J Math Chem (2009) 45:279–286
DOI 10.1007/s10910-008-9404-5

ORIGINAL PAPER

On Kekulé structures count

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Published online: 8 August 2008

Abstract Kekulé valence structures offer qualitative description of conjugated cyclic hydrocarbons, suggesting localization of CC single and CC double bonds. Generation of all geometric Kekulé structures for families of polyhex tori of a given tube cross-section, provided by the TORUS software, was performed by the new Kekulé Count software, developed on a coloring algorithm. The sets of all non-isomorphic Kekulé structures for the considered molecules, as the main result of this study, are presented.

Keywords Kekulé valence structures · Polyhex tori · Non-isomorphic Kekulé structures

1 Introduction

The notion of Kekulé structures is used in organic chemistry for quick estimation of molecular thermodynamic stability and is especially useful in the case of benzenoid molecules.

Kekulé valence structures offer a qualitative description of the conjugated cyclic hydrocarbons, suggesting the localization of CC single and CC double bonds. 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].

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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 for the associate molecular graph.

Clar recognized that a polycyclic system without Kekulé valence structures cannot exist [2]. Usually, a higher K value is associated with a higher stability of the molecule [1,3]. There are, however, 20 C_{60} isomers with $K > 12500$ (the K value of Buckminsterfullerene C_{60}) although they are less stable (non-spherical, non-IPR, strained isomers) [4,5].

Strain in the σ-frame is an important energetic factor, particularly in non-planar molecules, where it may revert the expected ordering. Thus, in toroidal polyhexes, the thin-tubed tori, with the highest strain, have the largest K value [4]. It appears that K alone is not a reliable guess of an energetically favorable structure.

There exist various techniques and methods for calculating the number of Kekulé valence structures K [1,6]. This number may be achieved either by generating all the possible solutions of geometric Kekulé structures or by using an algebraic evaluation.

In the case of benzenoid hydrocarbons we can take advantage of the fact that the absolute value of the constant term in the characteristic polynomial is the square of K and also the absolute value of the determinant of the adjacency matrix $\mathbf{A}$: $K^2 = \pm \det(\mathbf{A})$[3]. The necessary condition of using this method is the structure can be embedded in the plane (*i.e.*, the associate graph can be drawn in the plane with no edge crossing). Another necessary condition is the molecule must have no conjugated circuit with $4n\,\pi$-electrons [7].

Toroidal polyhex structures cannot be embedded in the plane, so that the method gives incorrect results in this case [4].

For all-polyhex hydrocarbons, the permanent of the adjacency matrix equals to the square of the Kekulé structures count, $K^2 = \mathrm{per}(\mathbf{A})$ [8]. The permanent is an analogue of a determinant where all the signs in the expansion by minors are taken as positive.

In the case of non-benzenoid hydrocarbons, e.g., fullerenes, neither of the two above methods can be applied.

For closed-shell structures, embeddable in the plane, K is easily calculated via the signed adjacency matrix $\mathbf{S}$: $K^2 = |det(\mathbf{S})|$ [9,10]. The signed adjacency matrix is related to the adjacency matrix of an oriented graph, with the distinction that some of its entries may be negative. The signs are such that: first, $\mathrm{S}(G)$ must be anti-symmetric; second, in any even face (*i.e.*, a minimal even-folded ring) the number of times a minus sign (anti-clockwise orientation of an edge) is encountered must be odd [6]. The signed adjacency matrix is not uniquely determined.

2 Geometric Kekulé structures and non-isomorphic Kekulé structures for polyhex tori

For generating all the possible solutions of geometric Kekulé structures we made use of the vertex coloring of the graph: no two adjacent atoms can have the same color and the number of colors is minimized. This Kekulé chromatic algorithm can be applied to any structure: planar molecules, fullerenes and toroids.

We used this algorithm to evaluate the number of geometric Kekulé valence structures for families of polyhex tori of a given tube cross-section, provided by the TORUS software [11]. The number of atoms in the cross-section is $c = 6$–10 (see below).

The sets of all non-isomorphic (symmetry distinct) Kekulé structures, in the above classes of tori, were obtained by using the following algorithm:

(1) generate the distance matrix—useful to find all the automorphisms;
(2) generate the group of automorphisms—by a simple backtracking algorithm;
(3) generate the geometric Kekulé structures;
(4) find the canonical Kekulé structures.

Naming polyhex tubular objects is given in Diudea terms [12,13]: a string 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.

We have two classes of simple tori and four classes of twisted tori:

(i) H-cut, H[c, n];
(ii) V-cut, V[c, n];
(iii) H-twist, H-cut HHt[c, n];
(iv) V-twist, H-cut, VHt[c, n];
(v) H-twist, V-cut, HVt[c, n];
(vi) V-twist, V-cut, VVt[c, n].

where c and n are as above and t is the number of twisted rows (see [14], Fig. 1).

Data about the Kekulé structure count K are listed in Tables 1–6. The software routines,developed for these calculations, are given in the Appendix.

Table 1 Values of Kekulé structure count for C_{60} tori

	Torus	Number of Kekulé structures	Number of symmetry distinct Kekulé structures
1	(6,3)H[6,10]		
	(6,3)VH6[6,10]	61100	645
2	(6,3)HH2[6,10]	62180	1204
3	(6,3)HH4[6,10]		
	(6,3)HH6[6,10]	39020	763
4	**(6,3)HV2[6,10]**	**38405**	755
5	**(6,3)HV4[6,10]**		
	(6,3)HV6[6,10]	**38405**	751
6	(6,3)VH2[6,10]		
	(6,3)VH4[6,10]	61097	1175
7	(6,3)VV2[6,10]		
	(6,3)VV4[6,10]	39437	777
8	(6,3)VV6[6,10]		
	(6,3)V[6,10]	39440	472

Table 2 Values of Kekulé structure count for C_{72} tori

	Torus	Number of Kekulé structures	Number of symmetry distinct Kekulé structures
1	(6,3)H[6,12]		
	(6,3)VH6[6,12]	539636	4131
2	(6,3)HH2[6,12]	547320	5282
3	(6,3)HH4[6,12]	285380	4249
4	(6,3)HH6[6,12]		
	(6,3)HV6[6,12]	263640	765
5	(6,3)HV2[6,12]	266601	4059
6	(6,3)HV4[6,12]	268545	4005
7	(6,3)VH2[6,12]		
	(6,3)VH4[6,12]	539633	7934
8	(6,3)VV2[6,12]		
	(6,3)VV4[6,12]	282132	4216
9	(6,3)VV6[6,12]		
	(6,3)V[6,12]	281268	2409

Table 3 Values of Kekulé structure count for C_{80} tori

	Torus	Number of Kekulé structures	Number of symmetry distinct Kekulé structures
1	(6,3)H[8,10]		
	(6,3)VH8[8,10]	1266049	8451
2	(6,3)HH2[8,10]		
	(6,3)HH8[8,10]	1165249	15152
3	(6,3)HH4[8,10]		
	(6,3)HH6[8,10]	980289	12787
4	**(6,3)HV2[8,10]**		
	(6,3)HV8[8,10]	**984577**	12810
5	**(6,3)HV4[8,10]**		
	(6,3)HV6[8,10]	**984577**	12800
6	**(6,3)VH2[8,10]**		
	(6,3)VH6[8,10]	**1265793**	16521
7	**(6,3)VH4[8,10]**		
8	(6,3)VV2[8,10]	**1265793**	8249
	(6,3)VV6[8,10]	983873	12966
9	(6,3)VV4[8,10]	992833	6778
10	(6,3)VV8[8,10]		
	(6,3)V8101	989217	6818

Table 4 Values of Kekule structures count for C_{84} tori

	Torus	Number of Kekulé structures	Number of symmetry distinct Kekulé structures
1	(6,3)H[6,14]		
	(6,3)VH6[6,14]	4815740	29748
2	(6,3)HH2[6,14]	4877284	59532
3	(6,3)HH4[6,14]	2112480	25855
4	(6,3)HH6[6,14]	1856588	22795
5	(6,3)HV2[6,14]	1876968	23070
6	(6,3)HV4[6,14]	1906669	23378
7	(6,3)HV6[6,14]	1849073	22709
8	(6,3)VH2[6,14]		
	(6,3)VH4[6,14]	4815737	58613
9	(6,3)VV2[6,14]		
	(6,3)VV4[6,14]	2054657	25197
10	(6,3)VV6[6,14]		
	(6,3)V[6,14]	2055209	13754

Table 5 Values of Kekule structure count for C_{96} tori

	Torus	Number of Kekulé structures	Number of symmetry distinct Kekulé structures
1	(6,3)H[8,12]		
	(6,3)VH8[8,12]	19294721	102763
2	(6,3) HH2[8,12]	17175809	181074
3	(6,3)HH4[8,12]		
	(6,3)HH8[8,12]	13251137	140355
4	(6,3)HH6[8,12]	12844289	68441
5	(6,3)HV2[8,12]	13004289	137269
6	(6,3)HV4[8,12]		
	(6,3)HV8[8,12]	13034049	137965
7	(6,3)HV6[8,12]	12962052	68933
8	**(6,3)VH2[8,12]**		
	(6,3)VH6[8,12]	**19294209**	202865
9	**(6,3)VH4[8,12]**	**19294209**	102020
10	(6,3)VV2[8,12]		
	(6,3)VV6[8,12]	13150148	138784
11	(6,3)VV4[8,12]	13219200	25048
12	(6,3)VV8[8,12]		
	(6,3)V[8,12]	13154448	71525

Table 6 Values of Kekule structure count for C_{100} tori

	Torus	Number Kekulé structures	Number of symmetry distinct Kekulé structures
1	(6,3)H[10,10]		
	(6,3)V[10,10]		
	(6,3)HH10[10,10]	25659185	131271
	(6,3)HV10[10,10]		
	(6,3)VH10[10,10]		
	(6,3)VV10[10,10]		
2	(6,3)HH2[10,10]		
	(6,3)HH8[10,10]	25457425	257065
3	(6,3)HH4[10,10]		
	(6,3)HH6[10,10]		
	(6,3)VV4[10,10]	25369225	256072
	(6,3)VV6[10,10]		
4	**(6,3)HV2[10,10]**		
	(6,3)HV8[10,10]		
	(6,3)VH2[10,10]	**25637825**	258761
	(6,3)VH8[10,10]		
5	**(6,3)HV4[10,10]**		
	(6,3)HV6[10,10]		
	(6,3)VH4[10,10]	**25637825**	258742
	(6,3)VH6[10,10]		
6	(6,3)VV2[10,10]		
	(6,3)VV8[10,10]	25457425	257065

From the tables it appears that the number K shows some degeneracy, *i.e.*, there are non-isomorphic molecular structures with the same K value. The boldface entries in tables mark the degenerate cases. Tables also include the identical graphs with different embedding (at one entry more than one structure); these identical graphs result as a consequence of the building procedure [15].

The results for the toroids C_{60} are identical to those reported by Cash [4], based on the permanent calculation.

3 Conclusions

Our chromatic algorithm for generating the geometric Kekulé valence structures can be applied to any structure, including the case of fullerenes and toroids. For the polyhex tori with the number of atoms larger than 60, the K-values and the number of non-isomorphic (symmetry distinct) Kekulé structures were reported here for the first time in literature.

Appendix

- **Kekulé chromatic algorithm for polyhex tori**

Generation of Kekulé structures is performed recursively, using the backtracking algorithm [16].

A solution (i.e., Kekulé structure) is recorded by arrays two strings (referred to as *Nod1* and *Nod2*, respectively), each having the number of elements equal to half of the number of atoms in the molecule. The elements in the corresponding position of the two arrays represent adjacent atoms, joined by a double bond.

The input parameter of the procedure is the position in the arrays of the solution.

```
Procedure findKekuleTwo(position k)
    If k = half the number of atoms in the molecule
    Then
        Found new solution
        Save solution
    Else execute
        Nod1[k] = atom at position k in the first color class
        For each atom x adjacent to the atom Nod1[k] and not contained in
Nod 2 execute
                    Nod2[k] = x;
                    findKekuleTwo(k+1);
        End for
    End if
End Procedure
```

- Finding canonical Kekulé structures

Let S be any set, ρ any relation of equivalence on S. We say that function $f : S \to X$is a canonizing function if:

$$f(s_1)\rho s_1 \text{ and } f(s_1) = f(s_2) \Leftrightarrow s_1 \rho s_2$$

and $f(s_1)$ is called canonical form of s_1. Obviously, $card(S/\rho)$ is equal to the number of elements identical to their canonical form. This technique is used to generate all the non-isomorphic Kekulé structures.

Let G be a labeled graph (having at least one Kekulé structure) which vertices are labeled 1,2,…,n. Denote by K the set of all Kekulé structures. The function $g : K \to \{1, \ldots, n\}^{\{1,\ldots,n\}}$ where $\{1, \ldots, n\}^{\{1,\ldots,n\}}$ is the set of all functions from $\{1, \ldots, n\}$ to $\{1, \ldots, n\}$ defined by:
$g(k)(i) = j$ if and only if ij is double bond in K.

It can be easily seen that the function K is an injection. The canonizing function on K is given by

$$F(k) = \min \{g(k') : k \text{ and } k' \text{ are isomophic}\},$$

where min uses lexicographical order defined by:

$x_1x_2...x_n < y_1y_2...y_n$ if and only if $(\exists i)((\forall j < i)(x_j = y_j) and x_i < y_i)$
Denote

- Let $P[NumAut][n]$ be a two-dimensional array in which the permutations that correspond to an isomorphism of the graph are stored
- Let $k[n/2][2]$ be a two-dimensional array in which the pairs of vertices covered by double bonds are stored
- $x$is the permutation that corresponds to $g(k)$
- $y$is the permutation that corresponds to $g(k')$ where k' is some permutation

The algorithm that calculates the canonical form is given in pseudo-code:
Put $x[k[i][0]] = k[i][1]$ and $x[k[i][1]] = k[i][0]$ for each $i = 1, ..., n/2$
Put $ThisIsSmallest = true$
For $ba = 1$ to $NumAut$
Put$y[P[ba][k[i][0]]] = P[ba][k[i][1]]$ and $y[P[ba][k[i][1]]] = P[ba][k[i][0]]$ for each $i = 1, \ldots, n/2$
If $y < x$ then put $ThisIsSmallest = false$ and end For-loop
If $ThisIsSmallest = true$ then this form is canonical.

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