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ORIGINAL PAPER

# Hydrocarbon links in an octet truss

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**Abstract** We use the octet truss of R. Buckminster Fuller to develop a geometric placement method for synthesizing braid representations of knots and links of oligo (phenylene ethynylene)s using the 60° *ortho*, 120° *meta* or 180° *para* phenyl ring substitution angles and respecting the van der Waals repulsion constraints. We show that any knot or link can be realized by a phenylene ethynylene oligomer modeled on the octet truss. Use of this lattice is motivated by the structural constraints of these phenylene ethynylene units. Where in bio-organic chemistry, questions often involve identifying existing knots, for example in DNA strands, organic synthesis is concerned with assembling molecular structures that can be verified to exist in a desired knot topology. This physical realization of a knot as a construction of common organic molecular subunits then facilitates further study of the properties of knotted molecules in general.

**Keywords** Knot · Link · Braid · Octahedron · Tetrahedron · Equiangular · Octet truss · Phenylene ethynylene · Equilateral

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## 1 Introduction

A key property of chain-like molecules is their ability to adopt a large number of conformations through rotations about single bonds along the chain [1]. In recent years, chemical synthesis has begun to address the creation of chain molecules with well-defined conformations [2], as is seen for proteins in nature, as well as knots of well-defined topologies [3], as are found in both natural and synthetic DNA [4]. Through elegant synthetic design and much experimental effort, a number of simple knots and links have been synthesized, but, to date, few systematic undertakings to create a variety of knots and links, let alone a comprehensive series of knots and links, have been attempted. The current paper describes a mathematical foundation for such a survey, showing that phenylene ethynylene oligomers, as they are idealized on the octet truss lattice, can be arranged to make any arbitrary braid, and these braids can be linked together to give knots and links of any topology.

The synthetic versions of these natural systems often require tethering strategies to hold the components of the knot in place while they are covalently attached to one another. To date, these synthetic limitations have determined which knots have been synthesized. Metal coordination or hydrogen bonding of two molecular fragments with side chains that could be covalently linked has afforded catenanes [5], or molecular links. Simple trefoil knots have been prepared using the same strategy [6]. All of these synthetic efforts have been limited by the templating motifs and the chemistry used to link the components together. To date, only simple links and knots have been synthesized, and there is no general strategy for the construction of a particular link using a particular molecular building block. Synthetically, the assembly of phenylene ethynylene oligomers into braids and knots can be facilitated by the use of appropriate functionality on the phenylene units to allow the tethering strategies that have previously been employed.

Recent years have seen advances in the synthesis of oligomeric phenylene ethynylenes of specific linkage geometries, particularly those that are *meta*- and *ortho*-linked ([7,8] respectively). These oligomers, by virtue of their phenylene and ethynylene moieties, are fairly rigid, but do allow conformational freedom along the chain by virtue of the C–C single bonds connecting the phenyl rings to the alkynes. This extent of conformational freedom has been exploited to create molecules that fold into helices [9], and to synthesize shape-persistent molecules on the nanoscale that exhibit aggregation and photophysical behavior [10]. They are synthetically accessible, if tediously, via Sonogashira cross coupling reactions, and their modular construction allows the incorporation of specific functional modifications of particular phenyl rings along the oligomer. These modifications have included functionality that could be extended to mimic the tethering actions of current knot syntheses [11]. Such synthetic flexibility makes them reasonable candidates for creating specific chain conformations, including those that are arranged into links or knots. A goal of such an endeavor would be the creation of any arbitrary knot; to do this requires a mathematical description and demonstration that a certain set of building blocks can be used to create an arbitrary knot. This is laid out below for idealized phenylene ethynylene units using their molecular structures arranged on an octet truss lattice model.

## 2 Braids to links

A *braid* is the intertwining of some $n$ strings attached to top and bottom "bars" (Fig. 1). Each string intersects any horizontal plane between the two bars exactly once; *i.e.*, each string always heads downwards from the top bar to the bottom bar. The *closure* of a braid is obtained by pulling the bottom bar around and gluing it to the top bar (Fig. 2). The closure of any braid is clearly a knot or link. Conversely, it was first proved by J. W. Alexander that every knot or link is a closed braid [12]. Thus, we may use braids to construct any knot or link.

The *braid index*, denoted $i\,(K)$, of a knot is the least number of strings in a braid corresponding to a closed-braid representation of the knot. For example, the braid index of the unknot is 1, the braid index of the trefoil knot is 2, and the braid index of the figure-8 knot is 3 [13].

In a braid diagram, we can arrange the drawing so that no two crossings in a braid occur at exactly the same height. However, to reduce the numbers of bonds, we may allow crossings to occur at the same height. We use the symbol $\sigma_i$, for $i = 1, \ldots, n-1$, to indicate a crossing of the ith string with the $(i+1)$th string. We obtain this crossing by switching the lower endpoints of the ith string and the $(i+1)$th string while keeping

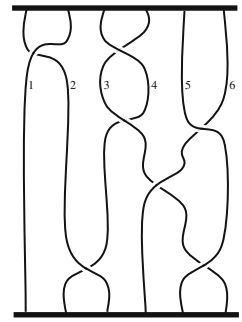


**Fig. 1** A braid

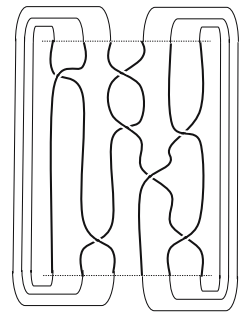

**Fig. 2** The closure of a braid

their upper endpoints fixed, with the ith string crossing *over* the $(i+1)$th string. If the ith string crosses *under* the $(i+1)$th string, we denote this crossing $\sigma_i^{-1}$.

An ordered combination of the $\sigma_i$ and $\sigma_i^{-1}$ symbols, reading a braid diagram from left to right (since we allow for two or more crossings to occur at the same height), then top to bottom, constitutes a *braid word*. Clearly, strings $i$ and $(i+1)$, for $i = 1, \ldots, n-1$, can be operated on by $\sigma_i$ or $\sigma_i^{-1}$ exactly once at a given height; thus, no two consecutive indices will occur in operations at the same height. Also, $i$ will be monotonically increasing at a given height. Therefore, the occurrence of consecutive indices in any pair of operations, or the occurrence of an index less than or equal to a preceding index in any pair of operations, indicates movement to a lower height for the second operation in the pair. For example, the braid word for the braid diagram in Fig. 1 is $\sigma_1^{-1}\sigma_3\sigma_3\sigma_5\sigma_4^{-1}\sigma_2\sigma_5^{-1}$.

The half-twists $\sigma_i$ and $\sigma_i^{-1}$ generate every braid word and hence every knot and link. Thus, to construct all knots and links from hydrocarbon complexes, it suffices to establish a set of strands, a left and a right half-twist move between a pair of strands that returns the strands to their previous vertical alignment, a means of concatenating the half-twists, and finally, a way of closing the braid in three-space.

## 3 Phenylene ethynylenes on the octet truss

Our goal is to construct all closed braids using phenylene ethynylene oligomers. Phenylene ethynylene units such as those shown in Fig. 3 offer the advantage of well-defined geometries and reasonably convenient synthetic access. Architecturally interesting macrocycles of predictable geometries have been synthesized and their physical properties studied [10]. The choice of these units restricts the resultant chains to have angles of 60, 120 and 180° because of the inherent bond angles. Clearly, the distance between the centers of the phenylene rings depends on the number of ethynylene units linking them. The distance for one ethynylene is 6.8 Å, and for a diethynylene is 9.5 Å (Fig. 3). The van der Waals radius for each ethynylene linker is 3.5 Å, or twice the radius of a carbon atom [14]. These geometrical properties lead us to consider the

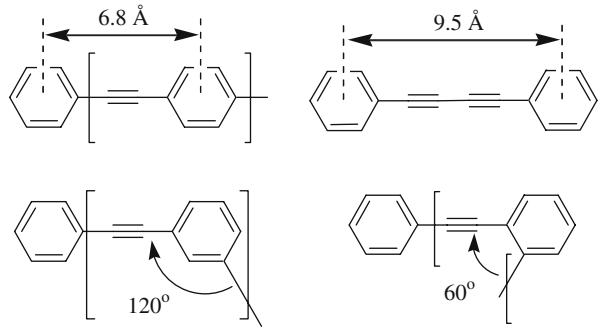


**Fig. 3** The structural parameters arising from the phenylene ethynylene bonding motifs

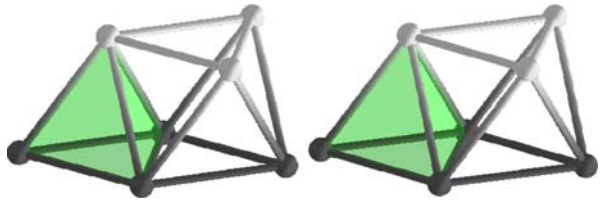

**Fig. 4** Stereoscopic projection of the basic space-filling tetrahedron/octahedron unit

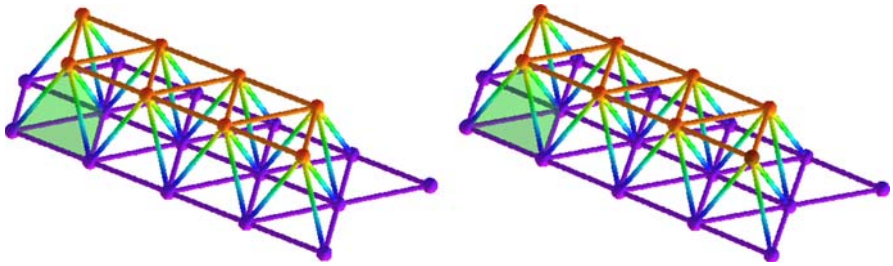

**Fig. 5** Stereoscopic projection of one horizontal layer of the octet truss. The purple edges lie in the $x$–$y$ plane and the red edges lie in the plane $z = \frac{\sqrt{6}}{3}d$, where $d$ is the distance between the centers of any two adjacent spheres

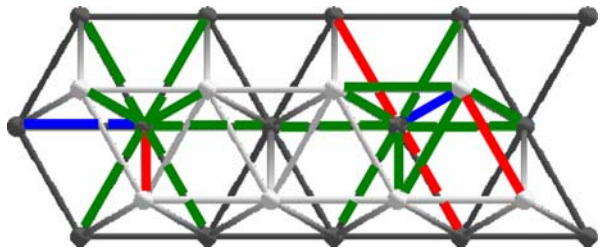

**Fig. 6** Projection onto the $x$–$y$ plane. Green edges represent attainable bond angles of 60, 120, or 180° with a blue edge; red edges indicate prohibited 90° angles with a blue edge

octet truss of R. Buckminster Fuller [15] as an ideal structure in which to arrange the phenylene ethynylene units.

The octet truss fills three-space with regular tetrahedra and octahedra (see Figs. 4 and 5), and is, in fact, the only semi-regular tiling of three-space (the cubic lattice being the only regular tiling). Thus, the only angles formed by the polyhedral edges are 60, 90, 120, and 180°, with the 90° angles formed by adjacent edges on an equator of an octahedron. We project this truss onto the $x$–$y$ plane and note that, in this projection, the 90° angles of the chain in three-space project to 90° angles in the two-space projection. Thus, all attainable bond angles in three-space correspond to angles other than 90° in the projection (see Fig. 6).

We also are constrained by the van der Waals radii of the atoms making up the sticks and junctions. In the octet truss, however, these do not overlap at all in the case of 9.5 Å long sticks (corresponding to the diethynylene moieties) and overlap within acceptable bounds in the case of ethynylene sticks that have a length of 6.8 Å. We

model the van der Waals radii of the hexagonal phenyl rings by spheres of diameter 7.4 Å. This distance corresponds to the distance between hydrogens *para-* to each other on the phenylene ring, 5.0 Å, plus two hydrogen van der Waals radii, 1.2 Å. This ensures that there is adequate spacing between phenyl rings in the folded chain, regardless of how the phenylene unit is oriented in space. See Figs. 7 and 8.

If there is an ethynylene stick between phenylene units contained in two spheres in a braid construction, the excluded space constraints are automatically satisfied. If two phenylene units occupy adjacent spheres in the truss without being neighbors along the oligomer chain, the excluded space constraints are also satisfied. The only concern is when phenylene units adjacent in the truss are coplanar; hydrogens on

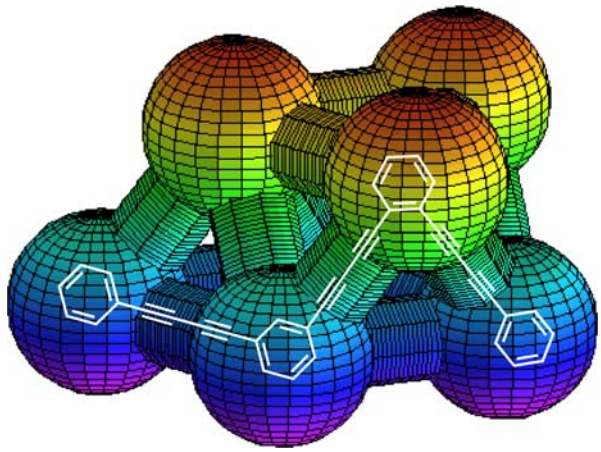

**Fig. 7** The basic tetrahedron/octahedron unit of Fig. 4, here shown with spheres of diameter 7.4 Å at distance 9.5 Å from center to center, and cylinders of diameter of 3.5 Å. Thus any molecule constructed within this geometry respects the excluded space constraints

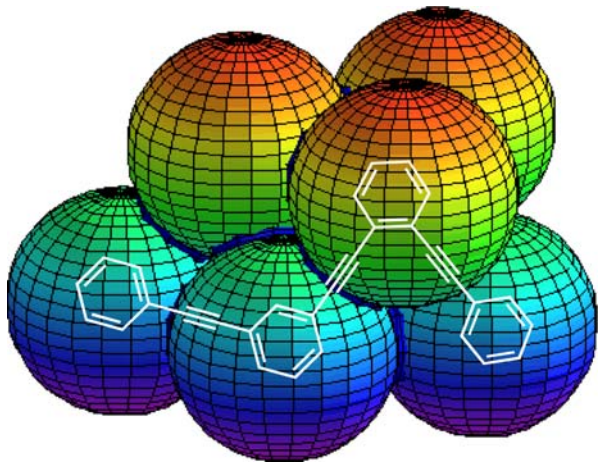

**Fig. 8** The basic tetrahedron/octahedron unit of Fig. 4, here shown with spheres of diameter 7.4 Å at distance 6.8 Å from center to center, and cylinders of diameter 3.5 Å

such phenyl rings are within the van der Waals radius of each other. However, this situation will not occur in the constructions given here, and even were it to, slight local perturbations, within the range of conformational flexibility these molecules, would permit the construct.

## 4 Building closed braids

As discussed above, we must establish a set of strands, a left and a right half-twist move between a pair of strands that returns the strands to their previous vertical alignment, a means of concatenating the half-twists, and finally a way of closing the braid in three-space. Once we have established these configurations, we can realize any knot or link by a phenylene ethynylene oligomer by finding a braid representation of it and then using the constructs below to place the half-twists and close the strands. We will establish these configurations within the geometry of the octet truss. For greater structural clarity in the diagrams, we use the smaller sphere and cylinder radii as in Figs. 4–6, and use the projection onto the $x$–$y$ plane as in Fig. 6.

### 4.1 Strands

We choose a line on the octet truss in the $x$–$y$ plane and start the braid strands at consecutive junctions along it. We then direct the braid strands in parallel at 60° from this line, as in Fig. 9.

### 4.2 Half-twists

The half-twist braid generators consist of an arrangement of six sticks using only 120° bond angles, as in Figs. 10 and 11. Figure 10 shows a configuration for a positive exponent twist in the braid word. In this figure, we view the white rods and balls as

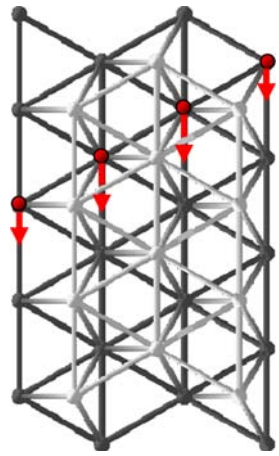

**Fig. 9** Starting the braid strands

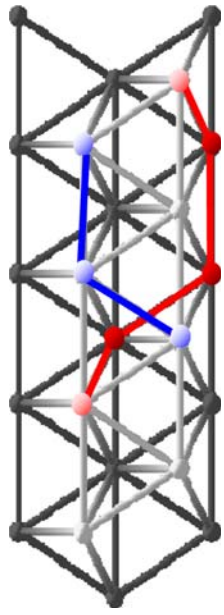

**Fig. 10** Positive twist

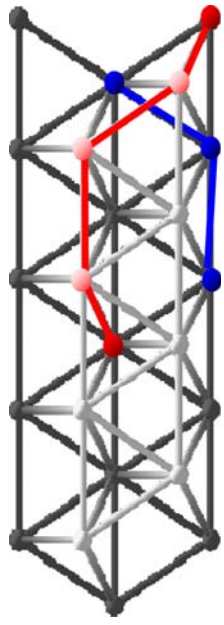

**Fig. 11** Negative twist

lying in the $x$–$y$ plane, with the black rods and balls lying below it. Figure 11 shows a configuration for negative exponent twist. Here, the black rods and balls as lie in the $x$–$y$ plane, with the white rods and balls lying above it.

### 4.3 Concatenating half-twists

We need to confirm that all necessary pairing of half-twists and straight segments are realizable with the allowed bond angles. These include a half-twist with a straight segment above or below either of its strands, a half-twist with itself, a half-twist with its inverse, and finally a half-twist with a neighboring half-twist, of either like or unlike exponent. Figure 12 shows a half-twist with all possible vertical segments, and Fig. 13 shows the concatenation of a half-twist with itself, resulting in a full 360° twist.

A half-twist may not be followed directly by its inverse, as this creates 90° angles, as in Fig. 14, which shows the concatenation of a half-twist immediately followed by its inverse, with the resultant 90° angles that prevent this configuration occurring at the green balls. Here we show both the plane above the $x$–$y$ plane and the plane below, with grey rods and balls lying in the $x$–$y$ plane. While this problem is easily addressed by inserting vertical segments, as in Fig. 15, which gives the concatenation of a half-twist followed by its inverse, legalized by inserting the vertical green rods, we note that this configuration is typically 'cancelled out' of the braid diagram via a Riedermiester II move. Figure 16 shows a half-twist with a neighboring half-twist, both with positive exponent, and Fig. 17 shows a half-twist with a neighboring half twist, the first with positive exponent, the second with negative exponent.

### 4.4 Closing the braid

We use 120° bonds to form the braid closure as well. We need to confirm that we can form a legal angle from any of the possible initial directions taken by the strand. This is illustrated in Fig. 18. Note that the half-twists extend only one layer either up or down from the $x$–$y$ plane, while the closure of the braid descends two layers down below the $x$–$y$ plane. Thus, there is no chance of intersection between the braid itself and the closure of the strands. Any of these closing strands may equally well be chosen to lie on the layers above instead of the layers below the twisting strands. Also, observe that the closure of a braid strand forms a legal angle with the braid strand in all cases: a straight segment, or a positive or negative twist. The blue edges may be omitted when 60° angles do not result, or if 60° angles are not undesirable. Figure 19 shows the three different alternative closures for 4-strand braids, here with some 60° bond angles. Again observe that the closures form legal angles with the braid strands in all cases: a straight segment, or a positive or negative twist. Figure 20 shows three different alternative closures for 4-strand braids, here achieved using only 120° bond angles.

Depending on the configurations at the ends of the joined pair of braid strands, closures using fewer bonds may be found, but we provide those shown here because they do suffice in all cases. For example, the closures for the trefoil in Fig. 22 and on the right of Fig. 21 were chosen to display symmetry.

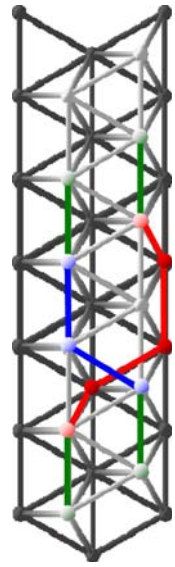

**Fig. 12** Half-twist with vertical segments

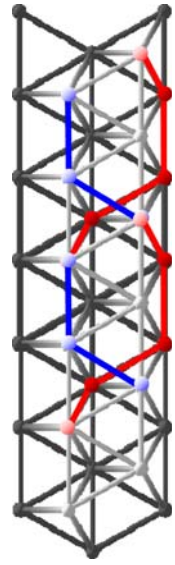

**Fig. 13** Half-twist concatenated with itself

## 5 Phenylene ethynylene trefoil

Using the construction rules outlined above, a trefoil consisting only of *para*- and *meta*-phenylene ethynylene units has been modeled. This trefoil consists of three linked twists which are then linked to all 180° *para*-phenylene ethynylene domains

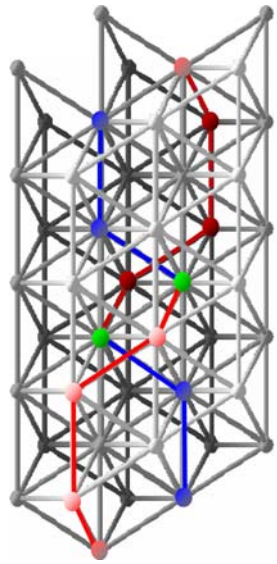

**Fig. 14** Half-twist followed by its inverse, resulting in 90° angles at the green balls

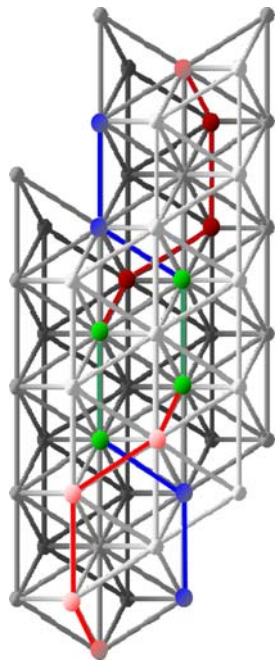

**Fig. 15** Half-twist followed by its inverse, with green vertical segments to remove the 90° angles

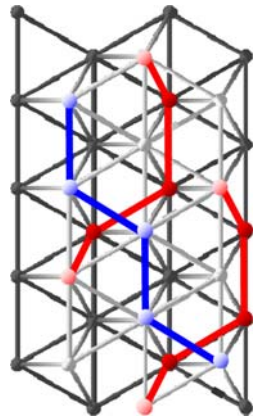

**Fig. 16** Two neighboring positive half-twists

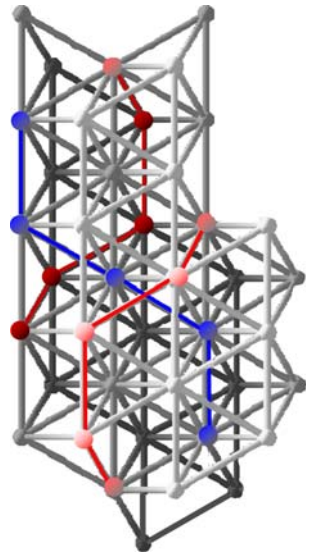

**Fig. 17** Neighboring half-twists with opposite signs

that connect the two ends. The left of Fig. 21 shows this construction on the octet truss; the green bars indicate the linear 180° domains. The right of Fig. 21 shows another possible trefoil in which the linear 180° domain on the right has been rotated to a higher level of the truss. The trefoil on the right was modeled in atomic detail because of its higher overall symmetry. The left of Fig. 22 suggests the positions of all of the atoms in such a trefoil. All of the phenylene rings occupy sites on the truss in one of two layers, the top shown in red and the bottom shown in blue. This molecule was modeled with molecular mechanics using the MM2 force field, and the right of Fig. 22 depicts an optimized geometry of this $C_{336}H_{168}$ hydrocarbon trefoil. Even with the shorter monoalkyne ethynylene sticks, the potential van der Waals contacts

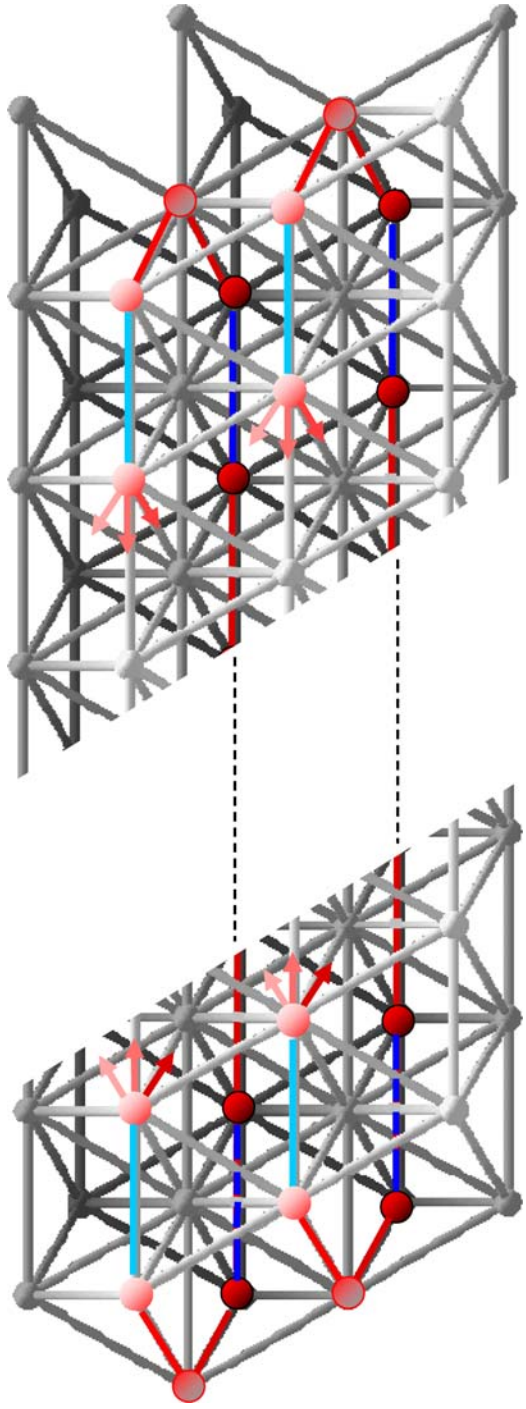

**Fig. 18** Closing the strands with 120° angles

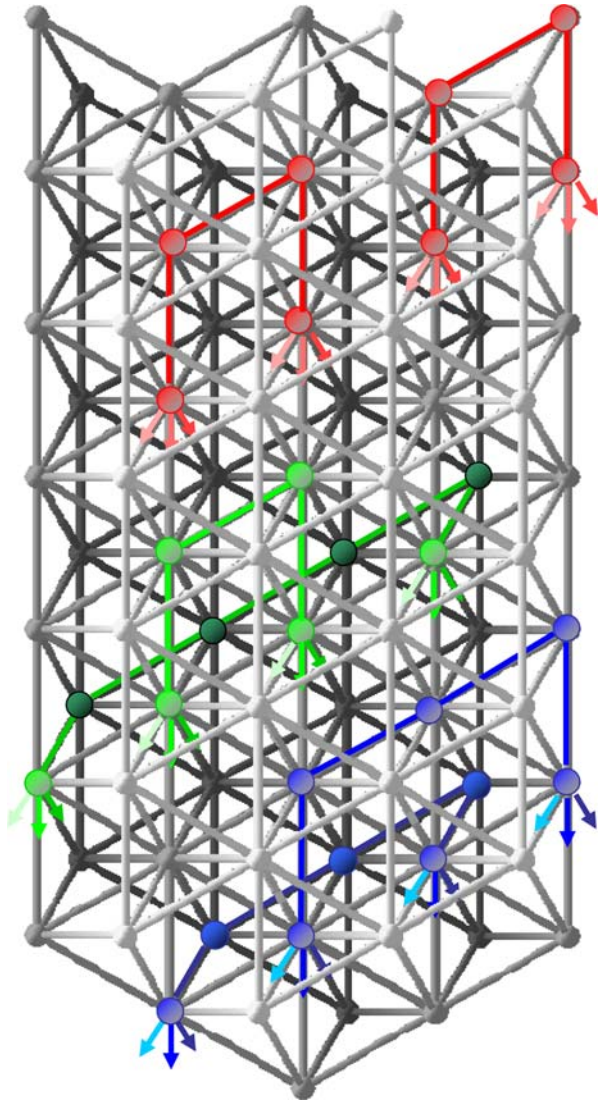

**Fig. 19** Alternative closures for 4-strand braids, with some 60° angles

between nonbonded, adjacent phenylenes does not prevent the molecule from adopting a conformation that lies more or less on the truss. Given the relative rigidity of the phenylene ethynylene backbone, it is reasonable to assume that strategically placed tethering groups at the sites indicated by the dotted green lines could be sufficient to allow formation of the trefoil by the formation of any number of single phenyl-ethynyl bonds.

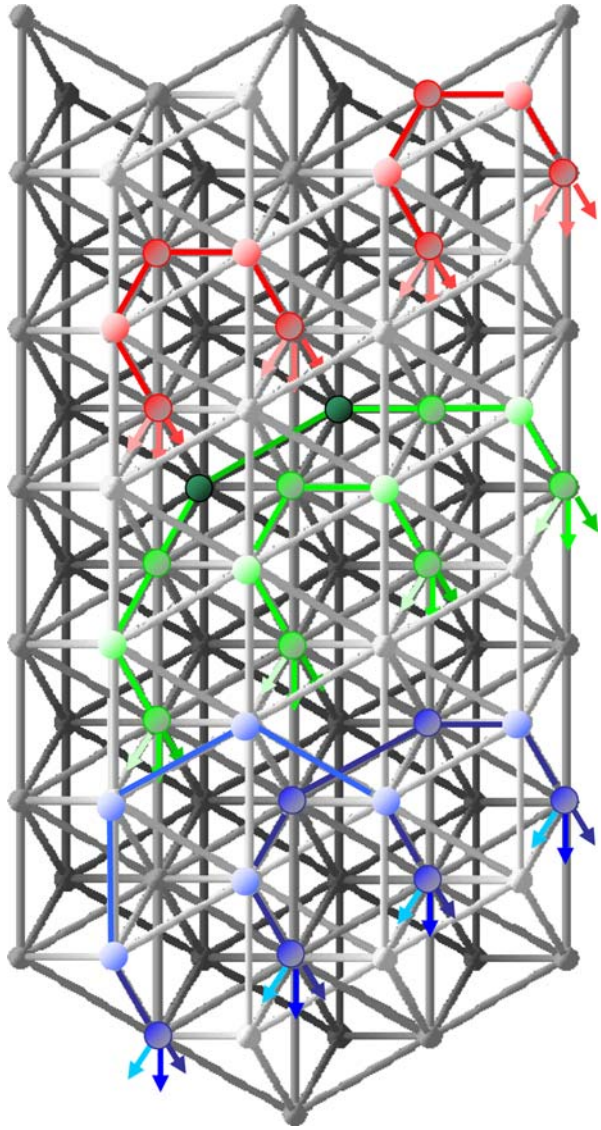

**Fig. 20** Alternative closures for 4-strand braids, with 120° angles only

## 6 Conclusion

We have shown that braids of phenylene ethynylene oligomers, consisting entirely of *para*- and *meta*-linkages, can be constructed on the octet truss lattice, and that these braids can be closed to make links. The use of the octet truss guarantees a physically accessible conformation of the phenylene ethynylene chains within the constructed link. The existence of half-twists and geometries with which they can be linked allows

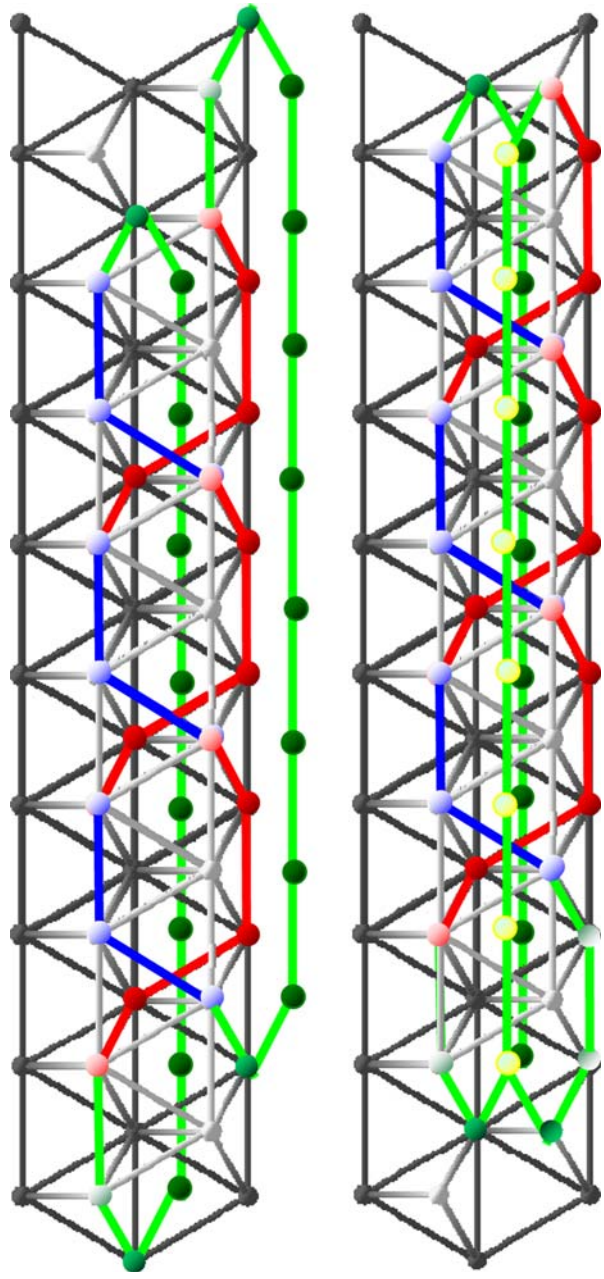

**Fig. 21** Two trefoils. The configuration on the left closes the braid below the half-twists, as in Fig. 18. The configuration on the right gains greater symmetry by using one chain above and one chain below the half-twists to close the braid

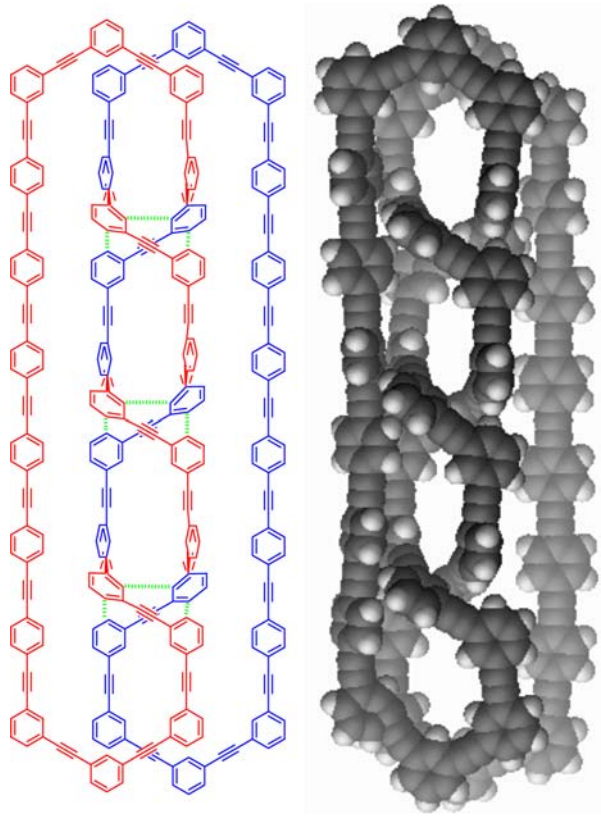

**Fig. 22** MM2 geometry optimized hydrocarbon trefoil of formula C336H168 Left: Red atoms lie in an upper level and blue atoms in a lower level of the octet truss; green dotted lines indicate non-local interactions that could aid the synthesis of the trefoil Right: Space-filling model of the trefoil

the modeling of any knot or link; the synthesis of any particular link depends then only on methods to keep half-twists templated while individual strands are covalently linked. Since phenylene ethynylenes can be synthesized to contain sequence-specific phenylene units bearing particular moieties, hydrogen-bonding or metal chelation sites could be installed; such moieties have been employed by others to assemble braids and knots. This general scheme could form the basis of a synthetic effort to access any arbitrary knot or link.

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