How to Design Non-Kekulé Polyhex Graphs?

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An efficient algorithm is proposed for designing alternant hydrocarbons with the same numbers of starred and unstarred carbon atoms but with no Kekulé structure. This algorithm is based on the interesting alternant properties of the non-zero coefficients of the NBMO (non-bonding molecular orbital) of special series of odd alternant hydrocarbon radicals.

INTRODUCTION

Among the vast number of polyhex graphs corresponding to polycyclic aromatic hydrocarbons several **graphs are known to have** a vexing property with respect to the perfect matching, or Kekulé structure counting problem.* Examples are *1*² and *2*³, which have the same number of starred | ● | and unstarred | ○ | atoms but have no Kekulé structure (See the left half of Figure 1). Further, both of them have the same number of »upward« and »downward« triangles for their dualist graphs, violating the rule proposed by Balaban for discriminating between closed and open shell systems.[2]

1   2

Henceforth let us call those bipartite graphs »quasi-isostellar« graphs, or simply QIS graphs, which have the same number of starred and unstarred points but have no Kekulé structure. The graphs with at least one Kekulé structure can be called »isostellar«, since they have obviously the same number of starred and unstarred points. On the other hand, both triangulene, or Clar's hydrocarbon, *3*, and the hexahex, *4*, are known to have no Kekulé structure.[3,4] These graphs may be called »non-isostellar«, since they have

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* Extension of the discussion in this paper to acyclic graphs is straightforward, and is not explicitly stated here.[1]

$$|\bullet| - |\circ| = 0 \quad \xrightarrow[\text{but}]{\text{thus}} \quad |\bullet| - |\circ| = 2$$

$$|NBMO| = 2$$
non-Kekulé

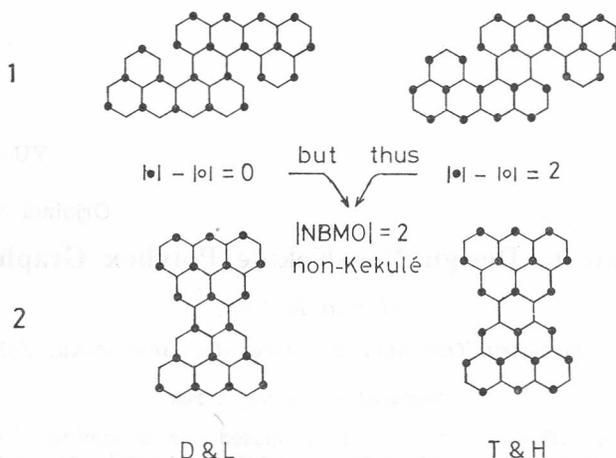D & L   T & H

Figure 1. Comparison of the starring processes by D&L and T&H.

different numbers of starred and unstarred atoms, or have different numbers of upward and downward triangles for their dualist graphs.

$$|\bullet| - |\circ| = 2$$
$$|\triangle| - |\triangledown| = 2$$
$$\Downarrow$$
$$|NBMO| = 2$$
$$K(G) = 0$$

3   4

In spite of the recent progress in the application of the graph theory to the resonance theory,[5] several important graph-theoretical theorems have been overlooked, especially on the conditions for the perfect matching, or 1-factor, problem.[6,7] On the other hand, some molecular orbital concepts, such as the NBMO (non-bonding molecular orbital) and perturbation calculation technique, are found to carry important information which the graph theory cannot yield for the construction and decomposition of graphs.[8-10] By combining these techniques, an aufbau principle for designing as many QIS graphs as possible will be presented in this paper.

THEOREMS BY TUTTE AND HALL

Among the existing theorems for judging the existence or non-existence of the perfect matching for a given graph the ones by Tutte[6] and Hall[7] have been shown to be useful, but have been scarcely recognized by chemists. Let us translate their theorems into chemistry.

Theorem (Modification of Tutte's and Hall's)

Divide the points in the given graph G with N points into two groups, A and B, so that no two elements of A are bonded, whereas the elements

of B may or may not be bonded among themselves. If grouping is possible so that $|A| > |B| = N - |A|$, G has no perfect matching.

By applying the discussion by Dewar and Longuet-Higgins to this theorem the following corollary was derived.

Corollary

The number of the NBMO's of G is at least $2|A| - N$.

Examples are shown in Figure 1 for *1* and *2* and compared with the conventional starring process (D&L) by Dewar and Longuet-Higgins for alternant hydrocarbons.[8-11] The Tutte and Hall method (T&H) can also be applied to acyclic and branched polyhex hydrocarbons, such as *5* and *6*, for which D&L has failed to predict the properties of their ground state.

It is to be noted here that Itoh has pointed out, on the basis of his own ESR argument, that the starred atoms in *5* and *6* are expected to have a

$$|\bullet| - |\circ| = 2$$
$$\Downarrow$$
$$|NBMO| = 2$$
$$K(G) = 0$$

5   6
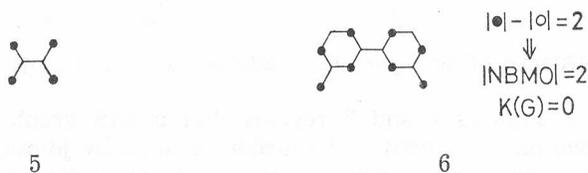
high spin density in the triplet ground state.[12] Both theoretical and experimental discussions related to this problem appeared recently.[13-16]

For a group of isostellar polyhex graphs with fixed double and/or single bonds, such as perylene, *7*, and zethrene, *8*, D&L and T&H starring patterns are different from each other, as shown in Figure 2, and the same conclusion can be drawn for the ground state.
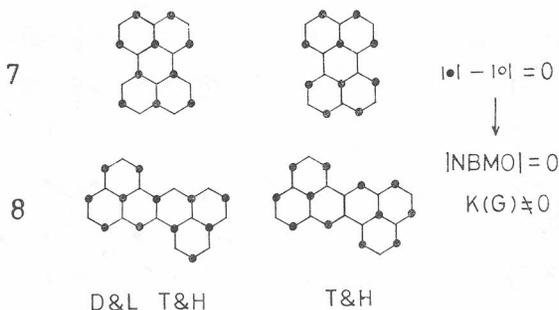

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$$|\bullet| - |\circ| = 0$$
$$\downarrow$$
$$|NBMO| = 0$$
$$K(G) \neq 0$$

8

D&L T&H   T&H

Figure 2. Examples of cases where both D&L and T&H methods give the same prediction for the ground state.

NBMO

By applying the zero-sum rule of NBMO's around each carbon atom to *1* and *2*, the coefficients of their NBMO's are found to be non-zero only on the starred atoms, as assigned by T&H (See Figure 1). They are obtained straightforwardly by the symmetric and antisymmetric combinations of those of the component odd alternant radicals, *9* and *10*, respectively, as shown

in Figure 3. Note that the NBMO coefficients are all zero on the two extrusive carbon atoms of *9* and *10*, which are used to form *1* and *2*, respectively. Then, the »inactive V region« is proposed to be defined for the regions marked with bold lines in Figure 3.
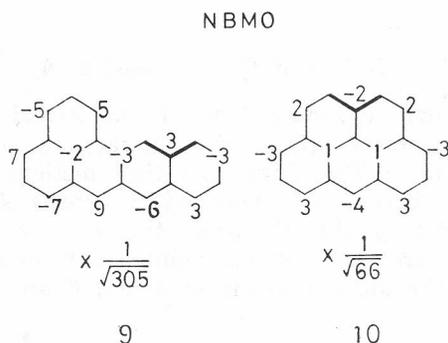
NBMO

Figure 3. NBMO's of two pentahex radicals with an inactive V region.

Inspection of Figures 1 and 3 reveals that a QIS graph might be constructed from two odd alternant hydrocarbon radicals by joining their inactive V regions. This is consistent with Dewar and Longuet-Higgins' finding that the Kekulé number, $K(G)$, of an alternant hydrocarbon G obtained by joining two odd alternants E and F can be enumerated from the product sum of the unnormalized coefficients of the NBMO's of E and F over the junctions, as exemplified in Figure 4,[9],*

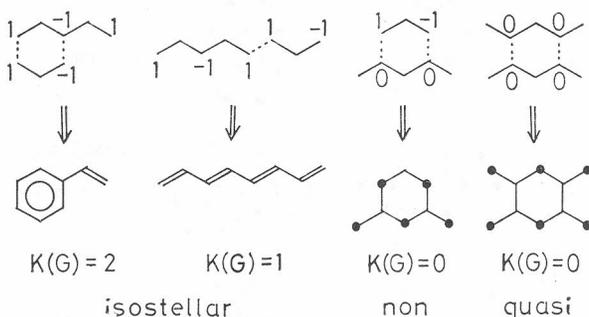$$K(G) = k \left| \sum_{(r-s)} C_{0r}^{E} C_{0s}^{F} \right|. \tag{1}$$

Figure 4. Examples of cases where the product sum of unnormalized coefficients of the NBMO's of the two component radicals gives the Kekulé number of the composite hydrocarbon.

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* Herndon proposed a method for enumerating the number of the Kekulé structures by adding the coefficients of NBMO of the radical obtained by deleting a certain carbon atom.[17] However, his method was found to be inapplicable to the QIS graphs like *1* and *2*.

Dewar also pointed out that the π-stabilization energy, ΔE, of G relative to the sum for E and F can be estimated from the above-mentioned product sum as[18]

$$\Delta E = k' \left| \sum_{(r-s)} C_{0r}^{\,E} C_{0s}^{\,F} \right|. \tag{2}$$

Either from Eqs. (1) and (2), the compounds *1* and *2* are predicted to have no first-order stabilization energy by joining two radicals, *9* and *10*, respectively, in the inactive V regions. This prediction was supported by the finding that graph *11*, which is obtained by joining the inactive V regions of *9* and *10*, belongs to QIS graphs.

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DESIGN OF QIS GRAPHS

The key problem for designing QIS graphs is to provide odd alternant hydrocarbons with an inactive V region in their NBMO's. No odd polyhex graph smaller than pentahex has an inactive V region, while among the seven pentahex radicals, only *9*, *10*, and *12* are found to have an inactive V region.
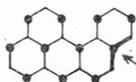
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Thus, by the possible combinations of *9*, *10*, and *12* with their inactive V region, one can design eight QIS undecahexes, as shown in Figure 5.*
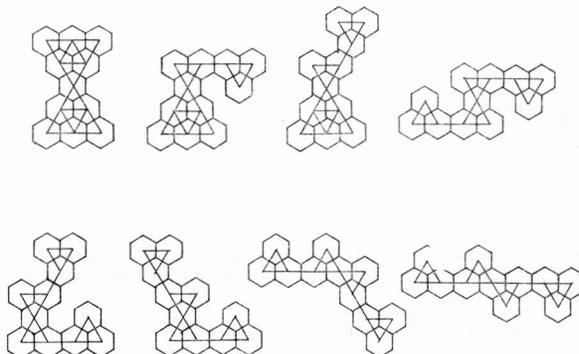

Figure 5. Eight possible QIS graphs constructed from two pentahex radicals.

Note that all of them have the same number of upward and downward triangles in their dualist graphs, but have no Kekulé structure.

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* The last entry of Fig. 5 was already pointed out to have no Kekulé structure by Gutman.[19]

An inactive U region may be defined for the bold line region of pen-
tahex *13*, as shown below.

13

Insertion of methyl radical into the mouth of the inactive U region of *13*,
however, leads to non-isostellar graph, *3*. Thus, the inactive U region does
not play so important a role in designing QIS graphs as the inactive V region.

Out of twenty-nine hexahex radicals[4] the seventeen graphs whose dualist
graphs are shown in Figure 6 have one or more inactive V regions. They
are grouped into two classes, A and B, with respect to the pericondensed
skeleton. Namely, the fifteen radicals of class A commonly possess ace-
naphthenyl or perinaphthenyl skeleton, *14*, while the remaining two radicals
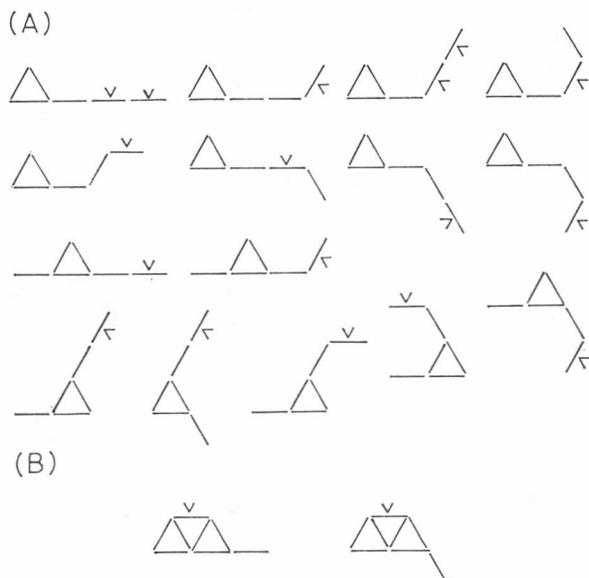of class B have skeleton *10*.

(A)

(B)

Figure 6. Seventeen hexahex radicals with inactive V regions. They are grouped
into A and B according to the pericondensed skeleton.

From a collection of the patterns of inactive V regions in Figure 6 one
can iduce several growing patterns of inactive V regions. They are graphi-
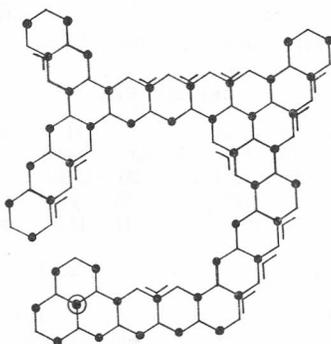

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Figure 7. Effect of kink and branching on the growing pattern of inactive V regions of the NBMO of polyhex graphs originated from the acenaphthenyl moiety.
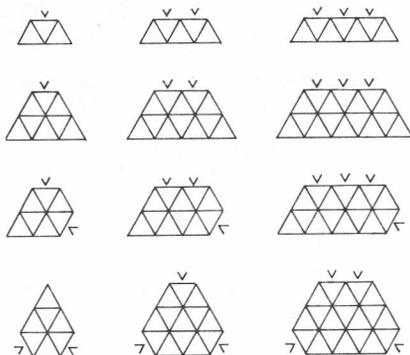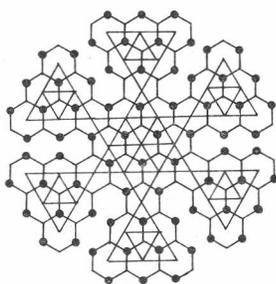

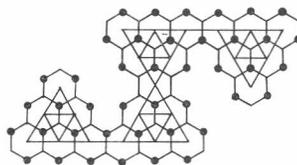Figure 8. Growing patterns of inactive V regions of the NBMO of pericondensed polyhexes.

cally illustrated in Figures 7 and 8. In Figure 7 the non-zero starred atoms grow from the center of the acenaphthenyl moiety (marked with a double circle) alternately along the chain of the catacondensed hexagonal units, and the side of inactive V regions changes alternately at every kink and branching point. Figure 8 shows the systematic growing of inactive V regions along the edges of various series of pericondensed polyhex radicals.

Now we can design as many QIS graphs as possible by combining these odd alternant radicals. In conclusion, two interesting examples are shown

$|\bullet| = 72$
$|\circ| = 66$
$\downarrow$
$|NBMO| = 6$

$|\triangle| = |\triangledown| = 18$

15

$|\bullet| = 42$
$|\circ| = 36$
$\downarrow$
$|NBMO| = 6$

$|\triangle| = |\triangledown| = 8$

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as *15* and *16*. Both of them have six NBMO's, which can correctly be predicted from the T&H starring but not from D&L.

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SAŽETAK

Kako konstruirati nekekuleovske poliheksagonalne grafove?

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Predložen je efikasni algoritam za konstruiranje parnih alternantnih ugljikovodika, koji posjeduju jednak broj atoma označenih zvijezdicom i onih bez te oznake, a koji nemaju kekuléovske strukture. Taj se algoritam temelji na interesantnim alternantnim svojstvima neiščezavajućih koeficijenata nevezne molekularne orbitale specijalnog niza radikala neparnih alternantnih ugljikovodika.