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Kekulé Valence Structures for Some Families of Tu(6,3)HH*t*[*c*,*n*] Tubes

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Abstract. The trend of Kekulé valence structures number (*K*) of some twisted families of polyhex tubes (Tu(6,3)HH*t*[*c*,*n*]) is presented. The polyhex tubes with thin diameter are more strained and have the largest *K* value. An analytical formula for calculating the *K* value of Tu(6,3)H[*c*,*n*] tubes is presented. Numerical calculations of strain energy and *K* for families of Tu(6,3)H[*c*,*n*] tubes are also given.

INTRODUCTION

A polyhex tube can be designed from a tetragonal (4,4) net embedded[1] on the cylinder. Next, the (4,4) pattern is modified (using cutting operations) to give a hexagonal (6,3) net.[2-6]

By deleting each second *horizontal* edge and alternating edges and cuts in each second row it results in a standard (6,3)H/Z pattern (Figure 1,a). A *vertical* action of the above algorithm leads to a standard (6,3)V/A pattern (Figure 1,b). The specifications Z (zigzag) and A (armchair) come from the shape of the tube cross-section.

The tubes thus generated are named by a string specifying the tiling and dimensions of the net: Tu(6,3)[*c*,*n*]), with the (integer) parameters in the tetragonal brackets being the number of atoms in the tube cross-section (*c*) and the number of cross-sections along the tube (*n*).

Twisted, chiral, tubes can be generated by horizontal twisting of a row of connections (Figure 2,a). Edge cutting is further needed to change squares into hexagons (Figure 2,b); an even number of layers is needed to be twisted to obtain a hexagonal net.[2,6]

(a) (6,3)H/Z pattern (b) (6,3)V/A pattern

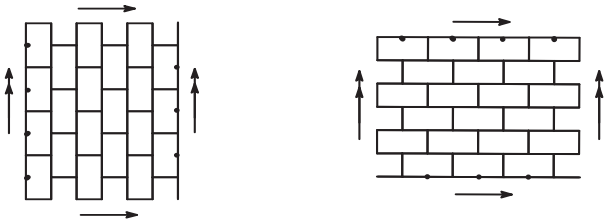


Figure 1: The (6,3) covering by H- (a) and V- (b) cutting of the (4,4) net.

(a) (4,4) net (a) (6,3) net

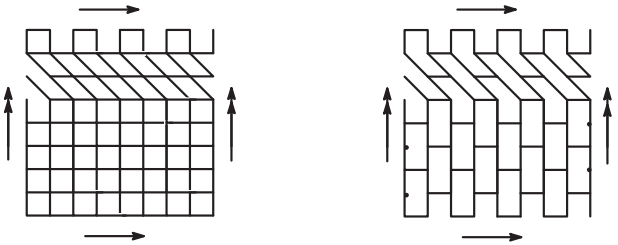
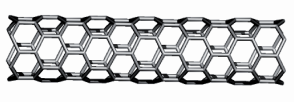


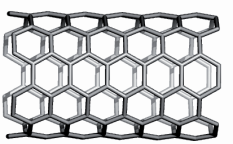
Figure 2: Twisted (4,4) pattern (a) and its (6,3) derivative (b).

In the name of tubes, Tu(6,3)HH*t*[*c*,*n*], the first H denotes the twisting, the second gives the type of cut and *t* denotes the number of twisted layers. The number of atoms on the *c*-dimension increases as *t* increases, concomitant with the shortening of *n*-dimension (in general, non-integer values, having a statistical meaning).[7] The twisting preserves the type of net (Z, in this case) and the total number of hexagons as well (*e*.g., (*c*/2) × (*n*-1)), the same as in the non-twisted tube. Correspondingly, the number of "zigzags" (*i.e*., the number of end-hexagons) increases, from *c*/2 up to twice the initial value (Figure 3). The final object will be Tu(6,3)HH*c*[*c*,*n*] = Tu(6,3)H/Z[2*c*,*n*/2]. Note that diameter doubling of single walled nanotubes has been observed experimentally [8,9] and termed "tube coalescence".

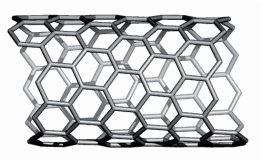
Tu(6,3)H/Z[12,12]



Tu(6,3)V/A[12,12]



Tu(6,3)HH10[12,12]



Tu(6,3)HH12[12,12];
Tu(6,3)HV12[12,12]= Tu(6,3)H/Z[24,6]

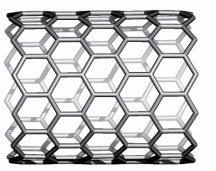


Figure 3: Nanotube twisting; diameter doubling at $t = c$ is evident by comparing the top left corner tube with the bottom right one.

KEKULÉ VALENCE STRUCTURES IN TWISTED H/Z POLYHEX TUBES

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.[10,11]

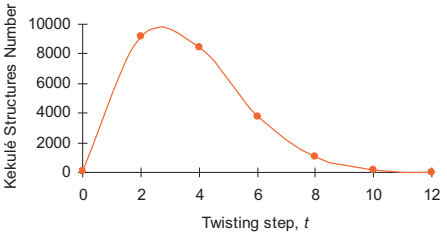
A Kekulé structure coincides with a perfect matching and a 1-factor in the Graph Theory. The number of Kekulé valence structures, *K*, of a molecule is the number of 1-factors of its associate molecular graph.

The tubes under study have been generated with TORUS 3.0 software package.[12] A Molecular Mechanics procedure (MM+) was used to optimize the tubes and, finally, a semi-empirical method (PM3). The strain energy was estimated in terms of POAV1 theory.[13-15]

In the following, the results obtained for the family of tubes Tu(6,3)HH*t*[12,6] are presented.

Generation of all Kekulé structures, has shown that, at the maximum twisting (*t*=*c*), the tube has the minimum value of *K* (Figure 4). The twisting leads to more relaxed tubes, by decreasing the strain of their surface, as shown in Figure 5. This is a consequence of the process

ending in diameter doubling of the tube.



t	*K*
0	64
2	9165
4	8408
6	3753
8	1086
10	167
12	8

Figure 4: Number of Kekulé valence structures for the family of tubes Tu(6,3)HH*t*[12,6]

The number Kekulé valence structures has a trend similar to that shown in Figure 4 for all the families of polyhex tubes Tu(6,3)HH*t*[*c*,*n*] we studied, with a minor variation: the twisting step *t* for which *K* shows the maximum value (listed in Table 1).

Table 1: Twisting step for which *K* has maximum value

	***n*=4**	**6**	**8**	**10**	**12**	**14**	**16**	**18**	**20**	**22**
***c*=6**	2	2	2	2	2	2	2	2	2	2
8	2	2	2	2	2	2	2			
10	2	2	2	2	2	4	4			
12	2	2	4	4	4					
14	2	4	4	4						
16	2	4	4	4						
18	2	4	4							
20	2	4	4							
22	2	4	4							
24	2	4	4							
26	2	4	4							
28	2	4	4							
30	2	4	4							
32	2	4								
34	2	4								
36	2	4								
38	2	6								
40	2	8								

The strain energy and the heat of formation for these families of tubes have the same trend as shown in Figures 5 and 6, respectively.

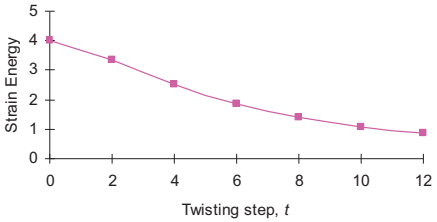


Figure 5: Strain energy for the family of tubes Tu(6,3)HH*t*[12,6]

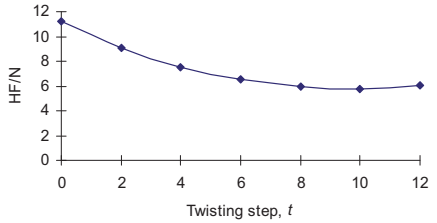


Figure 6: Heat of formation per atom for the family of tubes Tu(6,3)HH*t*[12,6]

KEKULÉ VALENCE STRUCTURES FOR UNTWISTED H/Z POLYHEX TUBES

For polyhex tubes Tu(6,3)H[*c*,*n*], we propose an analytical formula enabling the calculation of K number:

$$K(Tu(6,3)H[c,n]) = 2^n \qquad (1)$$

Proof. Let's consider a cross-section, being terminal at least in the left hand part (Figure 7).

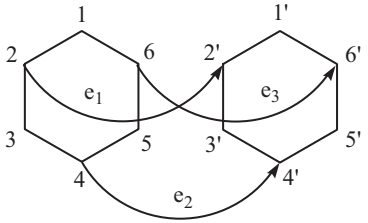


Figure 7: Section of Tu(6,3)H[6,n] (two cross-sections and the bonds joining them)

The size of the tube cross-section is always even. Double bonds and vertices covered by them are colored. If only one bond e_1, e_2, or e_3 is double (Figure 8,a), the terminal cross-section will remain with an odd number of vertices, therefore no perfect matching exists and K=0 for the section considered. If two bonds are double (Figure 8,b), the terminal cross-section will have one isolated vertex, therefore K=0. If all bonds e_1, e_2, e_3 are double (Figure 8,c), the terminal cross-section will have three isolated vertices, and again K=0. If all bonds e_1, e_2, e_3 are single, there are two ways for covering each cross-section by double bonds, therefore K=2 for each cross-section, and the pair sections in Figure 7 will have 2×2=4 Kekulé valence structures (Figure 9). The above argument can be generalized for any even dimension of the tube cross-section.

In conclusion, for a tube Tu(6,3)H[c,n], every Kekulé valence structure has all the double bonds on the cross-section bonds. Because the cross-section rings are bipartite (allways have an even number of atoms), there are only two ways of covering. That's why $K=2^n$ for the Tu(6,3)H[c,n] tube.

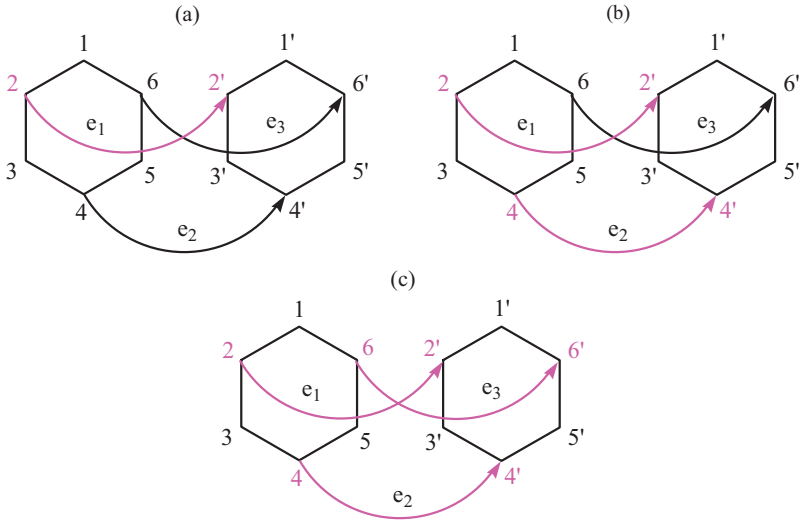


Figure 8: One bond e_1, e_2, e_3 is double (a); Two bonds e_1, e_2, e_3 are double (b); all bonds e_1, e_2, e_3 are double (c)

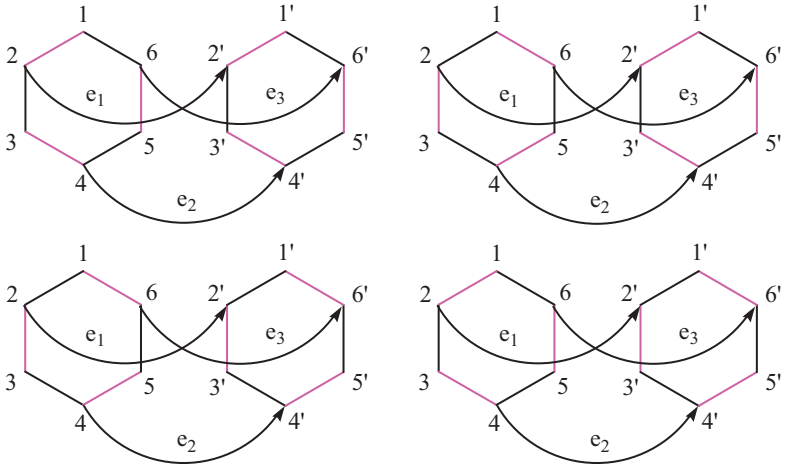


Figure 9: The 4 Kekulé structures of the section considered

The same result was obtained by Sachs *et al.*[16]

From the chemistry of planar benzenoid molecules, it is known that a molecule with a higher *K* value is more aromatic and more stable.[10,17] But in the case of non-planar molecules, the strain of the σ-frame becomes an important energetic factor which may revert the expected ordering.[18,19] As the tube cross-section increases, the molecular structure becomes less strained and the *K*-value decreases (Table 2). Therefore, a larger *K* value correlates here with a decrease in the tube stability.

Table 2. Trend of the Strain Energy/atom and K-values in tubes of increasing cross-section size.

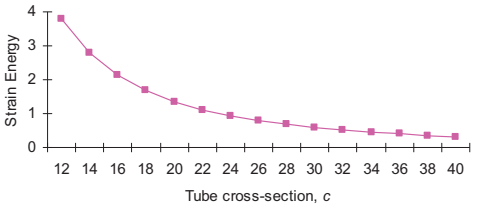
Polyhex Tube	Number of Atoms	Strain Energy	*K*
TuH[8,6]	48	9.9325	64
TuH[12,4]	48	3.807	16
TuH[16,3]	48	1.9842	8
TuH[8,7]	56	10.1073	128
TuH[14,4]	56	2.7987	16
TuH[12,5]	60	3.9271	32
TuH[20,3]	60	1.2454	8
TuH[10,7]	70	5.8269	128

Polyhex Tube	Number of Atoms	Strain Energy	*K*
TuH[12,8]	96	4.4171	256
TuH[16,6]	96	2.2667	64
TuH[24,4]	96	0.9369	16
TuH[32,3]	96	0.4589	8
TuH[14,8]	112	3.0421	256
TuH[16,7]	112	2.3148	128
TuH[28,4]	112	0.686	16
TuH[20,6]	120	1.4547	64

TuH[14,5]	70	2.8872	32
TuH[12,6]	72	4.0171	64
vH[18,4]	72	1.6841	16
TuH[10,8]	80	5.8945	256
TuH[16,5]	80	2.2137	32
TuH[20,4]	80	1.3595	16
TuH[12,7]	84	4.082	128
TuH[14,6]	84	2.956	64
TuH[28,3]	84	0.6119	8
TuH[18,5]	90	1.748	32
TuH[30,3]	90	0.5264	8

TuH[24,5]	120	0.9786	32
TuH[30,4]	120	0.5901	16
TuH[16,8]	128	2.3431	256
TuH[32,4]	128	0.5192	16
TuH[20,7]	140	1.4793	128
TuH[28,5]	140	0.7171	32
TuH[24,6]	144	1.0072	64
TuH[36,4]	144	0.4048	16
TuH[20,8]	160	1.4977	256
TuH[32,5]	160	0.5496	32

Let's consider the family of tubes Tu(6,3)H[c,4]. Because n has a constant value, all these tubes have the same K-value: $2^n=2^4=16$ (see formula (1)). However, the thin-tubed structures have the highest strain energy while the thick-tubed ones are the most relaxed (Figure 10). Thus, in the case of tubes Tu(6,3)H[c,n] (n =constant), the stability of structures does not depend on the Kekulé valence structures count. Similar results were obtained for tubes Tu(6,3)H[c,n] with $n \in \{3,5,6,7,8\}$.



Tube	SE	Tube	SE
H[12,4]	3.807	H[28,4]	0.686
H[14,4]	2.7987	H[30,4]	0.5901
H[16,4]	2.1352	H[32,4]	0.5192
H[18,4]	1.6841	H[34,4]	0.4555
H[20,4]	1.3595	H[36,4]	0.4048
H[22,4]	1.1198	H[38,4]	0.361
H[24,4]	0.9369	H[40,4]	0.3249
H[26,4]	0.7944		

Figure 10: Strain energy curve for Tu(6,3)H[c,4] tubes

CONCLUSIONS

In this article, it was shown that the twisting leads to more relaxed tubes, by decreasing the strain of their lattice. The number of the Kekulé valence structures was found larger in thinner tubes than in thicker ones but it is not involved in the stability of these molecular structures, as resulted by investigation of some twisted families of polyhex tubes

(Tu(6,3)HH*t*[*c*,*n*]). Our results confirm the previous finding that the thinnest polyhex tubes show the largest *K* value.

An analytical formula for the calculus of the Kekulé valence structures number in Tu(6,3)H[*c*,*n*] tubes was derived. Examples of numerical calculation of the strain energy and the *K*-values, in some families of polyhex tubes (Tu(6,3)H[*c*,*n*]) were also given.

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