Topological chirality and achirality of links

Chengzhi Liang and Kurt Mislow

Department of Chemistry, Princeton University, Princeton, NJ 08544, USA

Received 19 May 1995; revised 8 June 1995

Empirical and analytical methods employed in the detection of topological chirality and achirality (amphicheirality) in oriented and non-oriented links are critically examined. *U*-polynomials of non-oriented links are modified for use in the detection of topological chirality. By use of this method, all but eight (listed below) non-oriented links with up to four components and nine crossings are proven to be topologically chiral, including 4_1^2, the abstract model of the only topologically chiral, non-oriented catenane (chemical link) synthesized so far. The topological chirality of certain 3-Borromean links is similarly proven. The amphicheirality of 2_1^2, 6_2^2, 8_8^2, 9_{61}^2, 6_2^3, 8_4^3, 8_6^3, and 8_3^4 is proven by the demonstration that all eight non-oriented links can attain rigidly achiral presentations. Furthermore, we conjecture that 9_{61}^2 and a two-component, oriented link with an 11-crossing diagram are the first members of, respectively, a class of non-oriented and a class of oriented amphicheiral, non-alternating, prime links with odd crossing numbers. Amphicheirality combined with an odd crossing number is unprecedented among knots or links.

1. Introduction

When Wasserman reported the first synthesis of a molecule with two interlocked rings (a [2]-catenane) in 1960, he provided "the first demonstrated example of a compound in which the topology of the system must be considered in describing its structure" [1]. At about the same time, in a classic paper with Frisch [2], Wasserman introduced the concept of isomerism between knotted and unknotted and between interlocked (catenated) and non-interlocked rings, and thus launched the subject of "chemical topology". Numerous organic catenanes have since been prepared, thanks largely to the implementation of ingenious synthetic strategies devised by Sauvage, Schill, Stoddard, Vögtle, and their coworkers. Although these synthetic products are for the most part [2]-catenanes, a number of higher catenanes, such as [3]-catenanes [3], a [4]-catenane [4], and the [5]-catenane olympiadane [4], have also been prepared. Seeman and coworkers designed and carried out the synthesis of complex interlocked structures made up of single-stranded DNA; the most spectacular examples are polyhedra (a [6]-catenane in the form of a cube [5] and a [14]-catenane in the form of a truncated octahedron [6]) whose faces are made up of cyclic DNA's interlinked with their nearest neighbors. Also worth noting is the existence of a molecular-based magnet with a catenated structure [7] and of polycatenated interpenetrating organometallic networks [8].

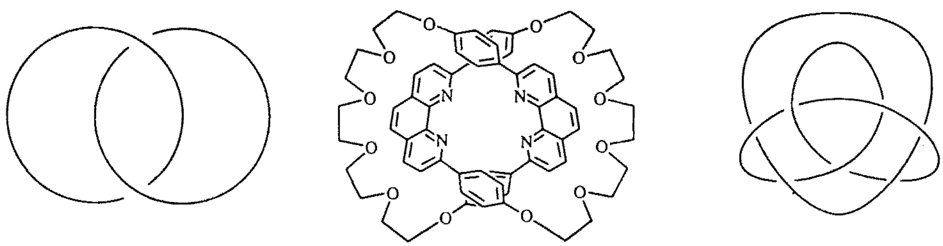
Catenated molecules in Nature were first discovered in the mitochondrial DNA of human cells by Vinograd and coworkers in 1967 [9]. A great variety of catenated DNA's have since been observed in diverse biological systems [10]. A number of catenated structures have also been recently observed among proteins [11].

In this paper we discuss general methods for establishing the chirality and achirality of topological links. These methods are directly applicable to catenanes, which are chemical entities that can be abstractly represented by such links. To provide the necessary background, we begin our account with an informal description of some basic concepts and terminology; for the corresponding treatment of knots, see [12].

A *topological link* is a finite union of mutually disjoint knots. A *knot* is a simple closed polygonal (or smooth) curve embedded in 3-space. A knot is therefore a link with only one component. Knots and links are non-trivial, and therefore topologically non-planar, if and only if they cannot be embedded in the plane without crossings. All the links referred to in this paper are non-trivial, but component knots often are not; such knots (or "unknots") may be thought of as empty triangles or as circles.

A given link can be distorted by continuous deformation in 3-space (*ambient isotopy*) into a variety of shapes (*presentations*) that form an equivalence class (*isotopy type*). In ambient isotopy, links are treated as though they were infinitely deformable, the only constraint being that there must be no cutting-and-rejoining of curves. Topologically equivalent presentations of a given isotopy type are said to be *isotopic*. For convenience in analysis, presentations of links are projected in the plane as *diagrams* in which each crossing is a transverse double point marked in a suitable manner so as to represent an over- or an undercrossing. Throughout the remainder of this paper, non-oriented links (see below) are symbolized by K and refer to isotopy types, that is, to complete sets of topologically equivalent presentations.

The number of crossings in a diagram may be reduced to a minimum by an ambient isotopy. For a link K that number is the *minimal crossing number*, $c(K)$. A diagram is said to be reduced if it contains no nugatory crossings. In particular, a diagram with a minimal crossing number is necessarily reduced. For example, $c(K) = 2$ in the reduced diagram (fig. 1(a)) of 2^2_1, the simplest non-trivial link (the Hopf link). This link is the abstract representation of the vast majority of reported chemical [2]-catenanes, one of which is depicted in fig. 1(b) [13]. Link types such as 2^2_1 are characterized by their crossing numbers according to a convention in which $c(K)$ is superscripted by the number of components in the link and subscripted by a numerical index, needed because two or more non-equivalent links



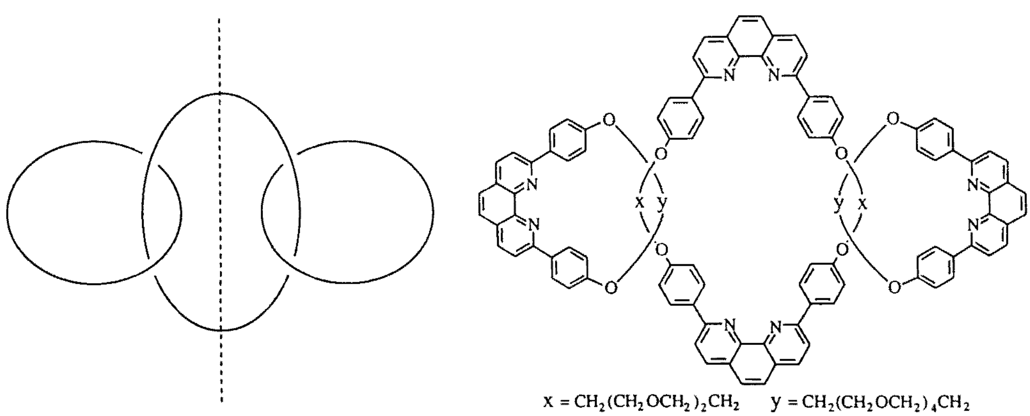
(a) (b) (c)

Fig. 1. (a) Reduced diagram of the Hopf link, 2_1^2. (b) A [2]-catenane [13] represented by 2_1^2. (c) Reduced diagram of the simplest non-alternating link, 7_8^2.

may share the same crossing number for links with $c(K) > 5$. For knots the superscript 1 is usually omitted, as for the trefoil knot, 3_1.

A link is *alternating* if overpasses alternate with underpasses all along the curves in the reduced diagram; otherwise it is *non-alternating*. For example, 2_1^2 is an alternating link while 7_8^2 (fig. 1(c)) is non-alternating. Alternating knots and links are listed first in knot and link tabulations such as Rolfsen's [14], followed by non-alternating knots and links.

Figure 2(a) is the reduced diagram of a three-component link that is representative of some [3]-catenanes. One of these [3c] is depicted in fig. 2(b). A plane perpendicular to the plane of projection (dashed line) and pierced in exactly two points cuts the link in half. If the open ends on both sides of the plane are now joined to form closed curves, two Hopf links result. The three-component link is an example of a *composite or product link*, $K_1\#K_2$, whose factors are *prime links*. Thus the three-component link in fig. 2(a) is denoted by $2_1^2\#2_1^2$, and the five-component link



(a) (b)

Fig. 2. (a) Reduced diagram of a composite link, $2_1^2\#2_1^2$. The dashed line is a projection of the plane that divides the component Hopf links. (b) A [3]-catenane [3c] represented by $2_1^2\#2_1^2$.

that represents olympiadane by $2_1^2\#2_1^2\#2_1^2\#2_1^2$. In contradistinction, 2_1^2 and 7_8^2 are prime links because they cannot be divided (factored) into smaller, non-trivial links.

2. Chirality and orientation

A knot or link is topologically achiral if and only if it can be mapped onto its mirror image by an ambient isotopy; otherwise it is topologically chiral. Topologically chiral knots or links exist as pairs of isotopy types or *enantiomorphs*, $\{K, K^*\}$, all of whose presentations are pairwise mirror-image related. For example, if the diagram in fig. 1(c) is associated with the topologically chiral link 7_8^2, then the full description of the pair of enantiomorphs is $\{K(7_8^2), K(7_8^2)^*\}$.

If directions (denoted by arrows along the curves) are assigned to the component curves that constitute a link, that link is said to be *oriented*. Otherwise it is *non-oriented*. As will be discussed in further detail below, all but eight of the 130 non-oriented, prime links with up to four components and nine crossings in Rolfsen's tabulation [14] are topologically chiral (for example, 7_8^2), yet only one catenane has so far been synthesized [15] whose structure can be represented by a topologically chiral non-oriented link. That link is 4_1^2. Diagrams of the enantiomorphic pair $\{K(4_1^2), K(4_1^2)^*\}$ are depicted in figs. 3(a) and (b), along with their molecular realizations in figs. 3(c) and (d), respectively. In contrast, topologically achiral non-oriented links such as 2_1^2 and $2_1^2\#2_1^2$ have been amply realized in molecular form, as mentioned above.

In general, any given diagram D of a non-oriented link K with m indistinguishable components yields upon orientation a set of 2^m oriented diagrams. If we assume that all of the oriented knot components are *invertible* [16], then this number is cut in half because reversing the orientation of *all* the components that make up the link does not yield a new link. The resulting set of 2^{m-1} diagrams, D_i' ($i = 1$, $2, 3 \cdots 2^{m-1}$), is partitioned into subsets, each of which is associated with an oriented link K'. We illustrate the above with three examples involving two-component links ($m = 2$), for which two oriented diagrams are expected.

The diagram in fig. 1(a) is a projection of the achiral link 2_1^2. Orientation yields the two oriented diagrams in figs. 4(a) and (b), i.e. $D(2_1^2) \rightarrow \{D_1'(2_1^2)\ ,\ D_2'(2_1^2)\}$, where $\rightarrow$ symbolizes orientation. In this case, $D_1'(2_1^2)$ and $D_2'(2_1^2)$ are diagrams of two topologically non-equivalent, chiral links that are related as enantiomorphs. That is, $K(2_1^2) \rightarrow \{K'(2_1^2), K'(2_1^2)^*\}$. Molecular realizations [17] are depicted in figs. 4(c) and (d). Consider next the chiral link 4_1^2. The two diagrams in figs. 3(a) and (b) are projections of the enantiomorphs of 4_1^2, and, upon orientation, each of these yields a pair of diagrams: $D(4_1^2) \rightarrow \{D_1'(4_1^2), D_2'(4_1^2)\}$ and $D(4_1^2)^* \rightarrow \{D_1'(4_1^2)^*, D_2'(4_1^2)^*\}$. In this case, the members within each pair are associated with topologically non-equivalent, chiral links that are *not* related as enantiomorphs: $K(4_1^2) \rightarrow \{K_a'(4_1^2), K_b'(4_1^2)\}$ and $K(4_1^2)^* \rightarrow \{K_a'(4_1^2)^*, K_b'(4_1^2)^*\}$. Finally, orientation of the diagram in fig. 1(c), which is the projection of one of the enantiomorphs of the

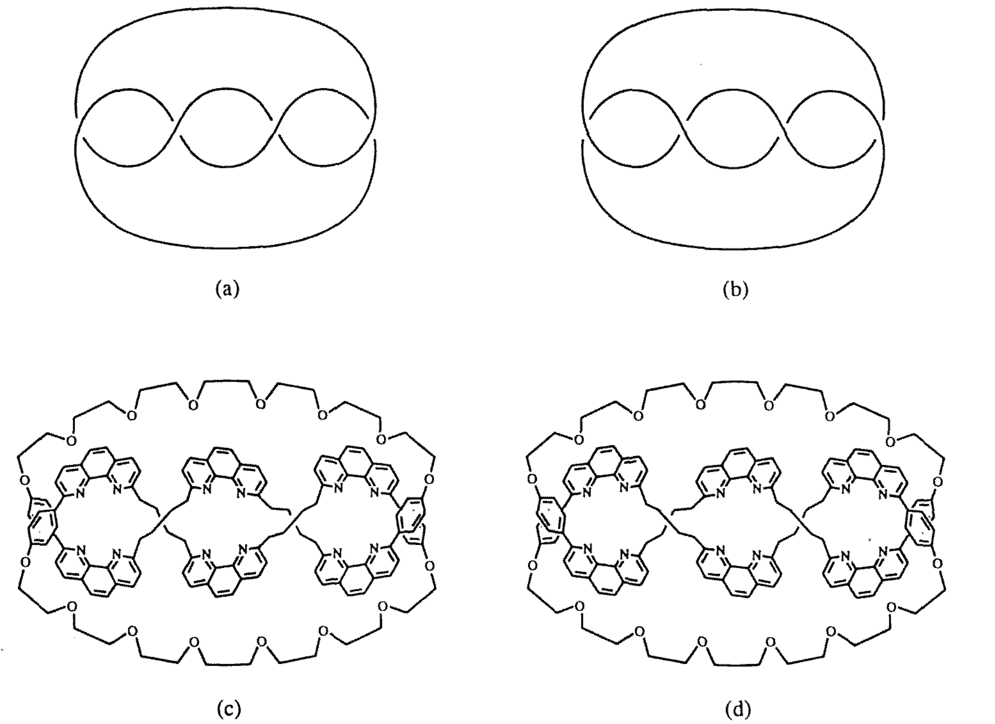


Fig. 3. (a) Reduced diagram of the simplest topologically chiral, non-oriented link, 4^2_1. (b) The enantiomorph of (a). (c) A [2]-catenane [15] represented by (a). (d) The enantiometer of (c), represented by (b).

chiral link 7^2_8, yields diagrams of two topologically *equivalent*, chiral links. That is, $D(7^2_8) \rightarrow \{D'_1(7^2_8) \sim D'_2(7^2_8)\}$, where $\sim$ denotes topological equivalence. Hence $K(7^2_8) \rightarrow K'(7^2_8)$ and $K(7^2_8)^* \rightarrow K'(7^2_8)^*$. The last example illustrates the fact that on occasion all 2^{m-1} diagrams obtained upon orientation of a non-oriented diagram are topologically equivalent and are thus associated with just one oriented link; that is, partitioning of the set of oriented diagrams may on occasion yield the trivial subset.

Finally, note that an achiral [2]-catenane is modeled by 2^2_1 and therefore cannot attain topological chirality merely through introduction of conformationally chiral features [18] or through attachment of geometrically chiral but topologically planar residues [19]: orientation of both of the cyclic components remains the conditio sine qua non for topological chirality.

3. How to tell whether a link is topologically chiral or achiral

In the preceding sections we asserted that certain links are topologically chiral

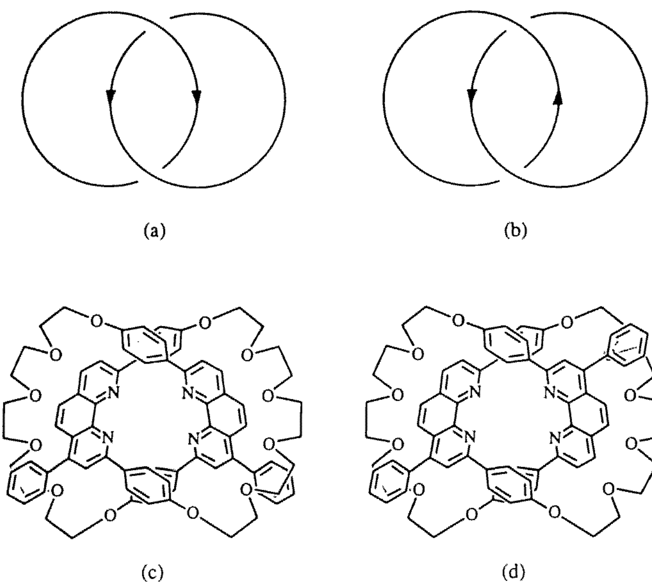


Fig. 4. (a) Reduced diagram $D_1'(2_1^2)$ of an oriented Hopf link $K_1'(2_1^2) = K_2'(2_1^2)^*$. (b) Reduced diagram $D_2'(2_1^2)$ of $K_2'(2_1^2) = K_1'(2_1^2)^*$. (c) A [2]-catenane [17] represented by $D_1'(2_1^2)$. (d) The enantiometer of (c), represented by $D_2'(2_1^2)$.

while others are topologically achiral, but without offering any evidence in support of these claims. In the following sections we describe general methods that are available to establish topological chirality or achirality in links.

All methods of this kind can be categorized as being either *empirical or polynomial*. Empirical methods were used with remarkable success in the 19th century, primarily by the foremost pioneer of knot theory, the physicist Peter Guthrie Tait [20], to identify all 20 topologically achiral (or "amphicheiral", as Tait called them, and as we shall refer to them in what follows) prime knots with up to 10 crossings. By definition, all that is required to prove a knot's amphicheirality is to demonstrate that a chiral presentation can be converted into its own mirror image by continuous deformation. Such a demonstration can be achieved by manipulating a piece of string in the form of a knot; no mathematical skill whatever is required, only patience, the ability to recognize mirror-image relationships, and some luck. The same method can be used to prove the amphicheirality of links, as described in section 4. Unfortunately, however, the *inability* to convert a chiral presentation into its mirror image is inadmissible as evidence for the topological chirality of a knot or a link, since it can never be proven that all possible conversion paths have been explored. To prove topological chirality demands the use of the polynomial methods discussed in section 5.

4. Proofs of topological achirality by empirical methods

As explained above, empirical methods are suitable for establishing the topological achirality, but not the chirality, of knots or links. We first show how these methods work with the non-oriented links in Rolfsen's tabulation [14], and then proceed to a discussion of the corresponding oriented links.

4.1. NON-ORIENTED AMPHICHEIRAL LINKS

In a previous paper [21] we stated, without proof, that of the 126 non-oriented, prime links with up to three component knots and up to nine crossings listed in [14], six (2^2_1, 6^2_2, 8^2_8, 6^3_2, 8^3_4, 8^3_6) are amphicheiral. Among the four links with four components listed in [14], 8^4_3 is also amphicheiral. We recently discovered an eighth member in this class, 9^2_{61}, whose odd crossing number renders it unique among all known amphicheiral knots and links and which will therefore be discussed in greater detail at the end of this article. As will be shown below, all other links in [14] are topologically chiral.

Two methods, both empirical, are available to prove the amphicheirality of these links. The first method, interconversion by ambient isotopy of mirror-image related chiral presentations, is entirely general and applicable to all knots and links, whether oriented or not. As an example, the interconversion path in fig. 5 proves that 8^2_8 is amphicheiral. The second method, which is applicable only to certain invertible knots [22], depends on the attainment of a *rigidly achiral presentation*, in which the symmetry of the presentation belongs to one of the achiral point groups. For example, 8^2_8 can attain a rigidly achiral presentation with S_4 symmetry (fig. 5). In the case of prime knots, the only possible point groups [12] are S_{2n}, $n = 1, 2, \cdots$, but this constraint does not apply to links. This is illustrated in fig. 6, which depicts the Borromean link (6^3_2) and three of its rigidly achiral presentations with different symmetries [21]. Finally, fig. 7 displays rigidly achiral presentations for 2^2_1, 6^2_2, 9^2_{61}, 8^3_4, 8^3_6, and 8^4_3. The amphicheirality of all eight links is thus firmly established.

4.2. ORIENTED AMPHICHEIRAL LINKS

Consider the oriented links derived from the eight amphicheiral non-oriented links described above. Upon orientation, diagrams of the two-component links 2^2_1, 6^2_2, 8^2_8, and 9^2_{61} yield in each case two diagrams that are associated with a pair of enantiomorphic links, as described above for 2^2_1. Orientation of 8^3_4 yields four diagrams, two of which are associated with an enantiomorphic pair (figs. 8(a) and (b)) while the other two (figs. 8(c) and (d)) correspond to a pair of links whose amphicheirality can be proven by ambient isotopy to rigidly achiral presentations (figs. 8(e) and (f)). Of the four diagrams obtained upon orientation of 8^3_6, two are associated with a pair of enantiomorphic links (figs. 9(a) and (b)) while the other

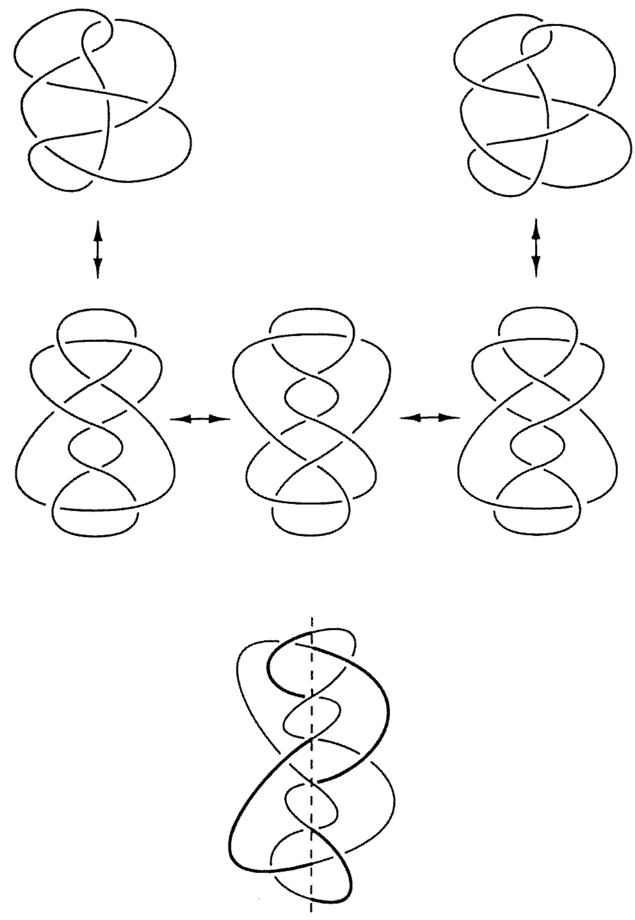


Fig. 5. Top: Mirror-image-related chiral presentations of 8_8^2 and a path for their interconversion by continuous deformation (ambient isotopy). Bottom: A presentation of 8_8^2 with S_4 symmetry. The dashed line indicates the S_4 axis.

two (figs. 9(c) and (d)) are topologically equivalent and correspond to a single amphicheiral link, as proven by ambient isotopy of 9(c) to 9(d) and by ambient isotopy of mirror-image related chiral presentations in 9(c). Of the eight diagrams obtained upon orientation of 8_3^4, two are associated with a pair of enantiomorphic links (figs. 10(a) and (b)), two (figs. 10(c) and (d)) are topologically equivalent and correspond to an amphicheiral link, and the remaining four (figs. 10(e)–(h)) are also topologically equivalent and correspond to a second amphicheiral link. The amphicheirality of 10(c) $\sim$ 10(d) is easily deduced from the fact that 10(c) is rigidly achiral (S_4 symmetry) and can be isotoped to 10(d). The topological equivalence of 10(e)–10(h) can be proven by ambient isotopy of 10(e) to 10(f)–10(h) and by ambient isotopy of mirror-image related chiral presentations in 10(e). Finally, all four diagrams obtained upon orientation of 6_2^3 (fig. 11) correspond to presentations

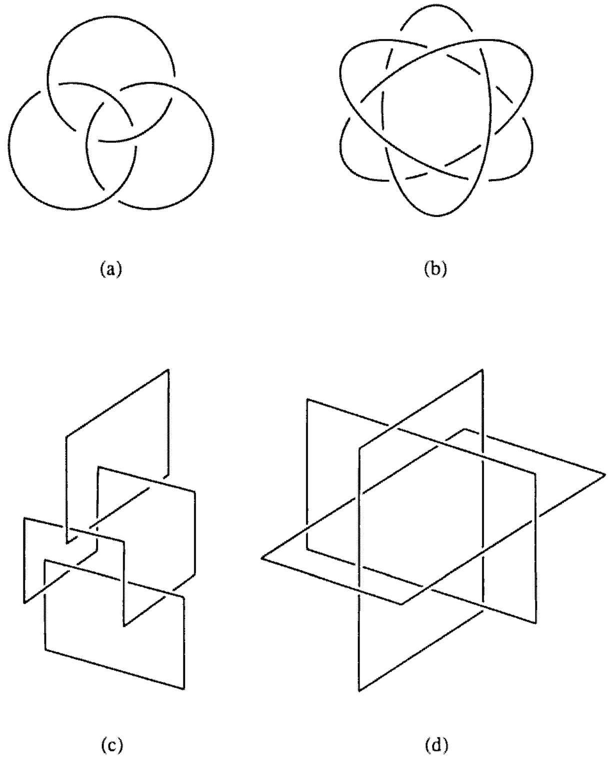


Fig. 6. The simplest Borromean link. (a) Reduced diagram of 6_2^3. (b) S_6, (c) D_{2d}, and (d) T_h are rigidly achiral presentations.

that are mutually interconvertible by ambient isotopy and are thus associated with a single oriented link. The amphicheirality of this link is also demonstrated with reference to the S_6 presentation of the non-oriented link (fig. 6(b)): no matter in which direction the three components are oriented, the resulting presentation remains centrosymmetric and therefore achiral.

Our results agree with those of Doll and Hoste [23], who tabulated all oriented, prime links with up to four components and nine crossings by use of skein polynomials (see section 5), and who found that the only amphicheiral links are 6_2^3, 8_4^3+++ (fig. 8(c)), 8_4^3++- (fig. 8(d)), 8_6^3, 8_3^4++++ (fig. 10(c)), and 8_3^4+++- (fig. 10(e)). Additional comments on this work are found in section 5.1.

5. Polynomial methods

Over a century ago, Tait expressed the need "to find all the essentially different forms" of a knot or link [20a]. Only empirical methods, of the sort discussed above,

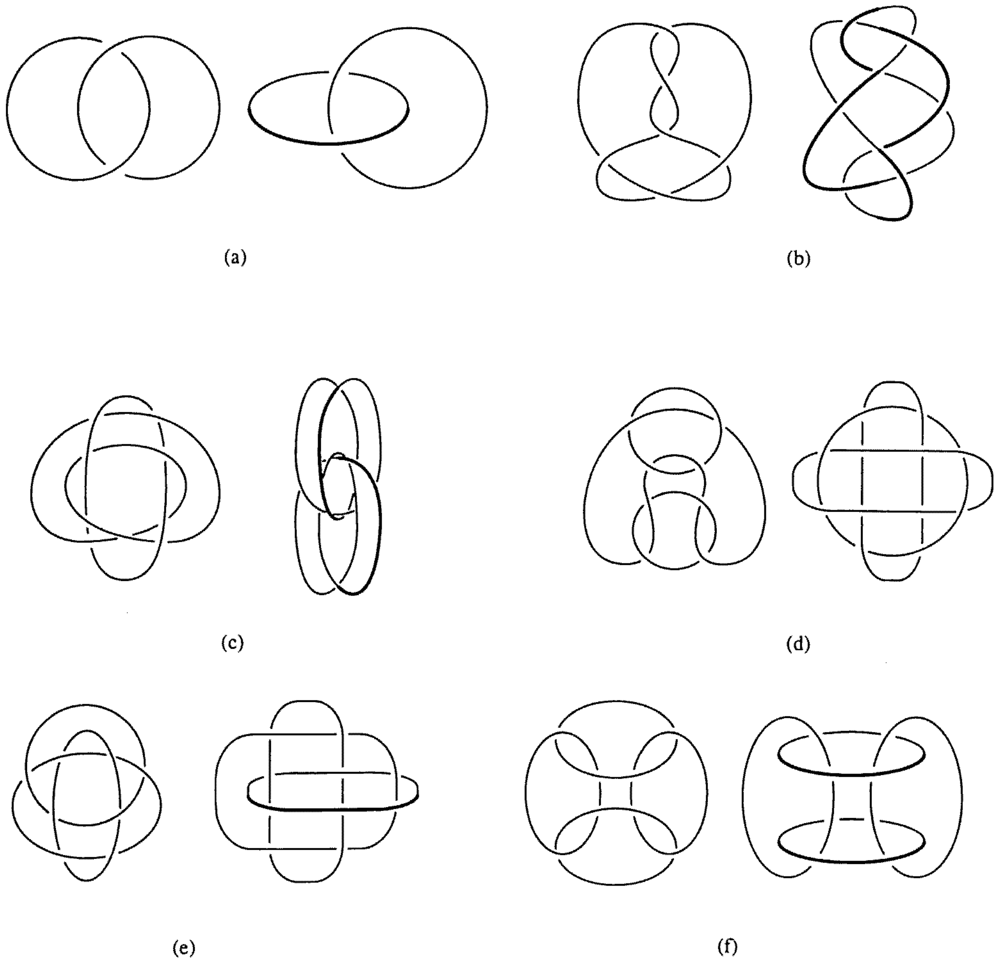


Fig. 7. Reduced diagrams of six amphicheiral links paired on the right with rigidly achiral presentations. (a) 2^2_1 (D_{2d}). (b) 6^2_2 (S_4). (c) 9^2_{61} (S_4); this presentation is equivalent to an array composed of the interlocked edges of two enantiomorphic Möbius strips. (d) 8^3_4 (S_4). (e) 8^3_6 (C_s). (f) 8^4_3 (D_{2h}).

were available during Tait's lifetime, and it was not until the advent of combinatorial topology that a systematic, non-empirical method was developed. The first example of the new approach was a proof, by Dehn in 1914 [24], that the trefoil knot exists in two topologically non-equivalent, enantiomorphic forms. The first knot *invariant*, that is, the first mathematical object that could be unambiguously associated with individual knot or link types independent of any particular presentation or diagram, was a polynomial discovered in 1928 by Alexander [25]. The Alexander polynomial failed, however, to distinguish between enantiomorphs.

This problem was not remedied until 1985, with Jones' publication of the one-variable polynomial $V(t)$ [26]. Jones' discovery triggered a burst of activity that led to more powerful two-variable polynomials, foremost among them the HOMFLY

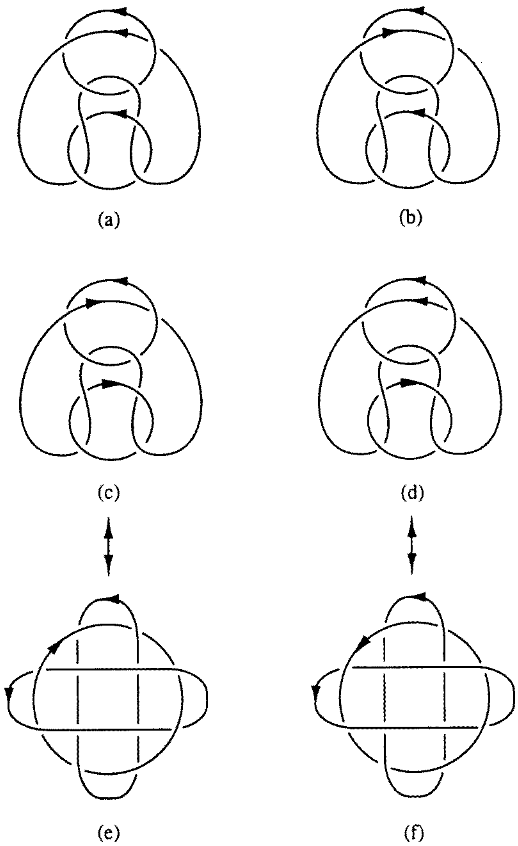


Fig. 8. The four reduced diagrams of oriented links derived from 8^3_4. (a) and (b) The enantiomorphic pair. (c) and (d) Two topologically non-equivalent amphicheiral links. (e) and (f) Rigidly achiral presentations that can be obtained by ambient isotopy from (c) and (d), respectively.

polynomial $P(l,m)$ [27] and the Kauffman polynomial $F(a,z)$ [28]. These three "skein polynomials" are normally capable of detecting topological chirality in an oriented knot or link. Although none of the three polynomials is infallible in this respect, as will be discussed below, $F(a,z)$ suffers the fewest failures as a chirality detector of oriented knots and links; furthermore, where it fails, so do $V(t)$ and $P(l,m)$. In what follows, we therefore restrict ourselves exclusively to applications of the Kauffman polynomial.

5.1. ORIENTED LINKS

Given an oriented link K', with D' an oriented diagram of K', the Kauffman polynomial of K', which was proved to be an isotopy invariant [28], is defined as

$$F_{K'}(a,z) = a^{-w(D')} L_D(a,z) \,, \tag{1}$$

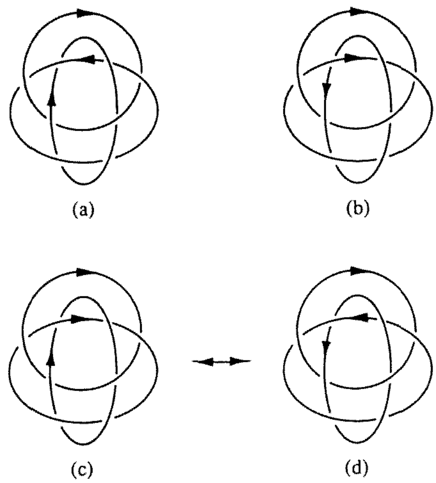


Fig. 9. The four reduced diagrams of oriented links derived from 8_6^3. (a) and (b) The enantiomorphic pair. (c) and (d) Two topologically equivalent presentations of the same amphicheiral link.

where $w(D')$ is the writhe of D', D is the corresponding non-oriented diagram, and $L_D(a, z)$, is called the L-polynomial of D. This two-variable Laurent polynomial was discovered by Kauffman [28]. The L-polynomial is mirror-image-sensitive but diagram-dependent [28c]; that is, the L-polynomial is not a topological invariant. We briefly digress to explain the meaning of "writhe".

Each crossing in the oriented diagram of a knot or link is associated with a *char-*

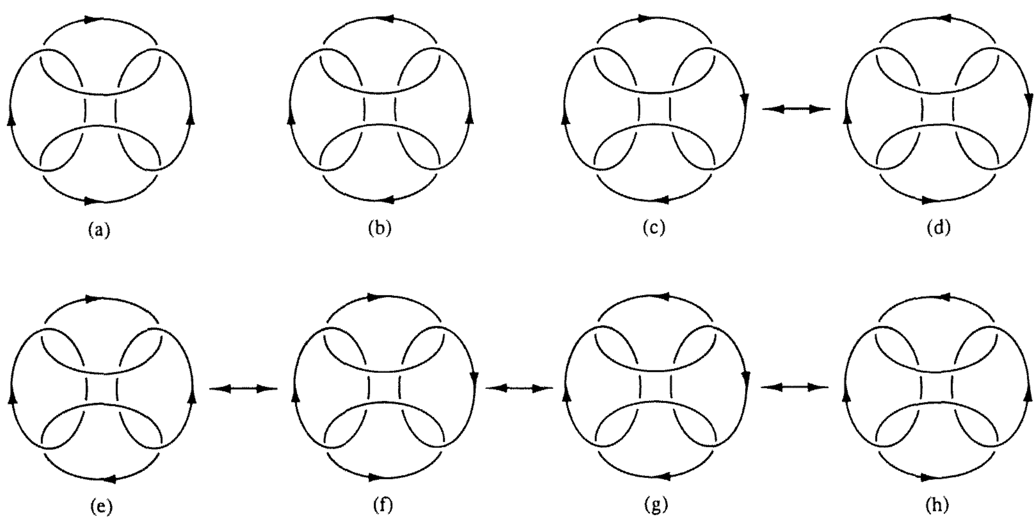


Fig. 10. The eight reduced diagrams of oriented links derived from 8_3^4. (a) and (b) The enantiomorphic pair. (c) and (d) Two topologically equivalent presentations of the same amphicheiral link. (e)–(h) Four topologically equivalent presentations of the other amphicheiral link.

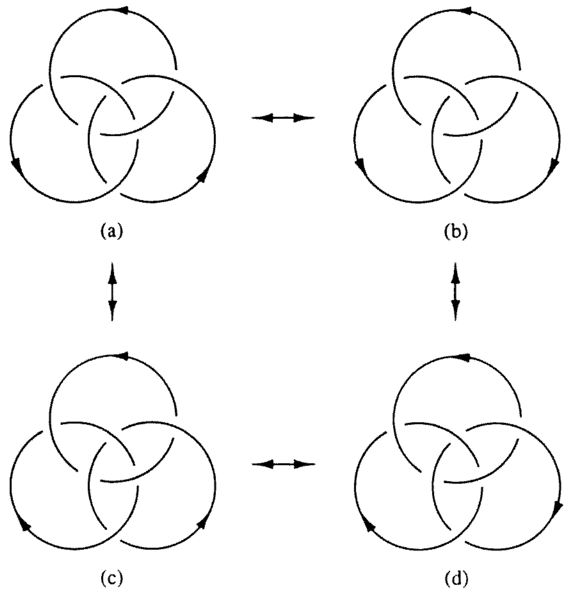


Fig. 11. Reduced diagrams of the four topologically equivalent presentations of the amphicheiral, oriented link derived from 6_2^3.

acteristic ε that can assume a value of $+1$ or -1. The *writhe*, $w(D')$, of an oriented knot or link diagram is the arithmetic sum of the crossing characteristics, i.e., $w(D') = \Sigma\varepsilon$. For example, by use of the convention in [12], $w(D') = -2$ and $+2$, respectively, for the enantiomorphs $D_1'(2_1^2)$ (fig. 4(a)) and $D_2'(2_1^2)$ (fig. 4(b)). Similarly, the writhes of the three oriented link diagrams derived from $2_1^2\#2_1^2$ (fig. 2(a)) are 0, $+4$, and -4, while those of the oriented link diagrams for 7_8^2 (fig. 1(c)) and the Whitehead link 5_1^2 (fig. 12) are -3 and -1, respectively.

All oriented links referred to in this paper are related to associated non-oriented links, and we therefore restrict ourselves exclusively to the oriented diagram set $\{D_i', i = 1, 2, \cdots, 2^{m-1}\}$ that corresponds to a non-oriented link diagram D with m indistinguishable components. For example, the Kauffman polynomials for the two oriented Hopf links in figs. 4(a) and (b) are given by

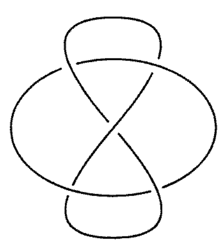


Fig. 12. The Whitehead link, 5_1^2.

$$F_{K_1'(2_1^2)}(a,z) = (a^3 + a)z + a^2 + (-a^3 - a)z^{-1},$$

$$F_{K_2'(2_1^2)}(a,z) = (a^{-3} + a^{-1})z + a^{-2} + (-a^{-3} - a^{-1})z^{-1}.$$

The inequality $F_{K_2'(2_1^2)}(a,z) \neq F_{K_1'(2_1^2)}(a,z)$ means that $K_1'(2_1^2)$ and $K_2'(2_1^2)$ are different isotopy types. Since we see the mirror-image relationship between the links in figs. 4(a) and (b), we conclude that $K_1'(2_1^2)$ and $K_2'(2_1^2)$ are enantiomorphs.

In general, the Kauffman polynomial has the following important property [28a]:

$$F_{K'^*}(a,z) = F_{K'}(a^{-1},z), \tag{2}$$

where K'^* is the mirror image of K', obtained by switching all the crossings in the D's of K'.

We call a Kauffman polynomial *asymmetric in a* if it satisfies the inequality in eq. (3a):

$$F_{K'}(a,z) \neq F_{K'}(a^{-1},z). \tag{3a}$$

Otherwise the polynomial is *symmetric in a*, or *self-conjugate* [27e]. From eqs. (2) and (3a) it follows that the oriented link K' and its mirror image K'^* have different Kauffman polynomials (eq. (3b)):

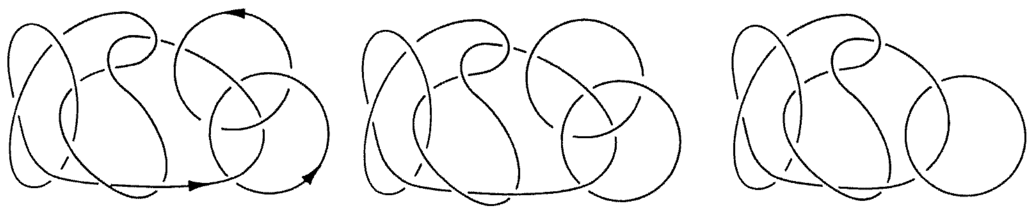
$$F_{K'}(a,z) \neq F_{K'^*}(a,z). \tag{3b}$$

Thus, inequality (3a) is a topological chirality detector for any given oriented link K'. For instance, asymmetry in a in *either* $F_{K_1'(2_1^2)}(a,z)$ *or* $F_{K_2'(2_1^2)}(a,z)$ proves that the oriented links $K_1'(2_1^2)$ and $K_2'(2_1^2)$ that are associated with $D_1'(2_1^2)$ and $D_2'(2_1^2)$ in figs. 4(a) and (b), respectively, are both topologically chiral, in harmony with the above conclusion.

While asymmetry in a is proof of topological chirality, symmetry in a does not, in general, serve as a proof of amphicheirality. That topological achirality of an oriented link or knot is a sufficient but not a necessary condition for symmetry in a is exemplified by the classic knots 9_{42} and 10_{71} [29] and by the 12-crossing knots 12_{126}, 12_{132}, 12_{214}, 12_{222}, and 12_{697} [29b]: although the oriented and non-oriented knots are chiral [27e,29,30], the Kauffman polynomials are symmetric in a. We call this phenomenon the "9_{42} syndrome". The same difficulty is encountered in links. Consider, for example, $F_{K'}(a,z)$ for the oriented, composite link $9_{42}\#6_2^3$ (fig. 13(a)):

$$F_{K'(9_{42}\#6_2^3)}(a,z) = F_{K'(9_{42})}(a,z) \cdot F_{K'(6_2^3)}(a,z).$$

Because the knot 9_{42} is one of the link's components, it follows by the uniqueness of prime decompositions that the composite link $9_{42}\#6_2^3$, as well as $9_{42}\#2_1^2$ (see below), is topologically chiral, *no matter whether it is oriented or not*. In general, because the 9_{42} syndrome cannot, in general, be rigorously excluded, symmetry in a



(a) (b) (c)

Fig. 13. Selected composite links. (a) $K'(9_{42}\#6_2^3)$. (b) $K(9_{42}\#6_2^3)$. (c) $K(9_{42}\#2_1^2)$.

does not *necessarily* imply topological achirality for oriented links (or knots). For example, we noted in section 4.2 that Doll and Hoste had identified all six amphicheiral, oriented, prime links with up to four components and nine crossings. Their method of identification was, in effect, the observation of symmetry in a for the six corresponding Kauffman polynomials, and they claimed that "within the range of this table, the Kauffman polynomial $F(a, x)$ detects all such cases [of amphicheirality]". In light of the ever-present possibility of misidentifying a chiral link as amphicheiral, due to the 9_{42} syndrome, their conclusion must in principle be regarded as fortuitously correct.

5.2. NON-ORIENTED LINKS

Several polynomials have been described for non-oriented links (or knots). A one-variable Laurent polynomial $Q_K(z)$, also called "absolute polynomial" [27b], was discovered by Brandt, Lickorish, and Millett in 1986 [31]. Unfortunately, the absolute polynomial is not mirror-image-sensitive because it "suffers from the same weakness with respect to the detection of chirality as does the Alexander polynomial" [27b]. In fact, $Q_K(z)$ is a special case of the Kauffman polynomial $F_{K'}(a, z)$ [27e]; that is, $Q_K(z) = F_{K'}(1, z)$. Recall the L-polynomial introduced earlier. The normalized version of L_D, called polynomial U_K of non-oriented links or knots, was defined by Kauffman [28a]:

$$U_K(a, z) = a^{-s(D')} L_D(a, z) , \tag{4}$$

where $s(D')$, the "self-writhe", is the sum of the characteristics of self-crossings in components of D'. For example, $s(D')$ of 5_1^2 in fig. 12 is -1. The polynomial U_K, hereafter referred to as the U-polynomial, is a topological invariant for non-oriented links [28a].

5.2.1. Detection of topological chirality

By combining eq. (1) and eq. (4), we have

$$U_K(a, z) = a^{2l(D')} F_{K'}(a, z) \tag{5}$$

in which $l(D') = [w(D') - s(D')]/2 = l(K')$, the *linking number* of the diagram D' and hence the linking number of the corresponding link K'. The linking number, an invariant of K' [32a], is one half the sum of the characteristics of the inter-component crossings. For example, $c(K) = 2$ and $l(K') = \pm 1$ for 2_1^2, while $c(K) = 5$ and $l(K') = 0$ for 5_1^2. Because $F_{K'}(a, z)$ and $l(K')$ are both invariants, it follows that $U_K(a, z)$ is also an invariant of K.

THEOREM

A non-oriented link K is topologically chiral if its U-polynomial $U_K(a, z)$ is asymmetric in a, that is,

$$U_K(a, z) \neq U_K(a^{-1}, z) . \tag{6}$$

Proof

Consider a non-oriented link K and its mirror image K^*, and a corresponding oriented link K' and its mirror image K'^*. By combining eqs. (2) and (5), and because $l(K') = -l(K'^*)$, it follows that

$$U_{K^*}(a, z) = a^{2l(K')+2l(K'^*)} U_K(a^{-1}, z) = U_K(a^{-1}, z) .$$

Because $U_{K^*}(a, z) \neq U_K(a, z)$, it follows that K is a different isotopy type than its mirror image K^*. Therefore, by definition, K is topologically chiral. This completes the proof. □

Hence, just as $F_{K'}(a, z)$ is a chirality detector for an oriented link K', $U_K(a, z)$ is a chirality detector for a non-oriented link K. For example, consider the non-oriented link 4_1^2 in fig. 3(b).

$$\begin{aligned} U_{K(4_1^2)}(a, z) \neq U_{K(4_1^2)}(a^{-1}, z) &= (a + a^{-1})z^3 + (a^2 + 1)z^2 \\ &+ (a^3 - 2a - 3a^{-1})z - 1 + (a + a^{-1})z^{-1} . \end{aligned}$$

The polynomial is asymmetric in a, proof that the non-oriented link 4_1^2 is topologically chiral. In this manner we were able to prove that all the links listed in Rolfsen's book [14], with the exception of eight links $\{2_1^2, 6_2^2, 8_8^2, 9_{61}^2, 6_2^3, 8_4^3, 8_6^3, 8_3^4\}$ whose U-polynomials are symmetric in a, are topologically chiral. The amphicheirality of these eight links could not be ascertained with absolute certainty by this method because the U-polynomial, like the $F_{K'}(a, z)$, may suffer from the 9_{42} syndrome. That is, if the U-polynomial is symmetric in a, we cannot conclude, in general, that the corresponding non-oriented link is amphicheiral. For example, the U-polynomials of the non-oriented composite links $9_{42}\#6_2^3$ and $9_{42}\#2_1^2$ (figs. 13(b) and (c)) are

$$U_{K(9_{42}\#6_2^3)}(a, z) = U_{K(9_{42})}(a, z) \cdot U_{K(6_2^3)}(a, z)$$

and

$$U_{K(9_{42}\#2_1^2)}(a,z) = U_{K(9_{42})}(a,z) \cdot U_{K(2_1^2)}(a,z)\,.$$

Both polynomials are symmetric in a, yet the corresponding links are both topologically chiral (see above). For this reason the empirical approach had to be employed to prove the amphicheirality of the eight links, as described in section 4.1.

5.2.2. Topological chirality of 3-Borromean links

An n-Boromean link is a nontrivial link in which n rings, $n \geqslant 3$, are combined in such a way that any two component rings form a trivial link [21]. We previously showed that amphicheirality in such links can be established empirically, by demonstrating the existence of rigidly achiral presentations [21]. Topological chirality, however, could only be conjectured for certain links and with an odd number of crossings, such as the two depicted in figs. 14(a) and (c) which correspond to figs. 5(d) and (e) in [21], respectively. By employing the procedure described in the preceding section, it is now possible to prove this conjecture.

Figure 14 depicts the first three members in two series of 3-Borromean links, $13+m$ $(m \geqslant 0)$ and $15+m$ $(m \geqslant 0)$. The U-polynomials are all asymmetric in a. For example, the U-polynomial of the link in fig. 14(a) ($U_{\text{fig.14a}}$) contains fourteen summands, the first eleven of which are asymmetric in a ($f_0(a,z) - f_{10}(a,z)$, taking the first terms as $f_0(a,z)$):

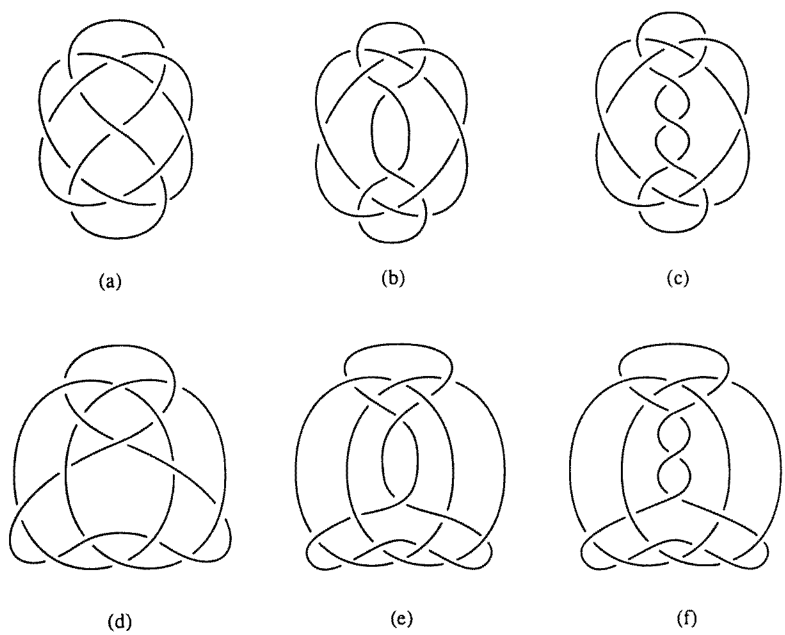


Fig. 14. Reduced diagrams of two series of 3-Borromean links. Members of the $13+m$ $(m \geqslant 0)$ series are shown with (a) 13, (b) 14, and (c) 15 crossings. Members of the $15+m$ $(m \geqslant 0)$ series are shown with (d) 15, (e) 16, and (f) 17 crossings.

$$
\begin{aligned}
U_{\mathrm{fig.14a}}(a,z) &= (9+9a^{-2})z^{12} + (27a+54a^{-1}+27a^{-3})z^{11} \\
&+ (36a^2+58+55a^{-2}+33a^{-4})z^{10} \\
&+ (30a^3-11a-87a^{-1}-25a^{-3}+21a^{-5})z^9 \\
&+ (17a^4-53a^2-169-172a^{-2}-66a^{-4}+7a^{-6})z^8 \\
&+ (6a^5-44a^3-57a-14a^{-1}-45a^{-3}-37a^{-5}+a^{-7})z^7 \\
&+ (a^6-20a^4+20a^2+128+125a^{-2}+31a^{-4}-7a^{-6})z^6 \\
&+ (-4a^5+20a^3+57a+63a^{-1}+43a^{-3}+13a^{-5})z^5 \\
&+ (6a^4+3a^2-15-11a^{-2}+a^{-4})z^4 \\
&+ (-2a^3-12a-16a^{-1}-4a^{-3}+2a^{-5})z^3 \\
&+ (-4a^2-12-12a^{-2}-4a^{-4})z^2+1+(-2a-2a^{-1})z^{-1} \\
&+ (a^2+2+a^{-2})z^{-2} .
\end{aligned}
$$

Since asymmetry in a of a single summand suffices as proof of topological chirality, we can state more simply:

$$U_{\mathrm{fig.14a}}(a,z)\colon\ f_0(a,z) = (9+9a^{-2})z^{12} .$$

Similarly,

$$U_{\mathrm{fig.14b}}(a,z)\colon\ f_0(a,z) = (9a^{-1}+9a^{-3})z^{13} ,$$

$$U_{\mathrm{fig.14c}}(a,z)\colon\ f_0(a,z) = (9a^{-2}+9a^{-4})z^{14} ,$$

$$U_{\mathrm{fig.14d}}(a,z)\colon\ f_0(a,z) = (10+10a^{2})z^{14} ,$$

$$U_{\mathrm{fig.14e}}(a,z)\colon\ f_0(a,z) = (10a+10a^{3})z^{15} ,$$

$$U_{\mathrm{fig.14f}}(a,z)\colon\ f_0(a,z) = (10a^2+10a^{4})z^{16} .$$

Thus all six 3-Borromean links in fig. 14 are topologically chiral.

Note that all the members of our series have reduced, alternating diagrams and hence [34a,35] have minimal crossing numbers.

6. Amphicheiral links with odd crossing numbers

As described in section 4.1, the non-oriented two-component link 9^2_{61} can attain a rigidly achiral presentation (fig. 7(c)) and is therefore amphicheiral. No other example is known so far of an amphicheiral link, whether oriented or not, whose $c(K)$ is odd. Furthermore, because no example is known of an amphicheiral knot with an odd $c(K)$, 9^2_{61} is sui generis among all known knots and links.

In this section we conjecture that 9^2_{61} is the first member in a class $\mathbf{K}$ of amphicheiral, non-oriented, non-alternating, two-component, prime links with $c(K) = 9 + 2n$, $n = 0, 1, 2, 3, \cdots$, that $\mathbf{K}$ is the union of two subclasses, $\mathbf{K}_{\text{even}}$ and $\mathbf{K}_{\text{odd}}$, characterized by the parity of n, and that the corresponding subclasses of oriented links, $\mathbf{K}'_{\text{even}}$ and $\mathbf{K}'_{\text{odd}}$, exhibit markedly different properties with respect to amphicheirality and writhe.

The members of $\mathbf{K}_{\text{even}}$, whose diagrams have $9 + 4m$ crossings, $m = 0, 1, 2, 3, \cdots$, may be constructed, as illustrated for the 13-crossing link diagram in fig. 15(a), by insertion of a pair of mirror-image-related double-helical tangles [33] with an even number of crossings into the two loops of the reduced diagram of 9^2_{61} that are marked by arrows in fig. 15(b). The corresponding rigidly achiral presentations are exemplified by the S_4 presentation of the 13-crossing link diagram in fig. 15(c). Similarly, the members of $\mathbf{K}_{\text{odd}}$, whose diagrams have $11 + 4m$ crossings, $m = 0, 1, 2, 3, \cdots$, may be constructed by insertion into 9^2_{61} of a pair of mirror-image-related double-helical tangles with an odd number of crossings, as illustrated for the 11-crossing link diagram in fig. 16(a). The corresponding rigidly achiral presentations are exemplified by the S_4 presentation of the 11-crossing link diagram in fig. 16(b). Every member in class $\mathbf{K}$ can be similarly deformed to an S_4 presentation.

Figure 17 depicts four oriented diagrams, derived from the enantiomorphs of 9^2_{61}, that illustrate membership in $\mathbf{K}'_{\text{even}}$. The Kauffman polynomial for $K_1'(9^2_{61})$, associated with $D_1'(9^2_{61})$ in fig. 17, had previously been calculated by Doll and Hoste [23], who found that $F_{K_1'(9^2_{61})}(a,z) \neq F_{K_1'(9^2_{61})}(a^{-1},z)$. From this it is easily shown that $D_1'(9^2_{61}) \sim D_2'(9^2_{61})^*$ and $D_2'(9^2_{61}) \sim D_1'(9^2_{61})^*$, and that $F(a,z) \neq F(a^{-1},z)$ for each of the four diagrams in fig. 17. The same kind of inequalities obtains for the HOMFLY and Jones polynomials. The two links associated with the four diagrams in fig. 17 are therefore topological enantiomorphs.

From the example of the links $K_1'(9^2_{61})$ and $K_1'(9^2_{61})^*$, which are associated with $D_1'(9^2_{61})$ and $D_1'(9^2_{61})^*$ in fig. 17, we conjecture that each member of $\mathbf{K}'_{\text{even}}$ exists as

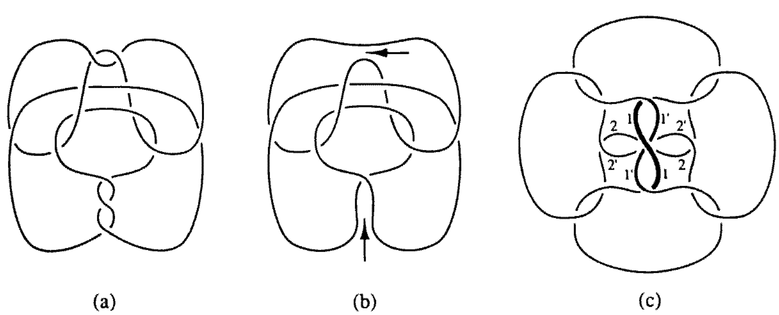
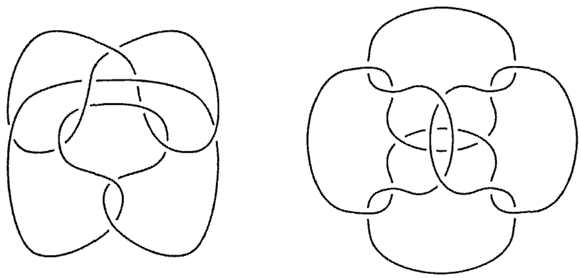


Fig. 15. Reduced diagrams of selected links belonging to $\mathbf{K}_{\text{even}}$. (a) A 13-crossing link diagram. (b) 9^2_{61}. (c) A rigidly achiral presentation of (a). The center of the projection is a transverse quadruple point, with segment 1 closest to the observer, and segments 1′, 2, and 2′ further away, in that order.



(a) (b)

Fig. 16. (a) An 11-crossing link diagram belonging to $\mathbf{K}_{\rm odd}$. (b) A rigidly achiral presentation of (a).

an enantiomorphic pair of oriented links. Note that the S_4 symmetry of the diagram in fig. 15(c) is destroyed upon orientation of the link. In contrast, each member of $\mathbf{K}'_{\rm odd}$ is amphicheiral because the S_4 symmetries of our diagrams for $\mathbf{K}_{\rm odd}$ are preserved upon orientation of both components of the links in this class. For example, whereas orientation of the S_4 presentation of 9^2_{61} (fig. 7(c)) yields two enantiomorphic links that are ambient isotopic with $K'_1(9^2_{61})$ and $K'_1(9^2_{61})^*$, orientation of the S_4 presentation of the 11-crossing link in fig. 16(b) yields two ambient isotopic links with S_4 symmetry (fig. 18).

Also noteworthy is the observation that two minimal crossing diagrams with different writhes, $w(D') = \pm 9$ and ± 7, are associated with 9^2_{61}; thus, with reference to fig. 17, $w(D') = +9, -7, -9$, and $+7$ for $D'_1(9^2_{61})$, $D'_2(9^2_{61})$, $D'_1(9^2_{61})^*$, and $D'_2(9^2_{61})^*$, respectively. This is similar to the Perko pair [32b], in which two minimal crossing diagrams with $w(D')$'s of $+10$ (or -10) and $+8$ (or -8) are associated with the same

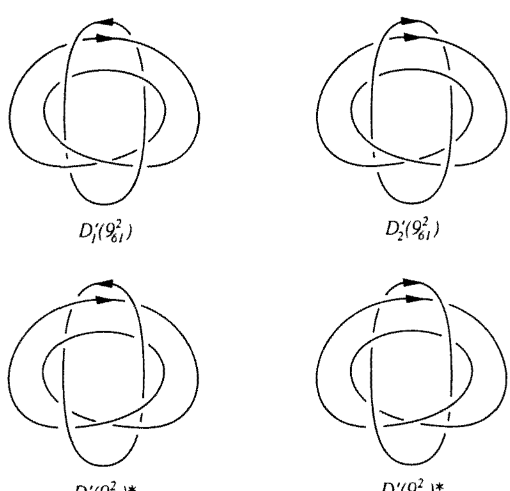


Fig. 17. Four reduced diagrams obtained by orientation of $D(9^2_{61})$ and $D(9^2_{61})^*$.

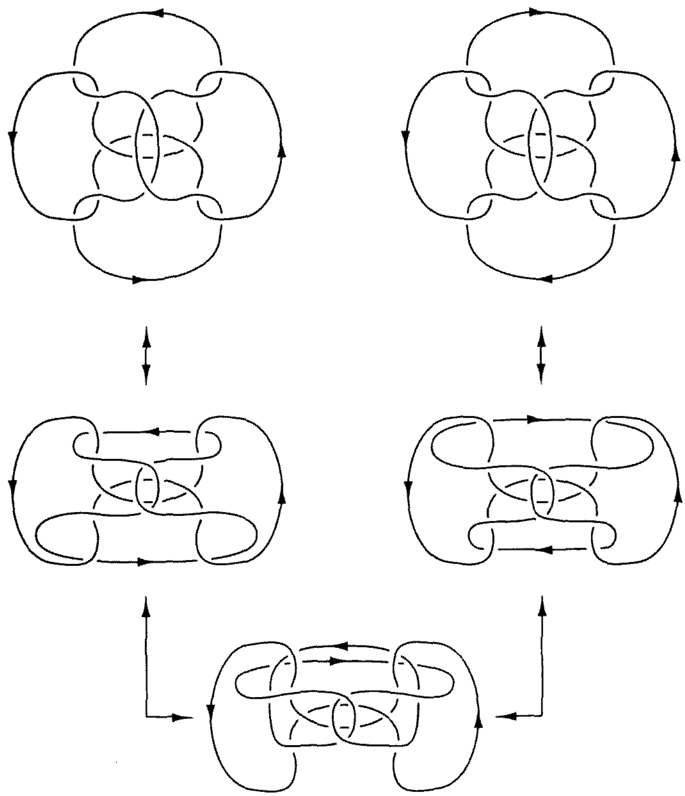


Fig. 18. Two diagrams with S_4 symmetry (top left and right), obtained by orientation of the S_4 presentation in fig. 16(b), and their interconversion by ambient isotopy.

topologically chiral, non-alternating, 10-crossing prime knot. Figure 19 depicts the Perko pair P_1 (left), with $w(D') = +10$, and P_2 (center), with $w(D') = +8$. In that sense, $D_1'(9^2_{61}) \sim D_2'(9^2_{61})^*$ or $D_2'(9^2_{61}) \sim D_1'(9^2_{61})^*$ parallels $P_1 \sim P_2$ or $P_1^* \sim P_2^*$.

Minimal crossing diagrams with different writhes, $w(D') = +1$ and -1, are also conjectured to be associated with each member of $\mathbf{K}'_{\text{odd}}$. For example, fig. 20

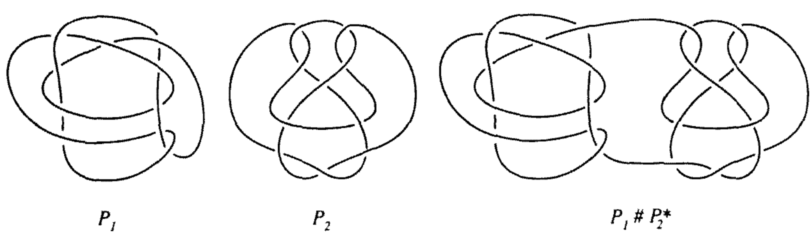


Fig. 19. The Perko pair: (a) P_1, with $w(D') = +10$, and (b) P_2, with $w(D') = +8$. (c) The composite knot $P_1 \# P_2^*$, with $w(D') = +2$.

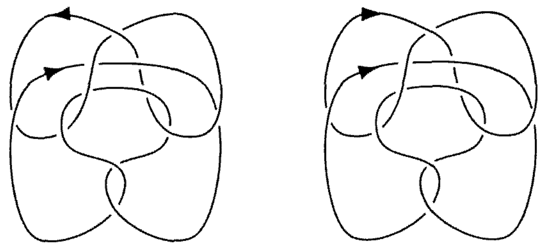


Fig. 20. Two reduced 11-crossing diagrams of the same amphicheiral, oriented link, both with $w(D') = +1$.

depicts two 11-crossing link diagrams of the same amphicheiral, oriented link, both with $w(D') = +1$, while the mirror-image diagrams have $w(D') = -1$.

Tait's conjecture, that any knot whose minimal crossing number is odd must be topologically chiral, has been proven for alternating knots [28a,34]. The suspicion that Tait's conjecture may not hold for some types of non-alternating knots is fueled by the existence of non-oriented (**K**) and oriented ($\mathbf{K}'_{\text{odd}}$) non-alternating links that are conjectured to have odd minimal crossing numbers yet are topologically achiral.

Acknowledgements

We thank Erica Flapan for helpful discussions, and Nicholas Cozzarelli and Nadrian Seeman for providing us with a copy of the program "Knotter" [36]. This work was supported by a grant from the National Science Foundation.

References

[1] E. Wasserman, J. Amer. Chem. Soc. 82 (1960) 4433. See also: E. Wasserman, D.A. Ben-Efraim and R. Wolovsky, ibid. 90 (1968) 3286; R. Wolovsky, ibid. 92 (1970) 2132; D.A. Ben-Efraim, C. Batich and E. Wasserman, ibid. 92 (1970) 2133.
[2] H.L. Frisch and E. Wasserman, J. Amer. Chem. Soc. 83 (1961) 3789; E. Wasserman, Sci. Amer. 207/5 (1962) 94. See also: N. van Gulick, New J. Chem. 17 (1993) 619 [manuscript originally submitted to Tetrahedron, August 1960].
[3] (a) G. Schill and C. Zürcher, Chem. Ber. 110 (1977) 2046. (b) G. Schill, K. Rissler, H. Fritz and W. Vetter, Angew. Chem. Int. Ed. Engl. 20 (1981) 187. (c) J.-P. Sauvage and J. Weiss, J. Amer. Chem. Soc. 107 (1985) 6108.
[4] D.B. Amabilino, P.R. Ashton, A.S. Reder, N. Spencer and J.F. Stoddart, Angew. Chem. Int. Ed. Engl. 33 (1994) 433, 1286.
[5] J. Chen and N.C. Seeman, Nature 350 (1991) 631. See also: N.C. Seeman, J. Chen, S.M. Du, J.E. Mueller, Y. Zhang, T.-J. Fu, Y. Wang, H. Wang and S. Zhang, New J. Chem. 17 (1993) 739.
[6] Y. Zhang and N.C. Seeman, J. Amer. Chem. Soc. 116 (1994) 1661.
[7] H.O. Stumpf, L. Ouahab, Y. Pei, D. Grandjean and O. Kahn, Science 261 (1993) 447.

[8] K.-W. Kim and M.G. Kanatzidis, J. Amer. Chem. Soc. 114 (1992) 4878; L.R. MacGillivray, S. Subramanian and M.J. Zaworotko, J. Chem. Soc., Chem. Commun. (1994) 1325; D.M.L. Goodgame, S. Menzer, A.M. Smith and D.J. Williams, Angew. Chem. Int. Ed. Engl. 34 (1995) 574; J.A. Real, E. Andrés, M.C. Muñoz, M. Julve, T. Granier, A. Bousseksou and F. Varret, Science 268 (1995) 265.

[9] B. Hudson and J. Vinograd, Nature 216 (1967) 647; D.A. Clayton and J. Vinograd, Nature 216 (1967) 652.

[10] A.D. Bates and A. Maxwell, *DNA Topology* (Oxford University Press, 1993) ch. 4.

[11] C. Liang and K. Mislow, J. Amer. Chem. Soc. 117 (1995) 4201.

[12] C. Liang and K. Mislow, J. Math. Chem. 15 (1994) 1.

[13] C.O. Dietrich-Buchecker, J.-P. Sauvage and J.-M. Kern, J. Amer. Chem. Soc. 106 (1984) 3043.

[14] D. Rolfsen, *Knots and Links* (Publish or Perish, Berkeley, 1976; second printing with corrections: Publish or Perish, Houston, 1990). Appendix C: Table of knots and links, pp. 388–429.

[15] J.-F. Nierengarten, C.O. Dietrich-Buchecker and J.-P. Sauvage, J. Amer. Chem. Soc. 116 (1994) 375.

[16] A. Kawauchi, Proc. Jap. Acad. 55, Ser. A (1979) 399; R.H. Fox, A quick trip through knot theory, in: *Topology of 3-Manifolds*, ed. M.K. Fort, Jr. (Prentice Hall, Englewood Cliffs, NJ, 1962) pp. 120–167; R.H. Crowell and R.H. Fox, *Introduction to Knot Theory* (Blaisdell, New York, 1963).

[17] J.-C. Chambron, D.K. Mitchell and J.-P. Sauvage, J. Amer. Chem. Soc. 114 (1992) 4625. See also: D.K. Mitchell and J.-P. Sauvage, Angew. Chem. Int. Ed. Engl. 27 (1988) 930; Y. Kaida, Y. Okamoto, J.-C. Chambron, D.K. Mitchell and J.-P. Sauvage, Tetrahedron Lett. 34 (1993) 1019.

[18] C. Piguet, G. Bernardinelli, A.F. Williams and B. Bocquet, Angew. Chem. Int. Ed. Engl. 34 (1995) 582.

[19] P.R. Ashton, I. Iriepa, M.V. Reddington, N. Spencer, A.M.Z. Slawin, J.F. Stoddart and D.J. Williams, Tetrahedron Lett. 35 (1994) 4835.

[20] (a) P.G. Tait, On knots, Trans. Roy. Soc. Edin. 28 (1876-77) 145–190. (b) P.G. Tait, On knots. Part II, Trans. Roy. Soc. Edin. 32 (1884) 327–342. (c) P.G. Tait, On knots. Part III, Trans. Roy. Soc. Edin. 32 (1885) 493–506. (d) P.G. Tait, On knots I, II, III. *Scientific Papers Vol. I* (Cambridge University Press, London, 1898) pp. 273–347.

[21] C. Liang and K. Mislow, J. Math. Chem. 16 (1994) 27.

[22] E. Flapan, Pac. J. Math. 129 (1987) 57; E. Flapan, Topological techniques to detect chirality, in: *New Developments in Molecular Chirality*, ed. P.G. Mezey (Kluwer, Dordrecht, 1991) pp. 209–239.

[23] H. Doll and J. Hoste, Math. Comput. 57 (1991) 747.

[24] M. Dehn, Math. Ann. 75 (1914) 402.

[25] J.W. Alexander, Trans. Amer. Math. Soc. 30 (1928) 275.

[26] V.F.R. Jones, Bull. Amer. Math. Soc. 12 (1985) 103.

[27] (a) K.C. Millett, Croat. Chem. Acta 59 (1986) 669. (b) K.C. Millett, Algebraic topological indices of molecular chirality, in: *New Developments in Molecular Chirality*, ed. P.G. Mezey (Kluwer, Dordrecht, 1991) pp. 165–207. (c) P. Freyd, D. Yetter, J. Hoste, W.B.R. Lickorish, K. Millett and A. Ocneanu, Bull. Amer. Math. Soc. 12 (1985) 239. (d) W.B.R. Lickorish and K.C. Millett, Topology 26 (1987) 107. (e) W.B.R. Lickorish and K.C. Millett, Math. Mag. 61 (1988) 3.

[28] (a) L.H. Kaufmann, Trans. Amer. Math. Soc. 318 (1990) 417. (b) L.H. Kauffman, Amer. Math. Monthly 95 (1988) 195. (c) L.H. Kauffman, *On Knots* (Princeton University, Princeton, NJ, 1987) pp. 444–473.

[29] (a) P. Ramadevi, T.R. Govindarajan and R.K. Kaul, Modern Phys. Lett. A 9 (1994) 3205. (b) C. Liang and K. Mislow, J. Math. Chem. 15 (1994) 35.

[30] G. Burde and H. Zieschang, *Knots* (Walter de Gruyter, Berlin, 1985) Appendix C: Tables, pp. 311–343.
[31] R.D. Brandt, W.B.R. Lickorish and K.C. Millett, Invent. Math. 84 (1986) 563.
[32] C.C. Adams, *The Knot Book: An Elementary Introduction to the Mathematical Theory of Knots* (Freeman, New York, 1994); (a) pp. 16–22; (b) p. 32.
[33] J.H. Conway, An enumeration of knots and links, and some of their algebraic properties, in: *Computational Problems in Abstract Algebra*, ed. J. Leech (Pergamon Press, New York, 1970) pp. 329–358.
[34] (a) K. Murasugi, Topology 26 (1987) 187. (b) M.B. Thistlethwaite, Topology 27 (1988) 311.
[35] M. Thistlethwaite, Topology 26 (1987) 297.
[36] J.H. Jenkins, Master's Thesis, University of California at Berkeley (1990).