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THE HUNT FOR CONCEALED NON-KEKULÉAN POLYHEXES

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Abstract

Concealed non-Kekuléan polyhexes are systems with no Kekulé structures, but with an equal number of black and white vertices. The history of the search for concealed non-Kekuléans is reviewed. Results for (a) computer-generations and enumerations on the one hand, and (b) graph-theoretical analyses on the other are reported. Polyhexes with and without holes are considered.

1. Introduction

Substantial parts of the material presented by one of us (S.J.C.) at the Third International Mathematical Chemistry Conference, Galveston, Texas (1989) were submitted to the J. Chem. Inf. Comput. Sci. [1]. Therefore, we shall not duplicate too much of that material in these proceedings, but we shall put emphasis on some highly relevant information which one of us gained at this very Conference. Furthermore, we include some original findings, some of them obtained from specific computer-generations of polyhexes which were running in Trondheim during the conference in Galveston.

The chemical implications of the studies of concealed non-Kekuléans (for a definition, see below) are not treated here. Nevertheless, this topic does have considerable chemical implications, but perhaps more mathematical interest, inasmuch as it gives more insight into the "anatomy" of the "hexagonal animals" (polyhexes). Finally, this research has aesthetical aspects, as will become apparent from some of the figures in the following.

2. Definitions

By "Conference", we mean the particular Conference referred to above.

A "polyhex" is taken in the sense as was explained by the contribution of Trinajstić and Nikolić at the Conference. A polyhex is Kekuléan or non-Kekuléan when it has or has not Kekulé structures, respectively.

We shall also treat polyhexes with holes and avoid the copious current designations for such systems (coronaphenes, circulenes, corona-condensed systems, coronoids, etc.). It is assumed that the hole should be larger than one hexagon. Among the polyhexes with holes, only systems with one hole each are taken into account here.

In order to define a concealed non-Kekuléan (polyhex, with or without hole) we need the concept of "color excess" or Δ-value. Assume that the vertices of a polyhex are colored in the usual way as black and white. Then Δ is the absolute magnitude of the difference between the number of black and white vertices. It is not necessary to count all the vertices in order to determine the value of Δ, since it has been found that Δ also is the absolute magnitude of the difference between the number of valleys and peaks. A valley (respectively, peak) is a vertex on a perimeter pointing south (respectively, north). More precise definitions have been given elsewhere. It seems unnecessary to go into further details here, but we give some examples in fig. 1. Note in particular that, in the case of polyhexes with holes, also the peaks and valleys on the inner perimeter (inside the hole) should be counted.

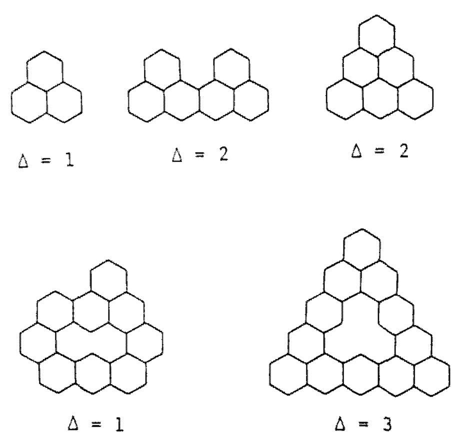

Fig. 1. Five obvious non-Kekuléans with the Δ values (color excess) indicated.

A Kekuléan polyhex obviously has $\Delta = 0$. Therefore, any polyhex with $\Delta > 0$ is non-Kekuléan and is called "obvious" non-Kekuléan. However, the condition $\Delta = 0$ is not sufficient for a polyhex to be Kekuléan. Non-Kekuléans with $\Delta = 0$ may be constructed and are the ones called "concealed" non-Kekuléans. In other words, a concealed non-Kekuléan is a polyhex with no Kekulé structure, but with an equal number of black and white vertices and an equal number of peaks and valleys.

The present authors have distinguished between non-Kekuléan benzenoids (without holes) and non-Kekuléan coronoids (with holes). This nomenclature does not conform with the one of Trinajstić and Nikolić advocated at the Conference. The controversy is avoided if we just speak about non-Kekuléans (with or without holes). Unfortunately, there are several incompatible nomenclatures currently used in this field of research. The authors look forward to a possible consensus on the basis of coming propositions, which were announced by Trinajstić at the Conference.

3. Historical

A systematic search for concealed non-Kekuléans appears to have started in 1974 with Gutman [2], who inferred that no concealed non-Kekuléans with less than eleven hexagons can be constructed, and depicted two such systems with $h = 11$. Here, h is used to designate the number of hexagons of the polyhex. These two concealed non-Kekuléans are marked **I** and **IV** in fig. 2. They have been quoted several times as Gutman's original findings, although Balaban [3] tried to share the credit for the "goblet" (**I** of fig. 2) between Gutman and Mallion with reference to a private communication from Mallion. This discussion, however, is uninteresting because Clar

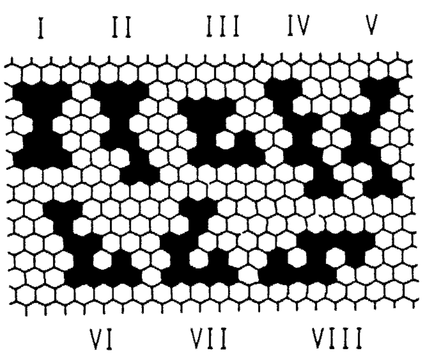

Fig. 2. The eight smallest (h = 11) concealed non-Kekuléans.

already in his well-known booklet of 1972 [4] depicted this system and characterized it completely such that it falls under our category of concealed non-Kekuléans. Therefore, we shall refer to **I** as the "Clar goblet". In 1981, Balaban [3] discovered the system **VIII** "by accident". Originally, he assigned this system to an incorrect category, but explained in a note added in proof with different wording, that it is a concealed non-Kekuléan. After a more conscious hunt for concealed non-Kekuléans, the same author [5] detected **III**, **V**, **VI** and **VII**. The remaining system of fig. 2, viz. **II**, was reported by Hosoya [6], who depicted for the first time the whole set of the smallest (h = 11) concealed non-Kekuléans (cf. fig. 2). The system **II** was also found independently by Cyvin and Gutman [7], who published the same eight concealed non-Kekuléans one year after Hosoya. None of these authors [6,7] claimed explicitly that the eight constructed concealed non-Kekuléans with $h = 11$ are the only such systems. However, this is in fact the case, as was first demonstrated by Brunvoll et al. [8]. This was done by computer-generations and classifications of polyhexes conducted independently in the People's Republic of China and Norway, using entirely different principles in the programming. Later, the same conclusion was reached by Zhang and Guo [9], who employed a graph-theoretical analysis.

4. More recent development for polyhexes without holes

The hunt for concealed non-Kekuléans has continued and accelerated substantially during the last two years. In the first place, it was natural to search for all the concealed non-Kekuléans with $h = 12, 13, \ldots$. Again, by independent computer analyses in PR China and Norway it was found that there are exactly ninety-eight concealed non-Kekuléans with $h = 12$ [10]. Furthermore, this result was later deduced by an extension of the graph-theoretical analysis [11]. However, the mathematical deductions do not always come after the computer-aided analysis. In the same work by Guo and Zhang [11], also the number of concealed non-Kekuléans with $h = 13$ (see table 1) was reported.

Table 1

Number of concealed non-Kekuléans and simply connected polyhexes in total

h	Concealed non-Kekuléans	Polyhexes total
11	8	141,229
12	98	669,584
13	1097	3,198,256
14	9781	15,367,577

One of the present authors was informed at the Conference that Jiang and Chen [12] derived the number 1097 for $h = 13$ independently of Guo and Zhang, and they extended their graph-theoretical analysis to $h = 14$ with the result shown in table 1. We wish to emphasize that these numbers (viz. 1097 and 9781) were obtained by mathematical analyses without computer aid. Brilliant achievements!

It is seen from table 1 that the concealed non-Kekuléans constitute a small fraction of the total number of polyhexes. More precisely, the percentage abundancies are 0.0057, 0.0146, 0.0343 and 0.0636 for $h = 11, 12, 13$ and 14, respectively. The numbers for polyhexes in total have been known for some time as far as $h = 11$ [13] and $h = 12$ [14] are concerned. The data for $h = 13$ and $h = 14$ (see table 1) were reported for the first time (together with the result for $h = 15$) by Trinajstić, as an achievement of the Düsseldorf–Zagreb group. Congratulations!

5. Polyhexes without holes and of specific symmetries

A further extrapolation of table 1 seems not to be of particular interest, but this is not the only possible way to study the concealed non-Kekuléans. Computer programming techniques have been developed [15,16] which allow a specific generation of certain classes of polyhexes. In particular, it is feasible to generate and enumerate polyhexes of specific symmetries.

Hosoya [17] described in 1986 a regular hexagonal (D_{6h}) concealed non-Kekuléan with forty-three hexagons, and conjectured that this is the smallest system of that kind. Soon thereafter, this was verified by computer analysis [16]. More precisely, it was found that the smallest concealed non-Kekuléan belonging to the D_{6h} symmetry is a unique system with $h = 43$, while four such systems of the C_{6h} symmetry and $h = 43$ can be constructed (cf. table 2). This table includes supplementary enumeration data for the polyhexes with hexagonal symmetries, the "snowflakes" [10,14,16,18,19].

Table 2

Numbers of concealed non-Kekuléans and simply connected polyhexes in total with hexagonal symmetry

	Concealed non-Kekuléan		Polyhexes	
h	D_{6h}	C_{6h}	D_{6h}	C_{6h}
43	1	4	13	527
49	0	42	20	2209
55	1	312	35	9470
61	1	*	60	*
67	4	*	104	*
73	7	*	183	*

*Unknown.

The forms of the five smallest ($h = 43$) concealed non-Kekuléans with hexagonal (D_{6h} and C_{6h}) symmetries have been given previously [10,16] and will not be reproduced here. Instead, we show in fig. 3 the seven concealed non-Kekuléans with D_{6h} symmetry and $h = 73$.

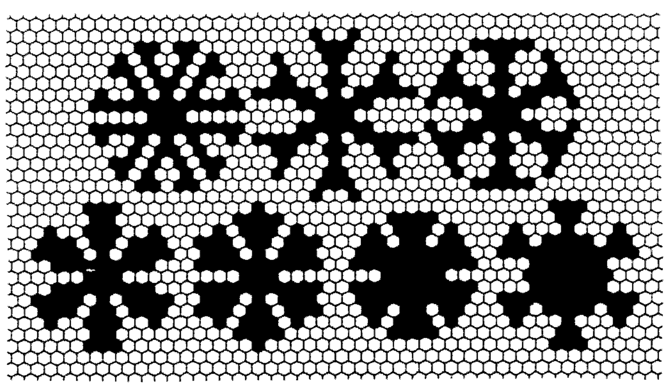

Fig. 3. The seven concealed non-Kekuléans with D_{6h} symmetry (snowflakes) and $h = 73$.

Some of the smallest concealed non-Kekuléans with D_{2h} symmetry were presented at the Conference (see fig. 4). Here, we recognize the first system with $h = 11$ as the Clar goblet.

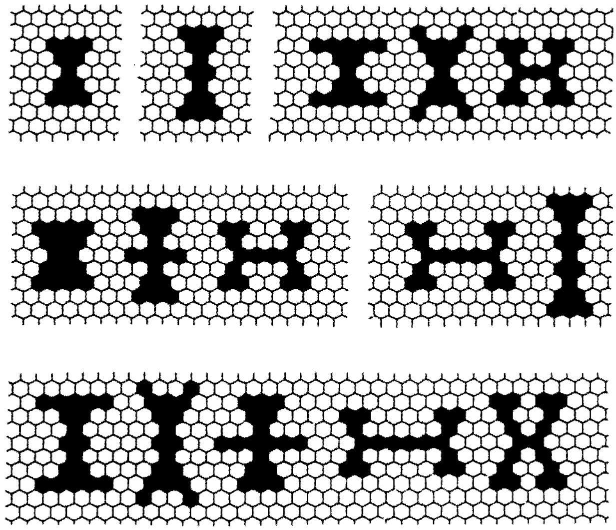

Fig. 4. The smallest concealed non-Kekuléans with D_{2h} symmetry.

The generation of concealed non-Kekuléans with the symmetries D_{6h}, C_{6h}, D_{2h} and C_{2h} is relatively easy in comparison with the derivations without regard to symmetry. In this connection, it is relevant to compare the numbers in tables 1 and 2. Furthermore, it is a fact that all polyhexes belonging to the four mentioned symmetry groups have $\Delta = 0$. Therefore, they are either Kekuléan or concealed non-Kekuléan, but never obvious non-Kekuléan. The situation is contrasted by the trigonal (D_{3h} and C_{3h}) polyhexes, for which an abundance of systems with $\Delta > 0$ is found. In conclusion, the concealed non-Kekuléans of trigonal symmetry really tend to hide themselves, so to speak; they are concealed! These systems are treated in some detail elsewhere [1].

6. Polyhexes with holes

Already in the early enumerations and classifications of polyhexes with holes [20], three concealed non-Kekuléan systems with $h = 15$ were depicted as the smallest ones, obtained by trial and error. Later, it was demonstrated by computer generations that $h = 15$ really is the smallest possibility as far as the polyhexes with naphthalenic holes are concerned [1]. Furthermore, it was deduced that there are exactly twenty-three concealed non-Kekuléan polyhexes with naphthalenic holes and $h = 15$. The forms are displayed in the cited reference [1].

Further investigations, which are not yet published, revealed that the above result is sound independently of the shape of the hole. For polyhexes with the phenalenic hole, for instance, the smallest concealed non-Kekuléans have $h = 16$, and there are exactly twenty-one systems. They are shown in fig. 5.

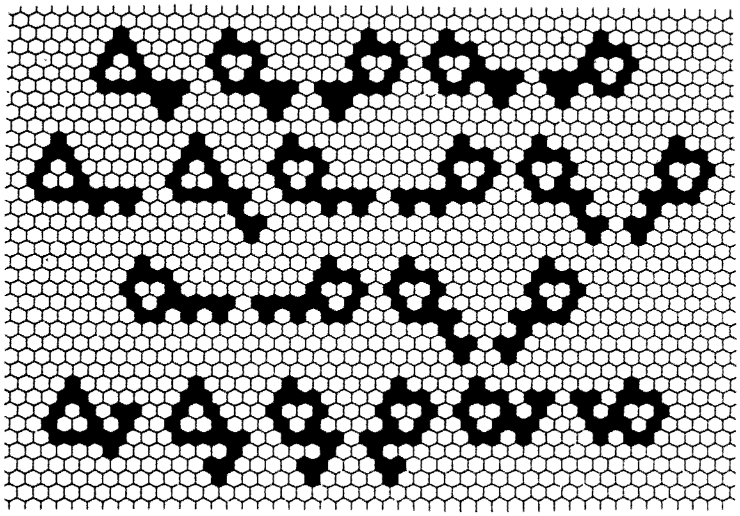

Fig. 5. The smallest (h = 16) concealed non-Kekuléan polyhexes with the phenalenic hole.

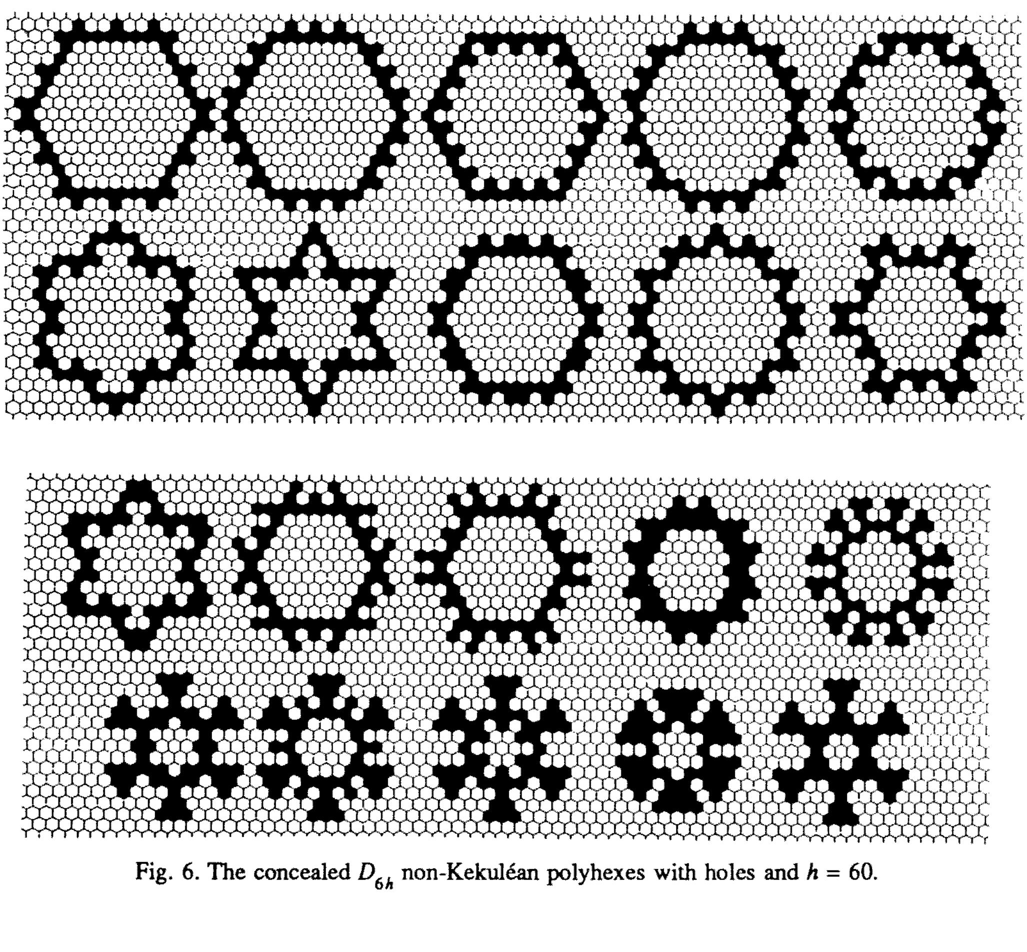

Fig. 6. The concealed D_{6h} non-Kekuléan polyhexes with holes and h = 60.

Polyhexes with holes and belonging to specific symmetries have also been studied to some extent. Further studies in this area are in progress. With regard to the concealed non-Kekuléans, some systems with the regular hexagonal symmetry (D_{6h}) have been deduced quite recently [19]. Specifically, it was found that the smallest system of this category is a unique polyhex with h = 48, and that there are three such systems with h = 54 and twenty with h = 60. The four smallest of these systems are depicted elsewhere [1,19]. In fig. 6, we show for the first time a pretty picture of the twenty D_{6h} concealed non-Kekuléan polyhexes with holes and h = 60.

Acknowledgement

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