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ORIGINAL PAPER

Analytical formulas for Kekulé structures number in (6,3)VH*t*[6,*n*] and (6,3)VH*t*[8,*n*] tori

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Abstract Analytical formulas for calculating the Kekulé structure number for families of polyhex tori are derived by using the transfer matrix method.

Keywords Kekulé valence structure · Transfer matrix · Analytical formulas · Polyhex tori

1 Introduction

A Kekulé structure is a valence structure covered by the maximal number of disjoint (double) edges so that all vertices are incident to exactly one of the disjoint edges [1]. The number of geometric Kekulé valence structures, K, for a molecule is the number of 1-factors (perfect matchings) of the associated molecular graph.

The number K is of interest as a measure of molecular stability: carbon compounds without Kekulé structures are unstable [1].

Various techniques and methods have been developed to calculate the number K [2,3]. This number may be evaluated either by generating all the possible solutions of geometric Kekulé structures or by using an algebraic evaluation.

One of the algebraic evaluations is the *transfer matrix* method [2]. This method is particularly useful for systems that have repeating sub-units e.g., polymers. The transfer matrix method is suitable for systems with rotational symmetry too. The first

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reported value for the number of Kekulé valence structures in buckminsterfullerene C_{60} was obtained using this method [1].

In the present paper we use the transfer matrix method to derive the analytical formulas of K for two families of polyhex tori.

2 Polyhex tori

Among the carbon allotropes, the torus is the only closed surface that can be tiled entirely with hexagons.

There are a couple of methods for generating a polyhex torus. For example the construction of such a torus can starts with embedding (i.e., drawing of a graph on a (closed) surface with no crossing lines) of the tetragonal (4,4) net on the toroidal surface. In this way we achieve a square torus. The squares are then changed to hexagons using cutting operations [4].

A *cutting operation* consists of deleting appropriate edges in a square lattice in order to produce some larger polygonal faces. To obtain the (6,3) lattice, each second edge is cut off. Two embedding isomers could result at each given $[c, n]$ pair, as the cut edges lye either horizontally or vertically (i.e., perpendicularly and parallel to the z-axis of the torus). The two isomers are called H and V, according to the cut-edge location [4,5]. By deleting each second *horizontal* edge and alternating edges and cuts in each second row it results in an H-isomer, while deleting each second *vertical* edge and alternating edges and cuts in each second column it results in a V-isomer.

Naming polyhex tori is given in Diudea terms [4]. The name of such a torus is a string of characters specifying the tiling and dimensions of the net, (6,3)$[c, n]$ with the (integer) parameters in the square brackets being the number of atoms in the tube cross-section and the number of cross sections around the large hollow of the torus, respectively.

Twisted tori can be generated by the following two procedures [4–6]:

(1) twisting the horizontal layer connections (Fig. 1c and e) and
(2) twisting the vertical layer (offset) connections (Fig. 1d and f).

We have two classes of simple tori and four classes of twisted tori in this constructive approach:

(a) H-cut: (6,3)H$[c,n]$;
(b) V-cut: (6,3)V$[c,n]$;
(c) H-twist, H-cut: (6,3)HH$t[c,n]$;
(d) V-twist, H-cut: (6,3)VH$t[c,n]$;
(e) H-twist, V-cut: (6,3)HV$t[c,n]$;
(f) V-twist, V-cut: (6,3)VV$t[c,n]$.

where c and n are as above and t is the number of twisted rows (Fig. 1).

The tori from Fig. 1 were generated with the TORUS software [6].

By construction, the maximum possible t-value of H-twisted polyhex tori is $t_{max}=c$. In the case of V-twisted polyhex tori, t can take values up to n (by construction). The maximum value of t to provide distinct topological objects, in a family of

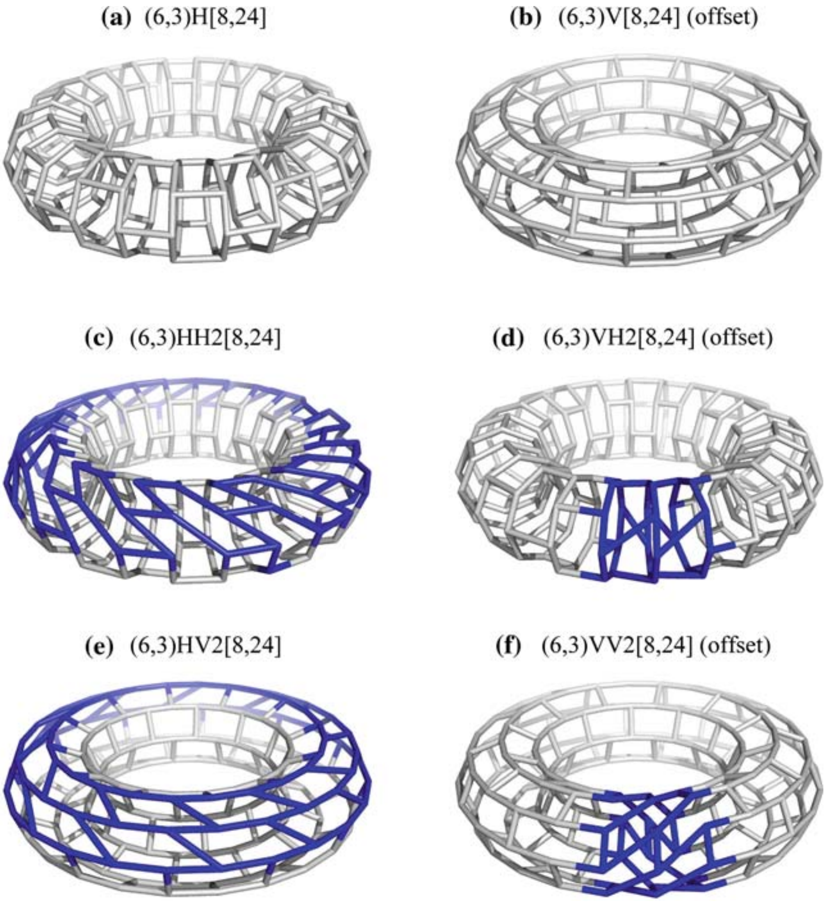


Fig. 1 The six classes of polyhex tori (non-optimized geometry)

V-twisted polyhex tori, equals $c/2$. Identical graphs in families of V-twisted polyhex tori are [5]:

$$\left.\begin{array}{l} \mathrm{VH}t_1[c,n] \equiv \mathrm{VH}t_2[c,n] \\ \mathrm{VV}t_1[c,n] \equiv \mathrm{VV}t_2[c,n] \end{array}\right\} \quad \text{where } t_1 \in \{0, 2, 4, \ldots, c/2\}$$
$$\text{and } t_2 \in \{c, c-2, c-4, \ldots, c/2\} \qquad (1)$$

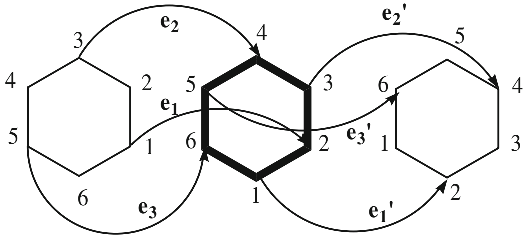
When $c/2$ is odd, then $t_{\max} = t - 1$

In the following, we study only the (6,3)VH$t[c,n]$ tori, $c = 6;8$.

3 Geometric Kekulé structures for (6,3)VH$t[c,n]$ tori

Let AT and AU be the transfer matrices of the twisted and untwisted units, respectively, of the (6,3)VH$t[c,n]$ torus (see the twisted unit in Fig. 2 and untwisted unit in Fig. 3).

Fig. 2 The twisted unit (with bold—6 atoms) for the (6,3)VHt[6,n] torus



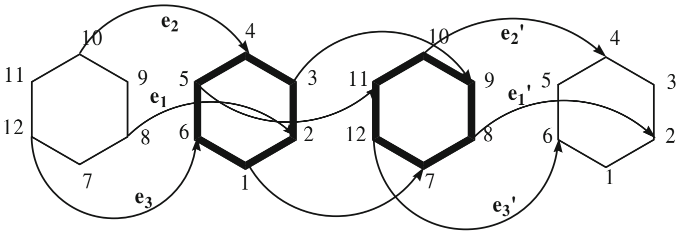


Fig. 3 The untwisted unit (with bold—12 atoms) for the (6,3)VHt[6,n] torus

For a polyhex torus with c atoms in the tube cross-section, $c/2$ CC bonds will connect two neighboring units. Each of these bonds can be either a CC double or a CC single bond.

A transfer matrix is constructed by considering all the possible assignments for the connecting bonds. The corresponding matrix elements [3] are given by the number of Kekulé valence structures for the unit when the $c/2$ connecting bonds take any of the $2^{c/2}$ possible assignments. The order of the matrix grows exponentially with the number of the connecting edges between neighboring units ($2^{c/2}$).

The AT and AU mat rices for the polyhex tori with 6 and 8 atoms in the tube cross-section are presented below.

$$AT_6 = \begin{pmatrix} 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 1 & 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \qquad AU_6 = \begin{pmatrix} 4 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 3 & 3 & 0 & 3 & 0 & 0 & 0 \\ 0 & 3 & 3 & 0 & 3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2 & 0 & 1 & 1 & 0 \\ 0 & 3 & 3 & 0 & 3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 2 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 & 2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

In the case of twisted unit for the (6,3)VHt[6,n] torus, when all the connecting bonds ($e_1, e_2, e_3, e'_1, e'_2, e'_3$) are simple bonds, the remaining unit is benzene ring, having 2 Kekulé structures. That's why the element from the first row and the first column in the AT_6 matrix will be 2. Similar reasons can be found for the other entries.

$$AT_8 = \begin{pmatrix}
2&0&0&0&0&0&0&0&0&0&0&0&0&0&0&0\\
0&1&1&0&1&0&0&0&1&0&0&0&0&0&0&0\\
0&1&1&0&1&0&0&0&1&0&0&0&0&0&0&0\\
0&0&0&1&0&1&0&0&0&1&0&0&0&0&0&0\\
0&1&1&0&1&0&0&0&1&0&0&0&0&0&0&0\\
0&0&0&0&0&1&1&0&0&1&1&0&0&0&0&0\\
0&0&0&1&0&0&1&0&0&0&1&0&0&0&0&0\\
0&0&0&0&0&0&0&1&0&0&0&1&0&0&0&0\\
0&1&1&0&1&0&0&0&1&0&0&0&0&0&0&0\\
0&0&0&0&0&0&0&0&0&1&1&0&1&0&0&0\\
0&0&0&1&0&1&0&0&0&0&1&0&1&0&0&0\\
0&0&0&0&0&0&0&0&0&0&0&1&0&1&0&0\\
0&0&0&0&0&1&1&0&0&0&0&0&1&0&0&0\\
0&0&0&0&0&0&0&0&0&0&0&0&0&1&1&0\\
0&0&0&0&0&0&0&1&0&0&0&0&0&0&1&0\\
0&0&0&0&0&0&0&0&0&0&0&0&0&0&0&1
\end{pmatrix}
\qquad
AU_8 = \begin{pmatrix}
4&0&0&0&0&0&0&0&0&0&0&0&0&0&0&0\\
0&4&4&0&4&0&0&0&4&0&0&0&0&0&0&0\\
0&4&4&0&4&0&0&0&4&0&0&0&0&0&0&0\\
0&0&0&3&0&2&1&0&0&1&2&0&1&0&0&0\\
0&4&4&0&4&0&0&0&4&0&0&0&0&0&0&0\\
0&0&0&2&0&4&2&0&0&2&2&0&2&0&0&0\\
0&0&0&1&0&2&3&0&0&1&2&0&1&0&0&0\\
0&0&0&0&0&0&0&2&0&0&0&1&0&0&1&0\\
0&4&4&0&4&0&0&0&4&0&0&0&0&0&0&0\\
0&0&0&1&0&2&1&0&0&3&2&0&1&0&0&0\\
0&0&0&2&0&2&2&0&0&2&4&0&2&0&0&0\\
0&0&0&0&0&0&0&1&0&0&0&2&0&1&0&0\\
0&0&0&1&0&2&1&0&0&1&2&0&3&0&0&0\\
0&0&0&0&0&0&0&0&0&0&0&1&0&2&1&0\\
0&0&0&0&0&0&0&1&0&0&0&0&0&1&2&0\\
0&0&0&0&0&0&0&0&0&0&0&0&0&0&0&1
\end{pmatrix}$$

The trace of an $n \times n$ square matrix A is defined to be the sum of the elements on the main diagonal. Let denote with *Tr(A)* the trace of the matrix A.

Using the notations given above we have the next formulas for computing the number of geometric Kekulé valence structures:

(a) (6,3)VH$t[c,n]$ torus

$$K_{VH}(x, y) = Tr(AT^{2y} \times AU^{x-y}), \text{ where } t = 2y \text{ and } n = 2x \tag{2}$$

(b) (6,3)H$[c,n]$ torus

$$K_H(x) = Tr(AU^x), \text{ where } n = 2x \tag{3}$$

Starting from the Jordan matrix decomposition of the AT and AU matrices, we derived analytical formulas to count the number of geometric Kekulé valence structures for H-cut and V-twisted polyhex tori ((6,3)VH$t[c,n]$).

The Jordan matrix decomposition is the decomposition of a square matrix M into the form

$$M = SJS^{-1} \tag{4}$$

where J is a matrix of Jordan canonical form (the classical canonical form) and S^{-1} is the matrix inverse of S [7].

The Jordan decomposition of our matrices is:

$$\begin{aligned} AT &= ST \times JT \times ST^{-1} \\ AU &= SU \times JU \times SU^{-1} \end{aligned} \tag{5}$$

In the following, we give the Jordan decomposition of the transfer matrices for (6,3)VH$t[c,n]$ tori with $c = 6$ and 8.

$$SU_6 = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ -1 & -1 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & -1 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad ST_6 = \begin{pmatrix} 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & -1 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & \frac{-1-i\sqrt{3}}{2} & \frac{-1+i\sqrt{3}}{2} \\ 1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & \frac{-1+i\sqrt{3}}{2} & \frac{-1-i\sqrt{3}}{2} \\ 0 & 0 & 0 & 1 & 0 & 0 & 1 & 1 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

$$JU_6 = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 4 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 4 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 9 \end{pmatrix} \quad JT_6 = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 3 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{1-i\sqrt{3}}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1+i\sqrt{3}}{2} \end{pmatrix}$$

$$SU_8 = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & -1 & -1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & -1 & -1 & 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & -\sqrt{2} & \sqrt{2} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 1 \\ -1 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & -\sqrt{2} & \sqrt{2} \\ 1 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 \\ -1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

$$ST_8 = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -1 & -1 & -1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 0 & -1 & 0 & -1 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -i\sqrt{2} & i\sqrt{2} & -\sqrt{2} & \sqrt{2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & -1 & 1 & 1 & 0 & -i & 0 & i \\
-1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & -i & 0 & i & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & -1 & 1 & 1 & 0 & i & 0 & -i \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & i\sqrt{2} & -i\sqrt{2} & -\sqrt{2} & \sqrt{2} & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & -1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 0 & 1 & 0 & 1 \\
-1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & i & 0 & -i & 0 \\
1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}$$

$$JU_8 = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 4 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 4 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 16 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 6-4\sqrt{2} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 6+4\sqrt{2}
\end{pmatrix}$$

$$JT_8 = \begin{pmatrix}
0&0&0&0&0&0&0&0&0&0&0&0&0&0&0&0\\
0&0&0&0&0&0&0&0&0&0&0&0&0&0&0&0\\
0&0&0&0&0&0&0&0&0&0&0&0&0&0&0&0\\
0&0&0&0&0&0&0&0&0&0&0&0&0&0&0&0\\
0&0&0&0&1&0&0&0&0&0&0&0&0&0&0&0\\
0&0&0&0&0&2&0&0&0&0&0&0&0&0&0&0\\
0&0&0&0&0&0&2&0&0&0&0&0&0&0&0&0\\
0&0&0&0&0&0&0&4&0&0&0&0&0&0&0&0\\
0&0&0&0&0&0&0&0&-i\sqrt{2}&0&0&0&0&0&0&0\\
0&0&0&0&0&0&0&0&0&i\sqrt{2}&0&0&0&0&0&0\\
0&0&0&0&0&0&0&0&0&0&2-\sqrt{2}&0&0&0&0&0\\
0&0&0&0&0&0&0&0&0&0&0&2+\sqrt{2}&0&0&0&0\\
0&0&0&0&0&0&0&0&0&0&0&0&1-i&0&0&0\\
0&0&0&0&0&0&0&0&0&0&0&0&0&1-i&0&0\\
0&0&0&0&0&0&0&0&0&0&0&0&0&0&1+i&0\\
0&0&0&0&0&0&0&0&0&0&0&0&0&0&0&1+i
\end{pmatrix}$$

We have

$$\text{H}[c,n]\text{: } K_n(x) = Tr(SU \times JUx \times SU^{-1}) \tag{6}$$

$$\text{VH}t[c,n] : K_{n,t}(x,y) = Tr(SU \times JUy \times SU^{-1} \times ST \times JTy \times ST^{-1}) \tag{7}$$

where $t = 2y$ and $n = 2x$ and

$$JUx_6 = \begin{pmatrix}
0&0&0&0&0&0&0&0\\
0&0&0&0&0&0&0&0\\
0&0&1&0&0&0&0&0\\
0&0&0&1&0&0&0&0\\
0&0&0&0&1&0&0&0\\
0&0&0&0&0&4^x&0&0\\
0&0&0&0&0&0&4^x&0\\
0&0&0&0&0&0&0&9^x
\end{pmatrix}
\quad JUy_6 = \begin{pmatrix}
0&0&0&0&0&0&0&0\\
0&0&0&0&0&0&0&0\\
0&0&1&0&0&0&0&0\\
0&0&0&1&0&0&0&0\\
0&0&0&0&1&0&0&0\\
0&0&0&0&0&4^{x-y}&0&0\\
0&0&0&0&0&0&4^{x-y}&0\\
0&0&0&0&0&0&0&9^{x-y}
\end{pmatrix}$$

$$JTy_6 = \begin{pmatrix}
0&0&0&0&0&0&0&0\\
0&0&0&0&0&0&0&0\\
0&0&1&0&0&0&0&0\\
0&0&0&2^{2y}&0&0&0&0\\
0&0&0&0&2^{2y}&0&0&0\\
0&0&0&0&0&3^{2y}&0&0\\
0&0&0&0&0&0&\left(\frac{1-i\sqrt{3}}{2}\right)^{2y}&0\\
0&0&0&0&0&0&0&\left(\frac{1+i\sqrt{3}}{2}\right)^{2y}
\end{pmatrix}$$

The matrices JUx_8, JUy_8 and JTy_8 have the same form like those for $c = 6$. In the case of polyhex tori with 6 atoms in the tube cross-section we have:

$$\mathrm{H}[6,n] : K_n(x) = 3 + 2^{1+2x} + 9^x, n = 2x \tag{8}$$

$$\begin{aligned}\mathrm{VH}t[6,n] : K_{n,t}(x,y) = 1 + 2^{1+2x} + 9^x + (1/2(1 - i\sqrt{3}))^{2y} \\ +(1/2(1 + i\sqrt{3}))^{2y}, n = 2x, t = 2y\end{aligned} \tag{9}$$

We are interested to compute the difference $K_n - K_{n,t}$:

$$\begin{aligned}K_n(x) - K_{n,t}(x,y) &= 3 + 2^{1+2x} + 9^x - (1 + 2^{1+2x} + 9^x + (1/2(1 - i\sqrt{3}))^{2y} \\ &\quad +(1/2(1 + i\sqrt{3}))^{2y}) = 2 - (1/2(1 - i\sqrt{3}))^{2y} \\ &\quad -(1/2(1 + i\sqrt{3}))^{2y} = 2 - \left(\cos\left(-\frac{\pi}{3}\right) + \mathrm{i} \times \sin\left(-\frac{\pi}{3}\right)\right)^{2y} \\ &\quad - \left(\cos\frac{\pi}{3} + i \times \sin\frac{\pi}{3}\right)^{2y} = 2 - \cos\left(-\frac{2y\pi}{3}\right) \\ &\quad -\mathrm{i} \times \sin\left(-\frac{2y\pi}{3}\right) - \cos\frac{2y\pi}{3} - i \times \sin\frac{2y\pi}{3} \\ &= 2 - 2\cos\frac{2y\pi}{3}, \quad n = 2x, t = 2y\end{aligned} \tag{10}$$

We have three cases:

(a) $y = 3k$

$$\begin{aligned}K_n(x) - K_{n,t}(x,y) &= 2 - 2\cos\frac{2y\pi}{3} = 2 - 2\cos\frac{2 \times 3k\pi}{3} \\ &= 2 - 2\cos(2k\pi) = 0\end{aligned} \tag{11}$$

(b) $y = 3k + 1$

$$\begin{aligned}K_n(x) - K_{n,t}(x,y) &= 2 - 2\cos\frac{2y\pi}{3} = 2 - 2\cos\frac{2(3k+1)\pi}{3} = 2 - 2\cos \\ &\quad \times \left(2k\pi + \frac{2\pi}{3}\right) = 2 - 2\cos\frac{2\pi}{3} = 2 - 2 \times \left(-\frac{1}{2}\right) = 3\end{aligned} \tag{12}$$

(c) $y = 3k + 2$

$$\begin{aligned}K_n(x) - K_{n,t}(x,y) &= 2 - 2\cos\frac{2y\pi}{3} = 2 - 2\cos\frac{2(3k+2)\pi}{3} = 2 - 2\cos \\ &\quad \times \left(2k\pi + \frac{4\pi}{3}\right) = 2 - 2\cos\frac{4\pi}{3} = 2 - 2 \times \left(-\frac{1}{2}\right) = 3\end{aligned} \tag{13}$$

It follows that:

$$\begin{aligned} K[(6,3)\text{VH2}[6,n]] &= K[(6,3)\text{VH4}[6,n]] \\ K[(6,3)\text{VH6}[6,n]] &= K[(6,3)\text{H}[6,n]] \end{aligned} \tag{14}$$

The first two results are just as expected, because of identical graphs (see relation 1).

An important observation is that the number of geometric Kekulé structures for (6,3)VHt[6,n] tori ($t \bmod 2 = 0, t \neq k \times c, k = 0, 1, 2, \ldots$) is with 3 smaller than the number of geometric Kekulé structures for the non-twisted (6,3)H[6,n] torus:

$$K[(6,3)\text{VH}t[6,n]] + 3 = K[(6,3)\text{H}[6,n]],\ t \bmod 2 = 0,\ t \neq k \times c,\ k = 0, 1, 2, \ldots \tag{15}$$

In the case of polyhex tori with 8 atoms in the tube cross-section we have:

$$\text{H}[8,n] : K_n(x) = 1 + 3 \times 2^{1+x} + 2^{1+2x} + 16^x + (6 - 4\sqrt{2})^x + (6 + 4\sqrt{2})^x,\ n = 2x \tag{16}$$

$$\begin{aligned} \text{VH}t[8,n] : K_{n,t}(x,y) = {} & 1 + (-i)^{2y}2^x + i^{2y}2^x + 2^{1+2x} + (1-i)^{2y}2^{1+x-y} \\ & + (1+i)^{2y}2^{1+x-y} + 16^x + (6 - 4\sqrt{2})^{x-y}(2 - \sqrt{2})^{2y} \\ & + (6 + 4\sqrt{2})^{x-y}(2 + \sqrt{2})^{2y} n = 2x,\ t = 2y \end{aligned} \tag{17}$$

In the case of polyhex tori with $c = 8$, the difference $K_n - K_{n,t}$ is:

$$\begin{aligned} K_n(x) - K_{n,t}(x,y) = {} & 3 \times 2^{1+x} + (6 - 4\sqrt{2})^x + (6 + 4\sqrt{2})^x - (-i)^{2y}2^x - i^{2y}2^x \\ & - (1-i)^{2y}2^{1+x-y} - (1+i)^{2y}2^{1+x-y} - (6 - 4\sqrt{2})^{x-y} \\ & \times (2 - \sqrt{2})^{2y} - (6 + 4\sqrt{2})^{x-y}(2 + \sqrt{2})^{2y} = 3 \times 2^{1+x} \\ & - 2(-1)^y 2^x - (-2i)^y 2^{1+x-y} - (2i)^y 2^{1+x-y} \end{aligned} \tag{18}$$

There are two cases to consider, depending on parity of y:

(a) y = even

$$\begin{aligned} K_n(x) - K_{n,t}(x,y) &= 3 \times 2^{1+x} - 2(-1)^y 2^x - (-2i)^y 2^{1+x-y} - (2i)^y 2^{1+x-y} \\ &= 4 \times 2^x - 4i^y 2^x = 2^{x+2}(1 - i^y) \end{aligned} \tag{19}$$

$$\text{We know that } i^y = \begin{cases} -1, & \text{if } y = 2 \times \text{odd number} \\ +1, & \text{if } y = 2 \times \text{even number} \end{cases}$$

$$K_n(x) - K_{n,t}(x,y) = 2^{x+2}(1 - i^y) = \begin{cases} 2^{x+3}, & \text{if } y = 2 \times \text{odd number} \\ 0, & \text{if } y = 2 \times \text{even number} \end{cases} \tag{20}$$

Table 1 Values of Kekulé structures for polyhex tori with $c = 6$

Torus	K	Torus	K
(6,3)H[6,12]	539,636	(6,3)H[6,16]	43,177,796
(6,3)VH6[6,12]		(6,3)VH6[6,16]	
(6,3)VH2[6,12]	539,633	(6,3)VH2[6,16]	43,177,793
(6,3)VH4[6,12]		(6,3)VH4[6,16]	
(6,3)H[6,14]	4,815,740	(6,3)H[6,18]	387,944,780
(6,3)VH6[6,14]		(6,3)VH6[6,18]	
(6,3)VH2[6,14]	4,815,737	(6,3)VH2[6,18]	387,944,777
(6,3)VH4[6,14]		(6,3)VH4[6,18]	

(b) $y = \text{odd}$

$$\begin{aligned} K_n(x) - K_{n,t}(x,y) &= 3 \times 2^{1+x} - 2(-1)^y 2^x - (-2i)^y 2^{1+x-y} - (2i)^y 2^{1+x-y} \\ &= 3 \times 2^{1+x} + 2^{x+1} + i^y 2^{1+x} - i^y 2^{1+x} = 2^{x+3} \end{aligned} \tag{21}$$

It follows that:

$$\begin{aligned} &K[(6,3)\text{VH8}[8,n]] = K[(6,3)\text{H}[8,n]] \\ &K[(6,3)\text{VH2}[8,n]] = K[(6,3)\text{VH4}[8,n]] = K[(6,3)\text{VH6}[8,n]] \\ &K[(6,3)\text{VH2}[8,2x]] + 2^{x+3} = K[(6,3)\text{H}[8,2x]] \end{aligned} \tag{22}$$

According to relation (1), (6,3)VH2[8,n] $\equiv$ (6,3)VH6[8,n]. That's why

$$K[(6,3)\text{VH2}[8,n]] = K[(6,3)\text{VH6}[8,n]] \tag{23}$$

But (6,3)VH2[8,n] and (6,3)VH4[8,n] are not identical graphs (the distance matrix eigenvalues are different). However they have the same number of geometric Kekulé structures. It means that in the case of (6,3)VHt[8,n] family, K has some degeneracy (there are non-isomorphic molecular structures with the same K value).

An important observation is that the number of geometric Kekulé structures for (6,3)VHt[8,n] tori ($t \bmod 2 = 0, t \neq k \times c, k = 0, 1, 2, \ldots$) is with $2^{n/2+3}$ smaller than the number of geometric Kekulé structures for the non-twisted, parent (6,3)H[8,n] torus:

$$K[(6,3)\text{VH}t[8,n]] + 2^{x+3} = K[(6,3)\text{H}[8,n]], \quad n = 2x, t \mod 2 = 0, \quad t \neq k \times c, k = 0, 1, 2, \ldots \tag{24}$$

In the case of polyhex tori with 10 atoms in the tube cross-section, the transfer matrix of the twisted torus unit and the transfer matrix of the untwisted torus unit are 32×32 matrices. In this case the Jordan matrix decomposition is a very difficult task. That's why we could not derive an analytical formula to compute the number of geometric Kekulé valence structures of this family. Anyhow, we give some values for K calculated with formulas (2) and (3). See the next table.

Table 2 Values of Kekulé structures for polyhex tori with $c = 8$

Torus	K	Torus	K
(6,3)H[8,10]	1,266,049	(6,3)H[8,14]	297,715,201
(6,3)VH8[8,10]		(6,3)VH8[8,14]	
(6,3)VH2[8,10]	1,265,793	(6,3)VH2[8,14]	297,714,177
(6,3)VH4[8,10]		(6,3)VH4[8,14]	
(6,3)VH6[8,10]		(6,3)VH6[8,14]	
(6,3)H[8,12]	19,294,721	(6,3)H[8,16]	4,636,018,689
(6,3)VH8[8,12]		(6,3)VH8[8,16]	
(6,3)VH2[8,12]	19,294,209	(6,3)VH2[8,16]	4,636,016,641
(6,3)VH4[8,12]		(6,3)VH4[8,16]	
(6,3)VH6[8,12]		(6,3)VH6[8,16]	

Table 3 Values of Kekulé structures for polyhex tori with $c = 10$

Torus	K	Torus	K
(6,3)H[10,10]	25,659,185	(6,3)H[10,16]	472,667,793,537
(6,3)VH10[10,10]		(6,3)VH10[10,16]	
(6,3)VH2[10,10]	25,637,825	(6,3)VH2[10,16]	472,665,501,697
(6,3)VH8[10,10]		(6,3)VH8[10,16]	
(6,3)VH4[10,10]	25,637,825	(6,3)VH4[10,16]	472,665,501,697
(6,3)VH6[10,10]		(6,3)VH6[10,16]	
(6,3)H[10,12]	673,941,712	(6,3)H[10,18]	12,577,743,194,960
(6,3)VH10[10,12]		(6,3)VH10[10,18]	
(6,3)VH2[10,12]	673,841,497	(6,3)VH2[10,18]	12,577,732,089,725
(6,3)VH8[10,12]		(6,3)VH8[10,18]	
(6,3)VH4[10,12]	673,841,497	(6,3)VH4[10,18]	12,577,732,089,725
(6,3)VH6[10,12]		(6,3)VH6[10,18]	
(6,3)H[10,14]	17,813,029,625	(6,3)H[10,20]	335,456,786,609,617
(6,3)VH10[10,14]		(6,3)VH10[10,20]	
(6,3)VH2[10,14]	17,812,552,865	(6,3)VH2[10,20]	335,456,732,462,977
(6,3)VH8[10,14]		(6,3)VH8[10,20]	
(6,3)VH4[10,14]	17,812,552,865	(6,3)VH4[10,20]	335,456,732,462,977
(6,3)VH6[10,14]		(6,3)VH6[10,20]	

The results from Tables 1 to 3 (VHt[10,10] tori family) are identical to those obtained by a computer programme based on generation of all possible solutions of geometric Kekulé structures.

4 Conclusion

Some analytical formulas for calculating Kekulé structure counts, K, for two families of polyhex tori ((6,3)VH$t[6,n]$ and (6,3)VH$t[8,n]$) are derived and examples are given for some tori of these families. Because of the limits imposed by the Jordan matrix decomposition, for (6,3)VH$t[c,n]$ tori with $c \geq 10$, attempts to derive an analytical formula to compute the number of geometric Kekulé valence structures, failed.

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