Bead-Chain Construction Set and Interlocking Puzzle Inspired by Polyhedranes

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Abstract

We introduce a new type of construction set which can be used to build valence sphere models of any cage-like hydrocarbon, of general formula $(CH)_{2n}$. Using n linear five-bead chains, one can connect these building units into a three-dimension arrangement that stands for its valence sphere model through n cross-linkings. More interestingly, the assembly processes of certain symmetric molecules, such as three Platonic hydrocarbons, including tetrahedrane, cubane, and dodecahedrane, are similar to solving interlocking puzzles. Hence, a bead chain construction set can also be considered as a new type of take-apart put-together puzzles.

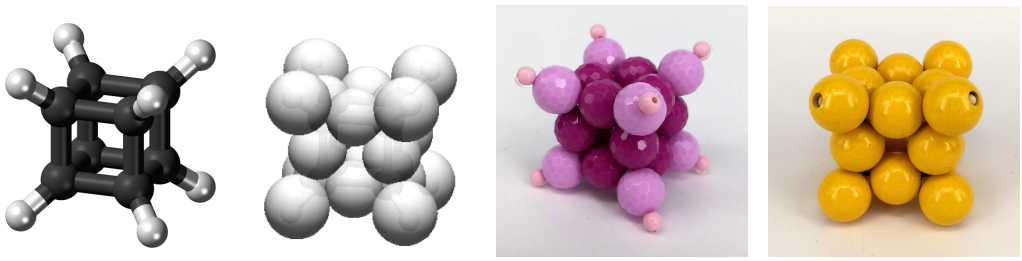
Introduction

In previous Bridges conferences, we presented systematic schemes to construct physical models of several families of compounds including fullerenes, carbon nanotubes, curved three-dimensional graphitic surfaces, space-filling tetrahedral zeolite structures, and higher-valence truss-like frameworks by the techniques of mathematical beading [1, 2]. We showed that bead models constructed by spherical beads can be viewed as the macroscopic realization of valence sphere models (VSMs) representing the three-dimensional distribution of electron pairs or ions of the corresponding molecules or crystals [3]. The saturation and directional characters of chemical affinity fall out naturally in bead models due to the balance between the hard-sphere repulsions among beads and the attraction generated by elastic cords that hold them together. In a way, constructing the bead model of a molecule with mathematical beading can be regarded as an analog computation, which can produce the approximate three-dimensional electron density profiles through suitable algorithmic procedures. Moreover, by using carefully chosen beads with different colors and shapes, we can create aesthetically pleasing molecular structures with different color patterns.

However, the beading procedure is essentially a slow sequential process. It may take many weeks to finish a bead model that contains thousands of beads, not to mention the possibility of making mistakes, which may require restarting the beading process from the position where the mistake occurred. Here, we introduce a new type of novel bead models for a whole family of cage-like hydrocarbons, or simply polyhedranes, the skeletons of which can be regarded mathematically as polyhedral cubic graphs. These models consist of pre-made bead chains, each of which is composed of a linear string of equal-size beads tightly connected by an elastic cord under tension.

Bead Chain Cube and Cubane

The simplest polyhedrane, the cubane molecule(C_8H_8) [4], consists of eight carbon atoms located at the corners of a cube, with one hydrogen atom connected to each carbon atom as shown in the Figure 1a. The molecular geometry and three-dimensional electron distribution of the cubane molecule can be described as a collection of twenty valence spheres approximated fairly well by floating spherical Gaussian functions (Figure 1b) [5]. The macroscopic physical model of a cubane molecule can be built by the standard beading techniques, in which each valence sphere is mimicked by a non-overlapping spherical beads as shown in



(a) **(b)** **(c)** **(d)**

Figure 1: *(a) Cubane, (b) Electron density profiles of Cubane optimized by the eFF method [5], (c) Bead VSM of Cubane, (d) BC-Cube (Bead-Chain Cube).*

Figure 1c. Tiny endcapped beads are required to hold beads representing CH bonds from falling apart, though. Moreover, one needs to be familiar with the beading techniques to handle beads and strings, in order to make the bead model, which can be hard for many beginners to the beading craft.

Interestingly, it is possible to avoid the whole beading process and still arrive at the same final structure for this molecule. The trick is to decompose the final bead models into simple building blocks which can be prepared in advance. The simplest building blocks are linear bead chains, which is easy to make even for beginners. The final structure can then be put together by combining these bead chains through cross-linkings.

The twelve CC single bonds and eight CH bonds of a cubane molecules are represented by twenty beads in a bead model. Suppose we choose the building blocks to be linear chains, the beads corresponding to eight CH bonds must be located at chain ends. One must need exactly four bead chains for a cubane molecule in order for a chain to start from one CH bond and end with another CH bond. To use as few basic building blocks as possible, each chain should contain $12/4 = 3$ non-terminal beads. Thus, a single type of five-bead chain is sufficient for making a VSM of a cubane molecule as shown in Figure 1d. The assembly process of a cubane model is similar to solving an interlocking puzzle due to the many possible ways of making cross-linkings among four chains. Therefore, we call it the Bead-Chain Cube (or BC-Cube) puzzle.

Platonic hydrocarbons

In addition to cubane, there are two other Platonic hydrocarbons, tetrahedrane and dodecahedrane, with chemical formula C_4H_4 and $C_{20}H_{20}$, respectively. Tetrahedrane has not yet been synthesized by chemists due to the large strain energy among neighboring CC bonds since the 60° angle in a regular triangle is too far away from the ideal bond angle of 109.5° for an sp^3 hybridized carbon atom. But, the dodecahedrane has

(a) **(b)** **(c)**

Figure 2: *Platonic bead chain puzzles: (a) Bead-Chain Tetrahedron, (b) Bead-Chain Cube, (c) Bead-Chain Dodecahedron.*

been successfully synthesized and the 108° angle of each regular pentagon is close to the ideal bond angle for an sp^3 hybridized carbon atom.

There are four vertices in a tetrahedrane molecule and a total of ten valence electron pairs with four pairs corresponding to CH bonds and six pairs CC bonds. Two linear five-bead chains can be utilized to build its bead model. The resulting bead model is shown in Figure 2a. Although we only need to make four cross-linkings between two five-bead chains to get the final tetrahedral arrangement, it may be still challenging for beginners to solve this puzzle.

Similarly, a total of ten five-bead chains are needed to make the valence sphere model for a dodecahedrane molecule. The possibility for different ways of making cross-linkings becomes very large. The systematic enumeration of the total number of distinct connected structures that can be obtained by cross-linking is an interesting problem to work out. But, here, we only wish to show the final dodecahedral framework as shown in Figure 2c and leave the construction procedure and the isomer counting problem for readers. Usually, we use two different colors to denote terminal and non-terminal beads which not only makes the assembling of complicated structures easier, but also results in final models that are aesthetically more pleasing.

Polyhedral Hydrocarbons as Cubic Graphs

More generally, it is possible to construct any cage-like hydrocarbon with the chemical formula $C_{2n}H_{2n}$ based only on one type of building blocks, namely five-bead chains. Mathematically, the carbon skeletons of these molecules correspond to cubic graphs or trivalent graphs in which all vertices have degree three. If we ignore CH bonds, each carbon atom is bonded to three neighboring carbon atoms. A cross-linking between two bead chains introduces a local tetrahedral arrangement for four beads. To satisfy the requirement that carbon atoms are located on the polyhedral skeleton and hydrogen atoms pointing outward, one needs exactly n five-bead chains for making the VSM of the corresponding polyhedrane molecule. Finding a procedure of constructing a bead chain model for a polyhedrane with five-bead chains is equivalent to finding a way to draw its skeletal polyhedron with n non-overlapping strokes, in which each stroke covers exactly three edges.

The possible bead models that a set of n five-bead chains can make grow quickly, since the total number of these cubic graphs grows exponentially as a function of n. In Figure 3, we list the bead models for all five isomers of $C_{10}H_{10}$. Notice that the total number of cubic graphs has already reached 7595 for $C_{20}H_{20}$ and only one corresponds to the dodecahedrane molecule. According to our experience, even though the corresponding bead-chain model can in principle be constructed, whenever an n-stroke solution for a polyhedrane exists. The actual assembling process from a given number of bead chains is still non-trivial.

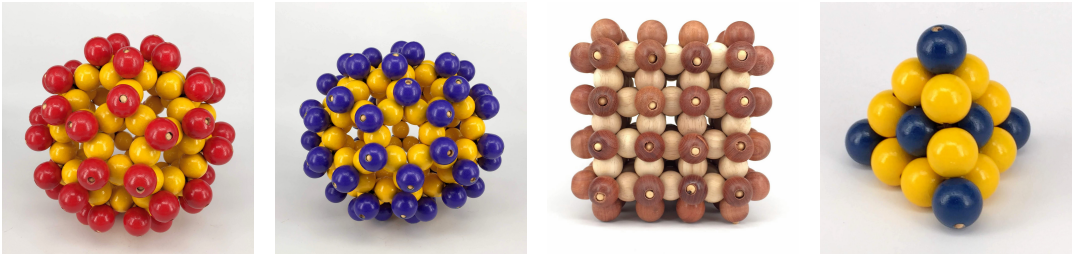
Figure 3: *All five isomers of $C_{10}H_{10}$.*

Conclusions

In this paper, we demonstrate that the VSMs of cage-like hydrocarbon molecules of general formula $(CH)_{2n}$ with carbon atoms located on the nodes of cubic graphs can be assembled from n linear five-bead chains through n cross-linkings. Two terminal beads of a bead chain stand for CH bonds, while three non-terminal

beads correspond to CC single bonds. As a result, $3n$ non-terminal beads form the skeletons of these molecules with n terminal beads pointing outward as little spikes.

Using similar assembly techniques, we have been able to construct many larger fulleranes such as $C_{60}H_{60}$ and $C_{70}H_{70}$ as shown in Figure 4a and 4b. Moreover, if we allow cross-linkings of three bead chains at a single position, more complicated nano structures that contain local octahedral arrangements of six spheres can also be mimicked. Figure 4c shows a bead model for a finite fragment of the perovskite structure which consists of 48 five-bead chains with 64 triple-chain crossings. Finally, we leave readers to figure out the puzzle on how to put together a close-packed tetrahedral arrangement of twenty spheres with four five-bead chains as shown in Figure 4d.



(a) **(b)** **(c)** **(d)**

Figure 4: *Bead chain models: (a) $C_{60}H_{60}$, (b) $C_{70}H_{70}$, (c) Perovskite of ReO_3 type consisting of a framework of octahedra sharing all vertices, (d) Bead chain tetrahedron with 20 close-packed spheres, which can be viewed as the bead model for an Au_{20} gold nanoparticle.*

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