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# Trend of Kekulé Valence Structures Number in H-cut V-twisted Polyhex Tori. Relation Between Stability and Kekulé Structures Count

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**Abstract.** Usually, a higher value for the number of Kekulé valence structures ($K$) is associated with a higher stability of the molecule. But there are also exceptions. The thin-tubed polyhex tori are more strained and yet have the largest $K$ value. Numerical calculations of strain energy and $K$ for families of polyhex tori are given. The trend of the number of Kekulé valence structures of some twisted families of polyhex tori (T(6,3)VH$t$[$c$,$n$]) are also presented.

## POLYHEX TORI

Among the carbon allotropes, the torus is the only closed (orientable) surface which can be tiled entirely with hexagons.

There are three methods for generating a polyhex torus.[1] The *graphite zone-folding* procedure[2-5] is the most often used to cover a torus by hexagons. The method defines an equivalent planar parallelogram on the graphite sheet and identifies a pair of opposite sides to form a tube. Finally the two ends of the tube are glued together in order to form a torus. The resulting polyhex torus is completely defined by four independent integer parameters,[3,4,6,7] reducible to three parameters.[3,5,8]

A second procedure uses the so-called topological coordinates, extracted from the adjacency matrix eigenvectors.[9-12]

The third method starts from the tetragonal (4,4) net embedded on the toroidal surface.[13,14] In this way, a square torus is achieved. The squares are then changed to hexagons by using cutting operations.[15-17]

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 edge-cut location.[1,15] 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's terms.[15] The name of such a torus is a string of characters specifying the tiling and dimensions of the net, T(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 *cutting* procedures in the following two ways:[1,15,18]

(1) twisting the horizontal connections (Figure 1 (c) and (e)) and

(2) twisting the vertical (offset) connections (Figure 1 (d) and (f)).

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

(a) H-cut: T(6,3)H[*c*,*n*];

(b) V-cut: T(6,3)V[*c*,*n*];

(c) H-twist, H-cut: T(6,3)HH*t*[*c*,*n*];

(d) V-twist, H-cut: T(6,3)VH*t*[*c*,*n*];

(e) H-twist, V-cut: T(6,3)HV*t*[*c*,*n*];

(f) V-twist, V-cut: T(6,3)VV*t*[*c*,*n*].

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

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* so that distinct topological objects are obtained, are given by the *Rules of* Valencia:[1]

**(i)** The maximum value of $t$ to provide distinct topological objects, in a family of H-twisted polyhex tori, equals $n/2$.

**(ii)** The maximum value of $t$ to provide distinct topological objects, in a family of V-twisted polyhex tori, equals $c/2$.

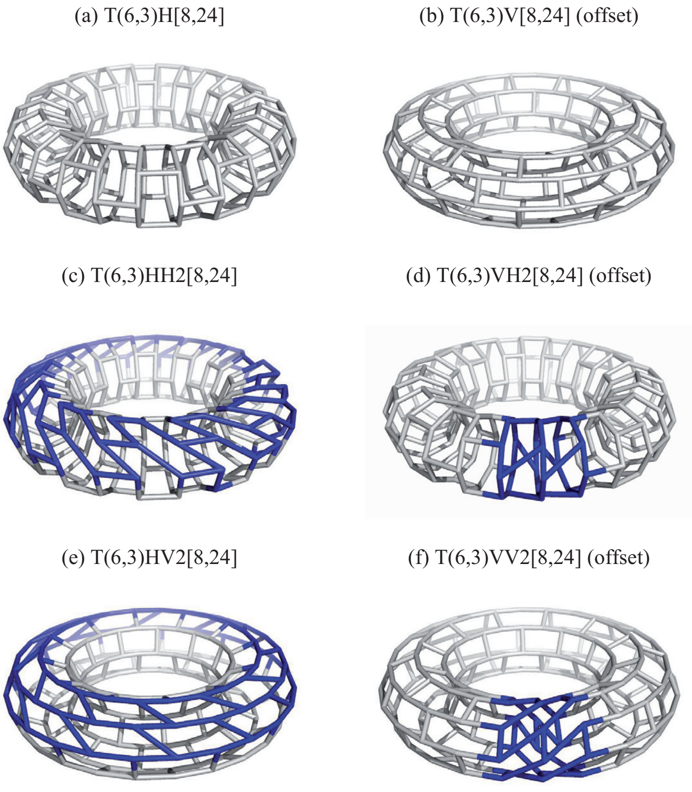


Figure 1: The six classes of polyhex tori (non-optimized geometry).

## KEKULÉ STRUCTURES IN FAMILIES OF V-twisted, H-cut POLYHEX TORI

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.[19,20]

A Kekulé structure coincides with a perfect matching and a 1-factor in the Graph Theory. The number of Kekulé valence structures, *K*, for a molecule is the number of 1-factors of the associate molecular graph.

To count the number of geometric Kekulé valence structures for V-twisted-H-cut-polyhex tori T(6,3)VH*t*[*c*,*n*], $c \in \{6,8\}$, we used the analytical formulas obtained with transfer matrix method:[21]

a) T(6,3)VH*t*[6,*n*], $t \in \{0,2\}$

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

**TVH*2*[6,*n*]:** $$K_{n,2}(x,y) = 2^{1+2x} + 9^x,\ \ n = 2x \tag{3}$$

b) T(6,3)VH*t*[8,*n*], $t \in \{0,2,4\}$

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

**TVH2[8,*n*]:** $$K_{n,2}(x,y) = 1 + 3\times 2^{1+x} + 2^{1+2x} + 16^x + (6-4\sqrt{2})^x + (6+4\sqrt{2})^x - 2^{x+3},\ \ n = 2x \tag{5}$$

**TVH4[8,*n*]:** $$K_{n,4}(x,y) = 1 + 3\times 2^{1+x} + 2^{1+2x} + 16^x + (6-4\sqrt{2})^x + (6+4\sqrt{2})^x - 2^{x+3},\ \ n = 2x \tag{6}$$

Because of the limits imposed by the Jordan matrix decomposition, for tori T(6,3)VH*t*[*c*,*n*] of $c \geq 10$ we were not able to obtain an analytical formula for the number of geometric Kekulé valence structures, *K*. For counting the values of *K* in the case of V-twisted, H-cut polyhex tori T(6,3)VH*t*[*c*,*n*], $c \in \{10,12,14,16,18,20\}$, we used the following formulas:[21]

a) T(6,3)VH*t*[*c*,*n*]

$$K_{VH}(x,y) = Tr(AT^{2y} \times AU^{x-y});\ \ t = 2y\ ;\ n = 2x \tag{7}$$

b) T(6,3)H[*c*,*n*]

$$K_H(x) = Tr(AU^x);\ n = 2x \tag{8}$$

where *Tr(A)* denotes the trace of the matrix *A*, and *AT* and *AU* denote the transfer matrices of the twisted and untwisted units of T(6,3)VH*t*[*c*,*n*].

The order of the matrices $AT$ and $AU$ grows exponentially with the number of atoms in the tube cross-section ($2^{c/2}$). By this reason, we calculated the values of $K$ only for families of polyhex tori up to 20 atoms in the tube cross-section.

More information about formulas (2)-(8), the reader can find in reference 21.

Figures 2-10 show the trend of $K$ in some families of twisted tori T(6,3)VH*t*[*c*,*n*], $c \in \{6,8,10,12,14,16,18,20\}$.

**T(6,3)VH*t*[6,n]**

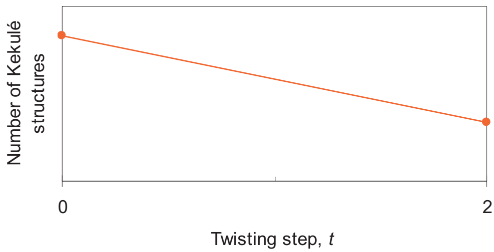


Figure 2: Trend of Kekulé valence structures number in T(6,3)VH*t*[6,*n*], *n*=6,8,10,… family

**T(6,3)VH*t*[8,n]**

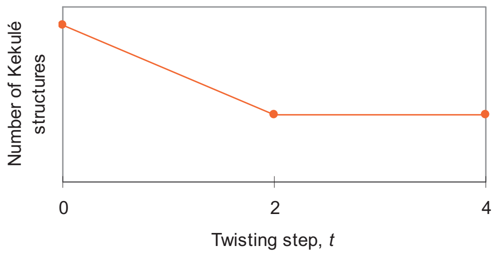


Figure 3: Trend of Kekulé valence structures number in T(6,3)VH*t*[8,*n*], *n*=8,10,12, … family

**T(6,3)VH*t*[10,n]**

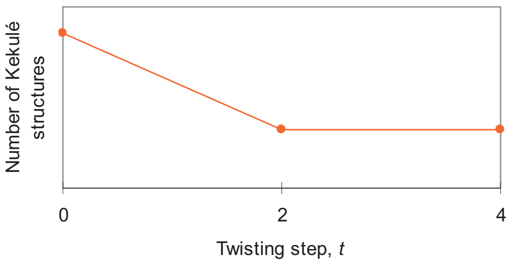


Figure 4: Trend of Kekulé valence structures number in T(6,3)VH*t*[10,*n*], *n*=8,10,…,100 family

**T(6,3)VH*t*[12,n]**

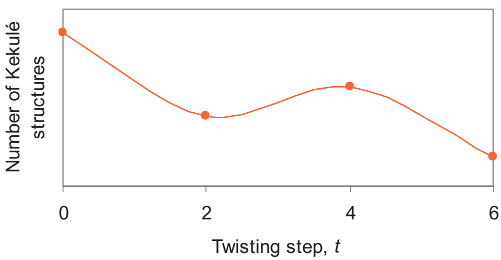


Figure 5: Trend of Kekulé valence structures number in T(6,3)VH*t*[12,*n*], *n*=6,8,…,60 family

**(6,3)VH*t*[14,n]**

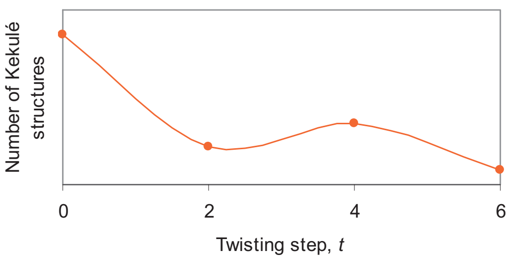


Figure 6: Trend of Kekulé valence structures number in T(6,3)VH*t*[14,*n*], *n*=8,10,…,44 family

**T(6,3)VH*t*[16,n]**

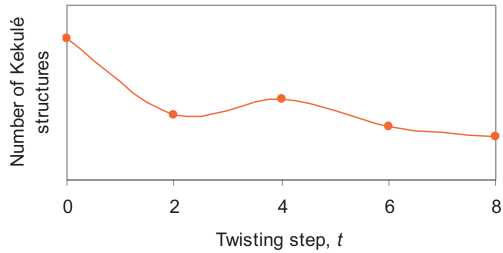


Figure 7: Trend of Kekulé valence structures number for (6,3)VH*t*[16,*n*], *n*=8,10,…,50 family of tori

**T(6,3)VH*t*[18,n]**

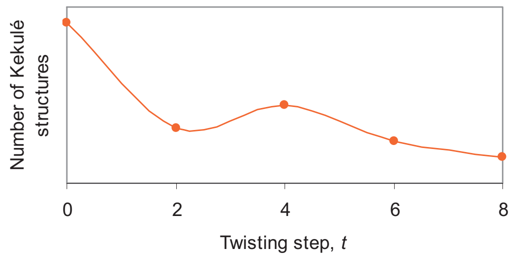


Figure 8: Trend of Kekulé valence structures number in T(6,3)VH*t*[18,*n*], *n*=8,10,…,36 family

**T(6,3)VH*t*[18,n]**

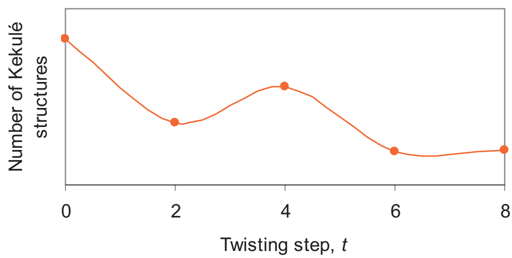


Figure 9: Trend of Kekulé valence structures number in T(6,3)VH*t*[18,*n*], *n*=38,40,…,56 family

**T(6,3)VH*t*[20,n]**

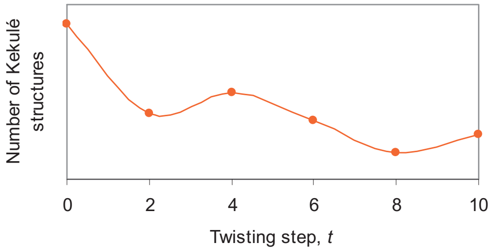


Figure 10: Trend of Kekulé valence structures number for (6,3)VH*t*[20,*n*], *n*=10,12,…,44 family

From the graphics (Figures 3 and 4) it appears that the number *K* has some degeneracy, *i.e*., there are non-isomorphic molecular structures with the same *K* value. Thus, the polyhex tori T(6,3)H[*c*,*n*] with 8 atoms in the tub cross-section, have the same number of Kekulé structures when 2, respectively 4 layer connections are twisted (*i.e*., *t*=2 and *t*=4, respectively). The same thing happens in the case of polyhex tori T(6,3)H[*c*,*n*] with 10 atoms in the tub cross-section.

In all the cases, the maximum value for *K* is reached for the untwisted torus (twisting step *t*=0). In the case of polyhex tori with 6,8,10,12,14,16 atoms in the tube cross-section, the minimum value for *K* is obtained when the twisting is maximum (twisting step $t = c/2 \text{ } if \text{ } c/2 \text{ } is \text{ } even \text{ } or \text{ } c/2-1 \text{ } if \text{ } c/2 \text{ } is \text{ } odd$). For the family of tori T(6,3)H[**18**,*n*], with *c*=18, the above finding is true up to *n*=36; n> 36, the minimum *K*-value is obtained when *t*= 6. In the case of T(6,3)H[**20**,*n*] family, with *c*=20, the minimum value of *K* is obtained at the twisting step *t*= 8. Finally, local minima/maxima are recorded for *t*=2 and *t*=4, respectively.

The tori from our study have been generated by TORUS 3.0 software package[18]. We used a Molecular Mechanics procedure (MM+) to optimize the tori in Table 1. The strain energy was estimated in terms of POAV1 theory.[22-24]

Usually, a molecule with a higher *K* value is more aromatic and more stable.[19,25] There are, however, 20 $C_{60}$ isomers, less stable (non-spherical, non-IPR, strained isomers), with *K* > 12500, which is the *K* value of Buckminsterfullerene $C_{60}$.[26]

In the case of non-planar molecules, the strain in the σ-frame is an important energetic factor which may revert the expected ordering. Thus, in toroidal polyhexes T(6,3)H[*c*,*n*], as the tube cross-section of tori increases, the structure becomes less strained and meanwhile the *K*-value decreases (see Tables 1 and 2). There are exceptions, amongst the studied cases: T(6,3)H[10,$n_1$] are more strained than T(6,3)H[12,$n_2$], ($10\times n_1 = 12\times n_2$), while smaller *K*-values are recorded.

Table 1. Strain energy/atom (kcal/mol) and *K*-value in polyhex tori; $N \leq 640$

| **Polyhex Torus TH[*c*,*n*]** | **N No. Atoms** | **Strain Energy** | **Kekulé Valence Structures Number** |
|---|---|---|---|
| [6,40] | 240 | 20.8037 | 12157667658080184356 |
| [8,30] | 240 | 11.0003 | 1162892088422301697 |
| [10,24] | 240 | 9.3648 | 239984311467844752 |
| [12,20] | 240 | 7.9419 | 295417896035533968 |
| | | | |
| [8,40] | 320 | 10.8858 | 1211071807802910030430209 |
| [10,32] | 320 | 8.7760 | 125182553077333588651137 |
| [16,20] | 320 | 6.1354 | 74724110026538983364609 |
| | | | |
| [6,60] | 360 | 20.9957 | 42391158277522046523508127156 |
| [10,36] | 360 | 8.4753 | 91145194531044333281676112 |
| | | | |
| [8,50] | 400 | 10.831 | 1268112485547288541280650395649 |
| [10,40] | 400 | 8.2088 | 66666933026281285404161681217 |
| | | | |
| [6,80] | 480 | 21.0667 | 147808829414348341167722439464732709956 |
| [8,60] | 480 | 10.8000 | 1329327408283709635421659976559493121 |
| [10,48] | 480 | 7.76110 | 36080406830883453872925278999557392 |
| [12,40] | 480 | 6.5393 | 83031252203688279528426787942996368 |
| [16,30] | 480 | 5.5626 | 15090599526434375752916536601794561 |
| [20,24] | 480 | 4.7634 | 13664460468885647476885222505347328 |
| | | | |
| [6,100] | 600 | 21.1039 | 515377520732011333571762330222080075695513932756 |
| [10,60] | 600 | 7.2630 | 14681270076404482401003780113505534329674192 |
| [12,50] | 600 | 6.0358 | 44554637804150176790714877135727741668853044 |
| [20,30] | 600 | 4.5314 | 4131354937436509571481868391492823407912784 |
| | | | |
| [10,64] | 640 | 7.1248 | 10925455416997565371127420402247070494617125377 |
| [16,40] | 640 | 5.1197 | 3143927968441616999566866746371525536609239041 |
| [20,32] | 640 | 4.4600 | 2783506221259044138095697187375654905511811073 |

Table 2. Strain energy/atom (kcal/mol) and $K$-value in polyhex tori; $N \geq 720$

| Polyhex Torus | N No. Atoms | Strain Energy | Kekulé Valence Structures Number |
|---|---|---|---|
| H[6,120] | 720 | 21.1284 | 17970102999144312104158382855011748714772832416584117955556 |
| H[10,72] | 720 | 6.9151 | 6078269162146626671474674605487572513190282597364112 |
| H[12,60] | 720 | 5.6494 | 23914117952111855436624910408837192462302763328010000 |
| H[18,40] | 720 | 4.7575 | 2319824659252931003637448250118043388511547051736804 |
| H[20,36] | 720 | 4.3232 | 1269423484114330499163674916369911620460871835543808 |
| | | | |
| H[8,100] | 800 | 10.7547 | 1606938257597038235825172307142159478070066911211326955061249 |
| H[10,80] | 800 | 6.7722 | 339724912148887735389157434968386141146242118850257786041 7 |
| H[16,50] | 800 | 4.7289 | 66963693070256067683442924940007394768841314379098901 7089 |
| H[20,40] | 800 | 4.1989 | 5819941720305932146212167004181584871225953044443098667 53 |
| | | | |
| H[6,140] | 840 | 21.7486 | 626578748217797037925622698193508014853458713877544935590478629 8356 |
| H[10,84] | 840 | 6.7222 | 2543097283320521339234163856087459974959955635846978986652752 |
| H[12,70] | 840 | 5.3532 | 12835956120213213051233154506115479088788876634455334578328756 |
| H[14,60] | 840 | 4.8608 | 1805991540343990027625400111934985214290650098388541555231393 |
| H[20,42] | 840 | 4.1409 | 394741522900917843761658538019947167809699572918813956154704 |
| | | | |
| H[8,110] | 880 | 10.7498 | 16849967126140887107651158106764486212543537257901541186974253 05601 |
| H[10,88] | 880 | 6.6854 | 190499489099342533463421333773717448455391865812900355329487481 7 |
| H[20,44] | 880 | 4.0858 | 26800432325978342877749183784049677974058565834492533254992115 3 |
| | | | |
| H[6,160] | 960 | 24.9882 | 21847450052839212624230656505913238417228855941320121546245389987974797441156 |
| H[10,96] | 960 | 6.6353 | 107067255459553318174789970235176765984999208768637881885655960879771 2 |
| H[12,80] | 960 | 5.1247 | 6889750235395324055798909295008109359555354209318250813237889753527568 |
| H[16,60] | 960 | 4.2939 | 1450218387494029807027925068557677695999761623220459202695921223598 09 |
| H[20,48] | 960 | 3.9853 | 1238661825823851119346792030714040852208072599712789692597260534458 88 |

**CONCLUSIONS**

In this article, the trend of the number of Kekulé valence structures of some families of twisted polyhex tori ((6,3) VH*t*[*c*,*n*]), $c \in \{6, 8, 10, 12, 14, 16, 18, 20\}$ is presented for the first time; regularities between the maximum/minimum value of $K$ and the twisting value were evidenced.

Numerical calculations of the Kekulé valence structures number and strain energy in some families of polyhex tori T((6,3)H[*c*,*n*]) were reported. Our results support the previous finding that the polyhex tori with thin-tube show the largest $K$-values although they are more strained. We also found exceptions: T(6,3)H[10,$n_1$] are more strained than T(6,3)H[12,$n_2$], ($10\times n_1=12\times n_2$), while smaller $K$-values are recorded.

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