph of triple-layered naphthalenophane and an infinite class of related graphs are all intrinsically chiral. Finally, we shall construct other classes of graphs which are also related to triple-layered naphthalenophane but are not intrinsically chiral.

2. A graph which is contractible to M_3 but is not intrinsically chiral

Consider the graph which is obtained from the triple-layered naphthalenophane graph by omitting all vertices of valence two (see figure 4). We call this graph the reduced graph of triple-layered naphthalenophane. Observe that this graph is contractible to M_3, in the sense that, if we replace the top diamond by a single edge and we replace the bottom diamond by a single edge, then we obtain a graph which is homeomorphic to M_3.

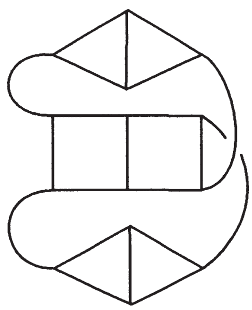

Figure 4. The reduced graph of triple-layered naphthalenophane.

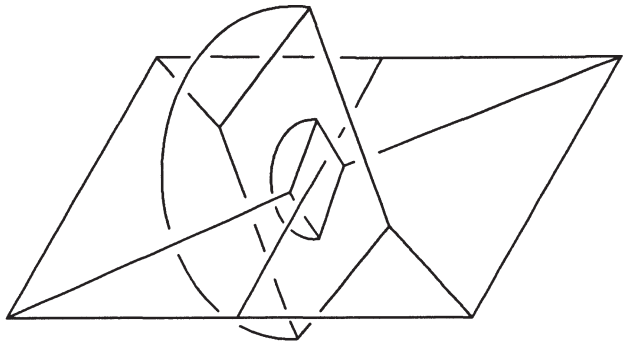

Figure 5. An achiral embedding of the reduced graph of triple-layered naphthalenophane.

Figure 5 illustrates a very different embedding of the reduced graph of triple-layered naphthalenophane. In figure 5, the two squares are contained in a horizontal plane which is a plane of symmetry for the embedding. Thus the reduced graph of triple-layered naphthalenophane is an example of a graph which is contractible to M_3, yet has a topologically achiral embedding. We see from this example that the property of being contractible to M_3 does not imply intrinsic chirality.

3. An intrinsically chiral family of graphs

We generalize the graph of triple-layered naphthalenophane by fusing together any number of benzene rings in place of each of the naphthalenes in the graph of triple-layered naphthalenophane. Figure 6 illustrates an embedding of such a graph with p benzene rings fused together on the bottom, q benzene rings fused together in the middle, and r benzene rings fused together on the top. We will denote the abstract graph which is embedded in figure 6 by $G(p,q,r)$. Observe that the graph of triple-layered naphthalenophane is $G(2,2,2)$, and if we replaced each naphthalene by an anthracene we would obtain the graph $G(3,3,3)$. We will prove below that if p, q, and r are all even then $G(p,q,r)$ is intrinsically chiral. It follows immediately from this theorem that the graph of triple-layered naphthalenophane is intrinsically chiral.

Theorem. If p, q, and r are even, then the graph $G(p,q,r)$ is intrinsically chiral.

Proof. We shall prove this by contradiction. Suppose that there is an embedding of $G(p,q,r)$ which is topologically achiral. We shall show that this assumption implies that there is an embedding of M_3 such that there is an orientation reversing homeomorphism $h:\mathbb{R}^3 \to \mathbb{R}^3$ with $h(M_3) = M_3$ which takes rungs to rungs and sides to sides. By our assumption there is an orientation reversing homeomorphism $h:\mathbb{R}^3 \to \mathbb{R}^3$ with $h(G(p,q,r)) = G(p,q,r)$, and h takes vertices to vertices and edges to edges. The embedding of $G(p,q,r)$ may not look at all like that of figure 6, however, since we do not know how $G(p,q,r)$ is embedded, we draw it as in figure 6. Now h takes

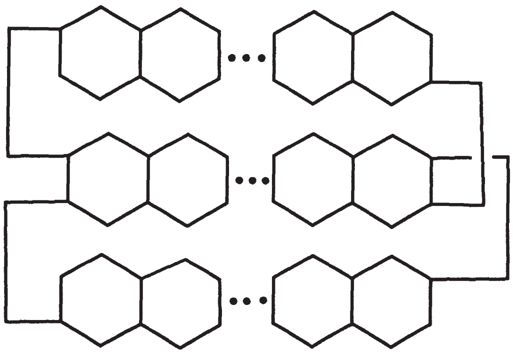

Figure 6. The graph $G(p, q, r)$.

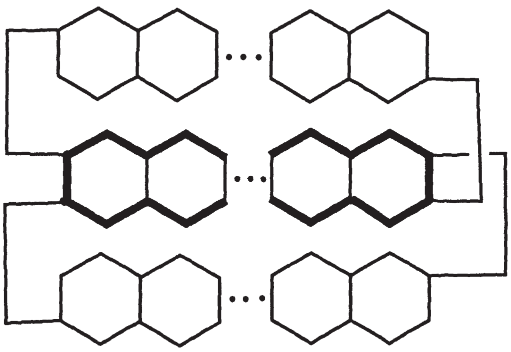

Figure 7. The circuit K is darkened in $G(p, q, r)$.

any circuit with six vertices to a circuit with six vertices. Since the only circuits with six vertices are the hexagons representing the benzene rings, this means that h takes each of these hexagons to itself or to another such hexagon. Furthermore, h must take any pair of adjacent hexagons to a pair of adjacent hexagons. So h must take each chain of fused hexagons to a chain of the same number of fused hexagons. The chain of q hexagons is the only chain of hexagons where the outer two hexagons each contain four vertices of valence three. So, h must take this chain of q hexagons to itself, possibly switching the two sides. Let K denote the perimeter of the chain of q hexagons. Then K contains $4q + 2$ edges, since each hexagon in the chain contributes four edges to the perimeter, except the terminal hexagons which each contribute five edges to K. It follows that h must take the set K to itself, though h may interchange the top and the bottom and/or the left and the right sides of K. In figure 7 we illustrate $G(p, q, r)$ with K as a darkened circuit.

It follows from the above paragraph that h must either take the chain of p hexagons to itself and take the chain of r hexagons to itself, or, if $r = p$, then h might interchange these two chains of hexagons. Let x, y, z, and w denote the vertices indicated in figure 8. Since h takes K to itself, h must take the set of points $\{x, y, w, z\}$ to itself, possibly permuting the four points. Recall that by hypothesis r is

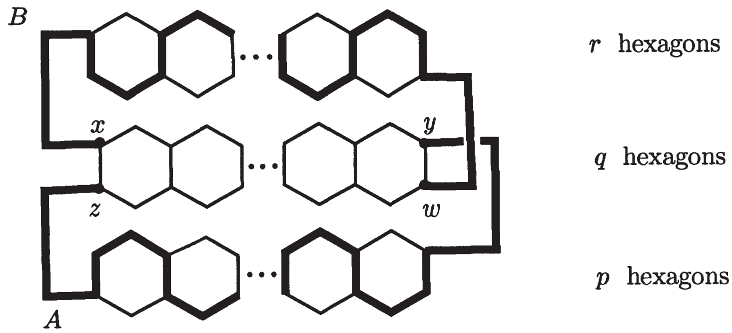

Figure 8. The arcs A and B are darkened in $G(p,q,r)$.

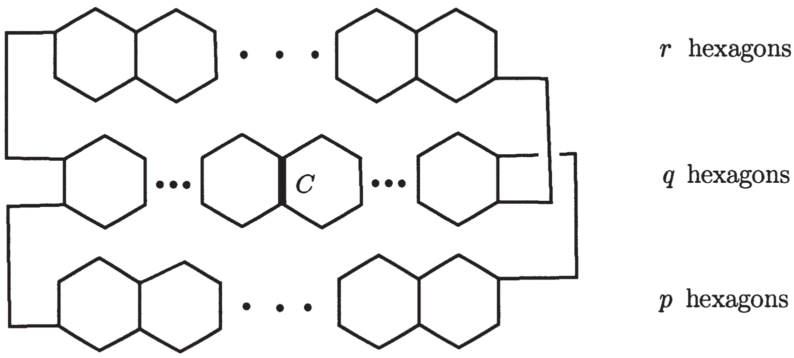

Figure 9. The arc C cuts K in half.

even. Thus the arc which zig-zags through the chain of r hexagons going down first, as in figure 8, will contain two edges more than the arc which zig-zags through the hexagons in the opposite way (initially going up rather than down). In particular, since r is even, there is a unique non-self-intersecting arc B in $G(p,q,r) - K$ with endpoints at x and w such that B contains $7+3r$ edges. Similarly, since p is even, there is a unique non-self-intersecting arc A in $G(p,q,r)-K$ with endpoints at y and z such that A contains $7+3p$ edges. The arcs A and B are darkened in figure 8. Now h either sends each of the arcs A and B to itself or possibly interchanges them when $r = p$.

Since q is even by hypothesis, there exists a unique edge C which splits the chain of q hexagons in half. That is, such that each component of $K - C$ contains half of the vertices of $K - C$. Since C is the unique edge with this property and $h(K) = K$, it follows that $h(C) = C$. The arc C is illustrated in figure 9.

Let M denote the graph obtained by taking the union of the circuit K together with the arcs A, B and C. We saw that $h(K) = K$ and $h(C) = C$, and h either interchanges A and B or takes each of A and B to itself. In either case, it follows that $h(M) = M$. We illustrate M on the left side of figure 10. On the right side of figure 10 we have deformed M to a nicer position. Observe that M is an embedding of a 3-rung Möbius ladder with sides K and rungs A, B, and C.

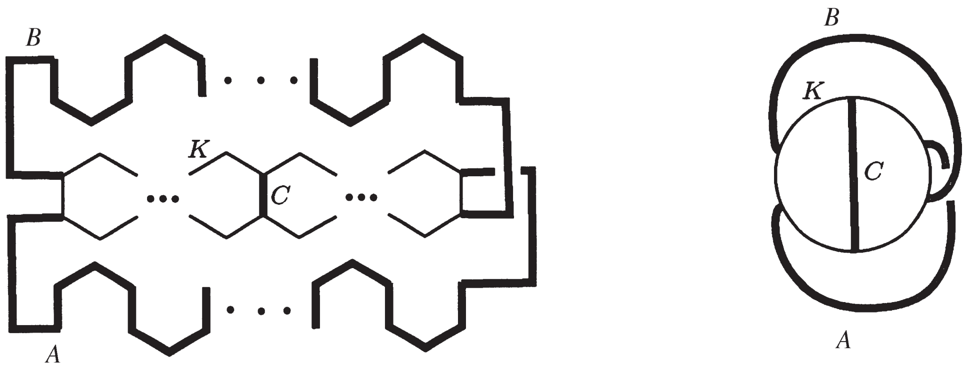

Figure 10. M is a 3-rung Möbius ladder.

Thus $h : \mathbb{R}^3 \to \mathbb{R}^3$ is an orientation reversing homeomorphism taking a 3-rung Möbius ladder to itself with rungs going to rungs and sides going to sides. Thus M is a topologically achiral embedding of a 3-rung Möbius ladder. This is not possible, since we know from [1] that the 3-rung Möbius ladder is intrinsically chiral. It follows that the graph $G(p, q, r)$ is intrinsically chiral, if p, q, and r are all even. □

4. Related graphs which are not intrinsically chiral

Now we want to consider the graph $G(p, q, r)$, where at least one of p, q, or r is odd. We shall show that, in this case, $G(p, q, r)$ has an embedding which is topologically achiral, and hence the graph $G(p, q, r)$ is not intrinsically chiral. First, we consider the case where at least one of p or r is odd and q is either even or odd. We shall illustrate a topologically achiral embedding of $G(3, 2, 2)$, then see how to generalize it to obtain a topologically achiral embedding of any $G(p, q, r)$, where p or r is odd. Figure 11 illustrates a simple embedding of the graph $G(3, 2, 2)$. Observe that this is the graph that we would obtain if we replaced one of the naphthalenes in triple-layered naphthalenophane by an anthracene.

In figure 12 we illustrate a topologically achiral embedding of $G(3, 2, 2)$. From a chemical point of view, of course, one benzene ring cannot pass through another. But if we consider $G(3, 2, 2)$ as an abstract graph, there is nothing wrong with the embedding illustrated in figure 12. In this figure, the chain of three hexagons is contained in a vertical plane, while the rest of the graph lies in a horizontal plane. The round arc at the top is actually the shared edge of the two largest hexagons. To obtain the mirror image, we first rotate the figure by 180° about a vertical axis going through the center of the three vertical hexagons. This rotation takes the horizontal plane to itself and takes the graph to its mirror image except for the circular arc, which is now at the bottom instead of the top of the picture. To correct this, we swing the circular arc over the rest of the figure so that it goes back to its original position. In this way we can deform the graph to its mirror image.

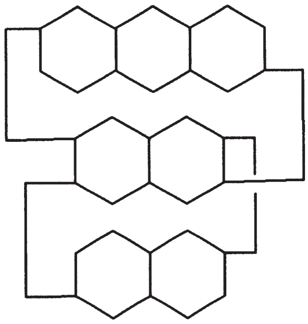

Figure 11. The standard embedding of the graph $G(3, 2, 2)$.

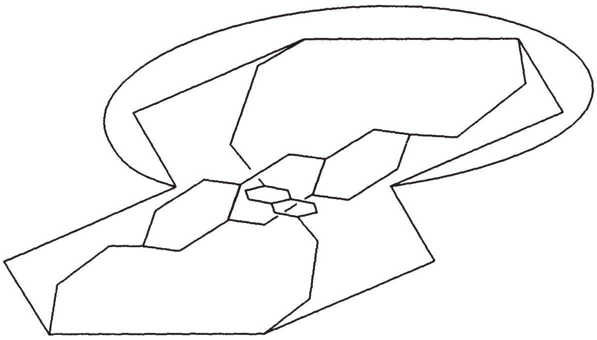

Figure 12. An achiral embedding of $G(3, 2, 2)$.

We have a similar achiral embedding for any $G(p, q, r)$, where p or r is odd. We can see from figure 12 that increasing the number of horizontal hexagons running through the center of the figure has no effect on the symmetry, as long as the number of vertical hexagons is odd. If q, the number of large hexagons, is odd we will end up with an even number of circular arcs so we will obtain the mirror image just by rotating the figure by 180° without having to swing a circular arc from the bottom to the top. We illustrate this with an achiral embedding of $G(3, 3, 3)$ in figure 13. This embedded graph can be rotated by 180° to obtain its mirror image (so, it actually is rigidly achiral). If q is even, we will have a circular arc which will have to be swung from the bottom to the top of the graph after rotating, as we did in for $G(3, 2, 2)$.

We cannot create a similar achiral embedding if p and r are both even and q is odd. Figure 14 illustrates a different achiral embedding which will work whenever q is odd. We illustrate it for $G(4, 3, 4)$. To obtain the mirror image, we first rotate the figure by 180° about an axis which is perpendicular to the plane of the paper. This will cause the four hexagons at the bottom to go to the top. Then swing the arc containing these hexagons back to the bottom of the picture. This gives us the mirror image of the graph through the plane of the paper.

Thus, figures 12–14 illustrate that if at least one of p, q, or r is odd then there is an achiral embedding of $G(p, q, r)$. We saw in the previous section that if p, q, and r

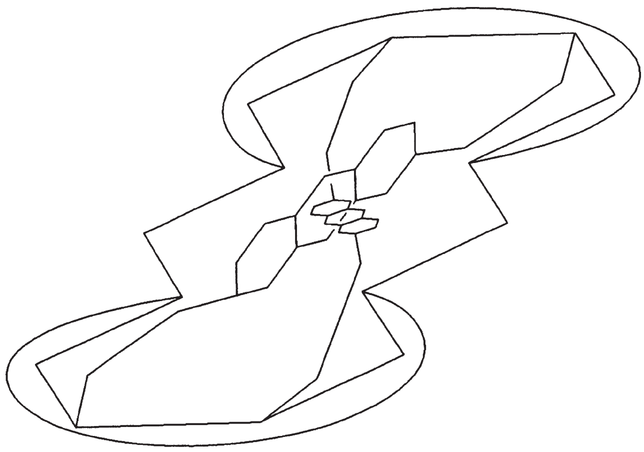

Figure 13. An achiral embedding of $G(3,3,3)$.

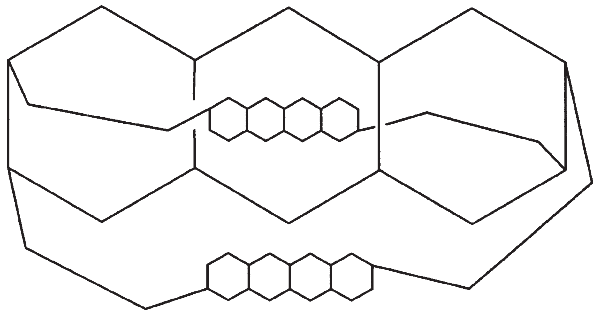

Figure 14. An achiral embedding of $G(4,3,4)$.

are all even then $G(p,q,r)$ is intrinsically chiral. So we have completely characterized when $G(p,q,r)$ is intrinsically chiral.

5. Conclusions

All of these examples illustrate that detecting when a graph is intrinsically chiral can be quite subtle. In particular, contracting a polygon to a single edge changes the graph and, hence, does not help us to determine whether the graph is intrinsically chiral. Elsewhere, we propose to model the topology of molecular graphs with cell complexes obtained by adding a polygonal surface to each impenetrable molecular ring [3]. There we show that the molecular cell complex of any of the graphs $G(p,q,r)$ is intrinsically chiral and that the particular embeddings of the graphs $G(p,q,r)$ which are illustrated in figure 6 of this paper are topologically chiral for any p, q, or r. In fact, it follows from [3] that any topologically achiral embedding of one of the graphs $G(p,q,r)$ will involve some piece of the graph passing through at least one of the hexagons, as we saw in figures 12–14.

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