

## REVIEW

### THE RECOGNITION OF POLYHEX HYDROCARBON RADICALS

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#### Abstract

Rapid topological tests for discerning radical benzenoids from nonradical ones are reviewed. These tests include Hückel  $B$  matrix, Gordon–Davison, Hall–Tutte, path, and excised internal structure inspection methods. The potential magnetic properties of type 2 diradicals are pointed out.

#### 1. Introduction

It is useful to be able to identify quickly whether or not a given hexagonal polycyclic hydrocarbon (polyhex) is a radical. Several tests are in common use, but their limitations are not always recognized. In this review paper, each is discussed and its basis in molecular orbital theory demonstrated. One class of structures is shown to have exceptional properties.

Recent enumerations of the polyhex having up to ten rings [1] have shown that >41% of the per-condensed polyhex are radical species. A number of papers have proposed rapid recognition tests for benzenoid radicals, many of them essentially equivalent, so comparisons between them should be useful for practising chemists. This paper reviews these tests and suggests the simplest forms for practical use.

A necessary and sufficient condition for a polyhex to correspond to a closed-shell molecule is that at least one Kekulé structure can be drawn for it. From this, the best-known test for a radical is that no Kekulé structure can be drawn for it which includes every C atom. This test has the major disadvantage that exhaustive trial and error is required before the non-existence can be proved. When a moderately large radical structure is being tested for a Kekulé structure, one needs some way of deciding when to end this trial and error process. Hence, a better test is desirable.

Some investigators restrict their use of *benzenoid* to nonradical polyhex molecular structures, whereas others are less restrictive and classify benzenoid hydrocarbons into Kekuléan (having at least one 1-factor subgraph) and non-Kekuléan (radical benzenoids). While it is true that small free radical ( $< C_{50}$ ) polyhex molecules have never been characterized, it is also true that free radicals play a very important role in reaction chemistry. Given the universe of possible free radicals that temporarily form during the course of chemical reaction, the conjugated polyhex radicals are among the more stable ones, i.e. they are the benzenoids of radical species. The existence of a polyhex Kekulé structure does not guarantee that the corresponding molecule will stably exist. It is well known that relatively large acenes and zethrenes, the latter for which  $K = 9$ , so not stably exist. However, all investigators refer to these unstable species as benzenoid hydrocarbons. Thus, stable existence of a polyhex molecule can not be used as a criterion for the term benzenoid, and the terminology used herein is the less restrictive one.

The number of unpaired electrons (or nbo's) per carbon atom ranges from 1/11 for triangulene to zero for an infinite graphite lattice (the ultimate macromolecular benzenoid). Since an infinite graphite lattice is not, in reality, achievable, it is reasonable to presume that finite graphite systems will often be polyradicals in which the number of nbo's is determined by the size and edge configuration. Thus, the study of polycyclic hydrocarbon radicals should give insight into the electronic mechanisms of carbonaceous materials.

## 2. The Hückel matrix $B$

Since all the structures which consist of hexagonal rings are alternant, it is always possible and convenient to write the Hückel matrix  $A$  with all the starred atoms first followed by the unstarred ones, so giving the partitioned form [2]:

$$A = \begin{pmatrix} 0 & B \\ B^T & 0 \end{pmatrix}.$$

In  $B$ , the rows refer to the starred atoms and the columns to the unstarred ones. This matrix  $B$  contains all the information about the structures of the molecule which is needed for this purpose.

If  $B$  is square, its determinant  $|B|$  is defined. Each non-zero product in the expansion of  $|B|$  corresponds to a permutation matrix whose unit elements are selected from those of  $B$  and gives a Kekulé structure so that  $|B|$  is the count of the number of structures. For six-membered rings, the parity of these permutations, and so of the structures, is equal so that even one Kekulé structure is sufficient to ensure that  $B$  is non-singular and hence that there are no non-bonding orbitals.

On the other hand, if the structure contains any ring with  $4m$  C atoms, both parities will occur and  $|B|$  can be zero and the structure a radical even if there are Kekulé structures. Cyclobutadiene with two structures of opposite parity is an obvious example. Hence, the test of finding one Kekulé structure applies only in the absence of such rings. When one is not present, the necessary and sufficient condition for a radical will be  $|B| = 0$  or a non-vanishing solution to  $Bv = 0$ .

### 3. Two types of radical

The necessary and sufficient condition for a radical is the existence of a non-bonding molecular orbital (nbo). For a rectangular  $B$ , this is trivial and either  $Bv = 0$  will have a non-vanishing solution  $v$  (the nbo), if  $B$  has more columns than rows, or  $u^T B = 0$  will determine  $u$  (the nbo), if there are more rows than columns. In either event, the remaining coefficients (on the minority set of atoms) in the nbo vanish. These equations will determine at least as many nbo's as the difference in the dimensions of  $B$ . In the radical, each nbo will be single occupied.

It is convenient to divide radicals into two types. The first type includes those which have an odd number of C atoms and so can be instantly recognized from their chemical formula. More precisely, it consists of the polyhex which have the number of starred atoms different from the number of unstarred ones, i.e.  $B$  is rectangular. The second type has a square but singular  $B$ . For these, the calculation of a non-vanishing nbo is a much faster test of singularity and radical nature, and more convincing than failing to draw a structure! These are usually diradicals.

### 4. The Gordon–Davison test

The fast test for a radical given by Gordon and Davison [3] can be written as

$$\wedge \neq \vee,$$

i.e. the number of peaks, upward pointing vertices on the periphery, is not equal to the number of valleys, downward ones. For this purpose, “up” and “down” can be chosen in three ways for every polyhex. The difference between the numbers up and down will be the same for these three ways, but one may be easier to use than the

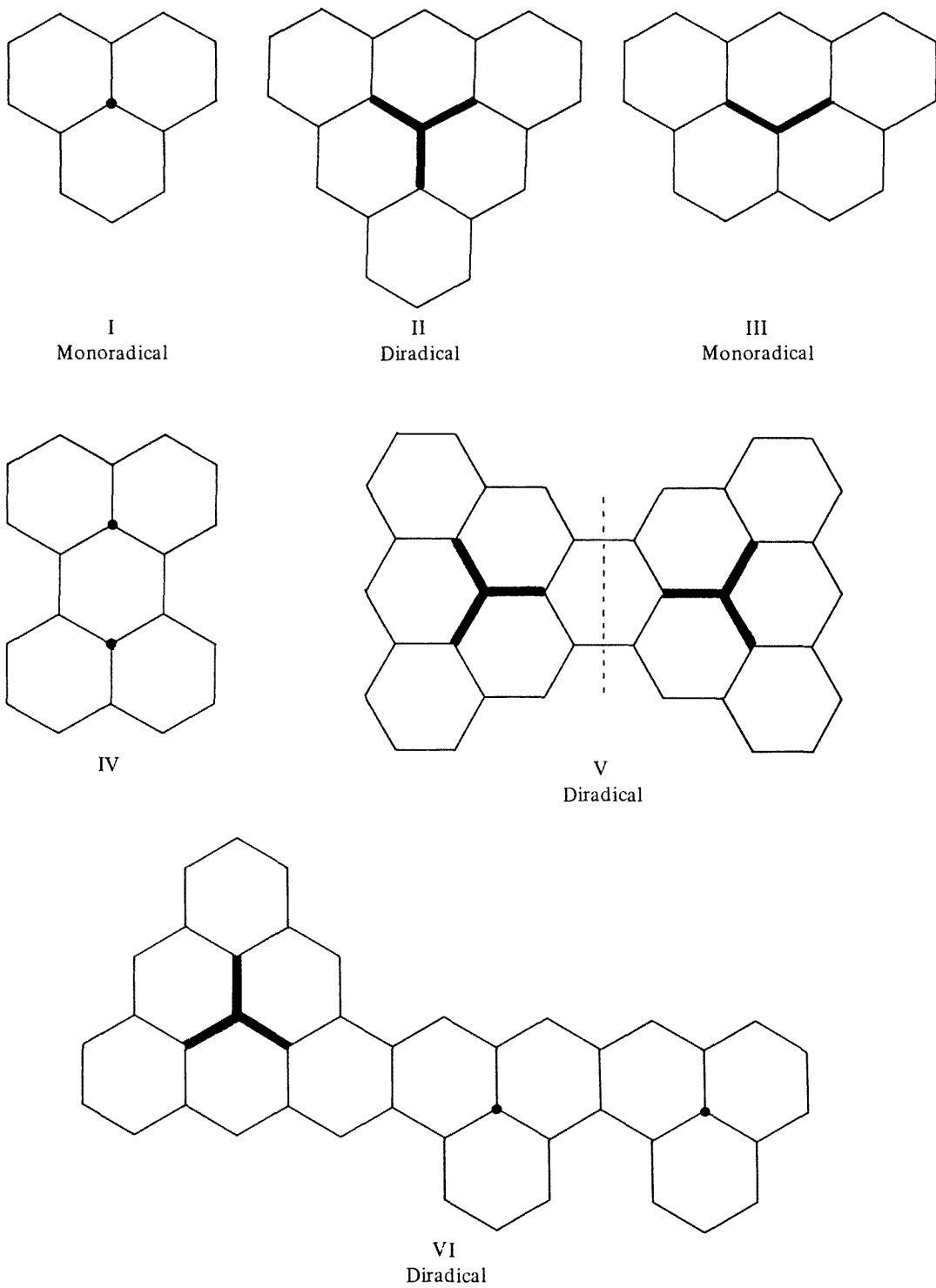
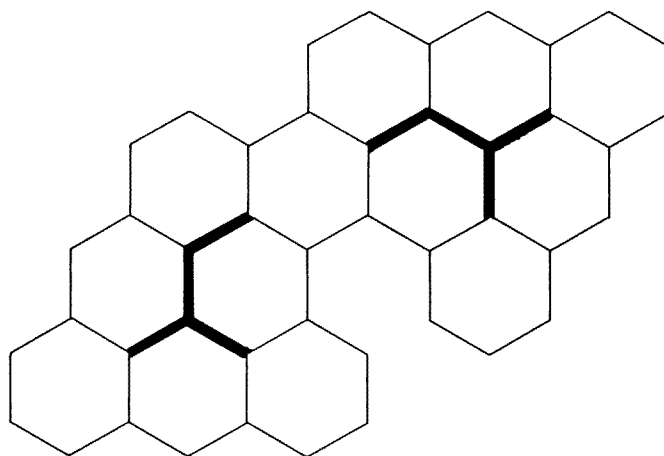


Fig. 1.



VII

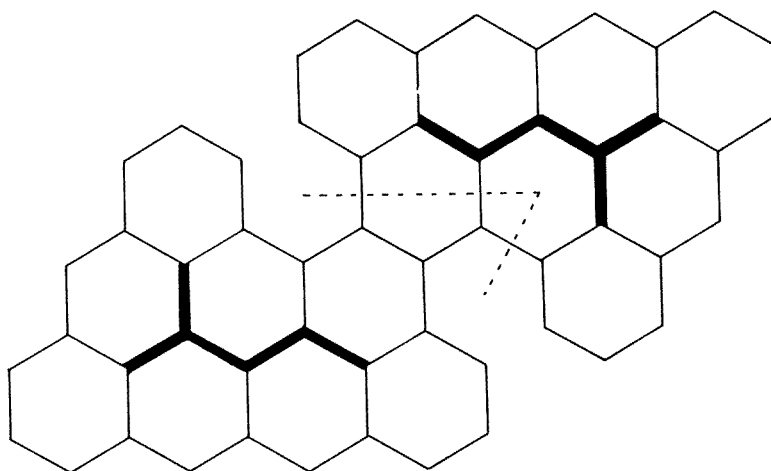
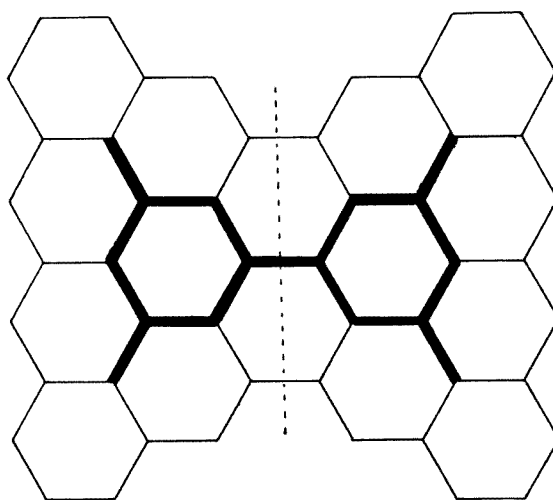
VIII  
DiradicalIX  
Diradical

Fig. 1 (continued).

others. This condition is easy to apply and gives a rapid visual test for all type 1 radicals whose structure is known whether or not the formula is available. Figure 1 shows a selection of polyhex species, and this test identifies I, II and III as type 1 radicals. The real problem concerns the type 2 radicals.

Balaban [4] has given a test which involves counting the number of upward and downward pointing triangles in the "dualist" graph (also known as the bual [15]). This is more elaborate than the Gordon–Davison test, but no more powerful.

## 5. The Hall–Tutte theorem

Hosoya [6] has noted that conditions for the drawing of a Kekulé structure were given, in different terminology, many years ago by Hall [7] and Tutte [8]. The essence of this method is to sort out the C atoms into two groups  $S$  and  $T$  so that no two atoms in  $S$  are bonded, whereas those in  $T$  are unrestricted. Then, if  $|S| > |T|$ , there is no possible Kekulé structure and the molecule is a radical. Figure 2 shows how two of the type 2 radicals in fig. 1 can be correctly identified by this test.

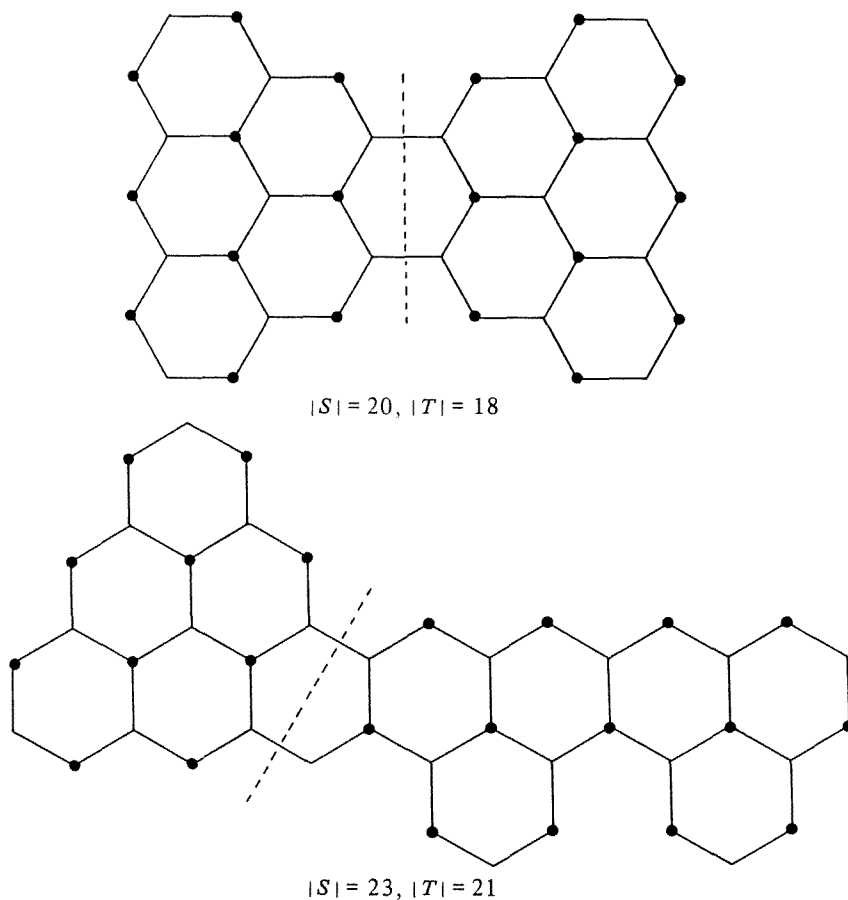


Fig. 2.

## 6. The path test

Gordon and Davison also proposed a more elaborate test which involves drawing paths through the molecule from each peak monotonically downwards to a valley. If this can be done for every peak and all the valleys are used, then the paths determine uniquely a Kekulé structure for the molecule. Along each path, the oblique bonds are double and the vertical ones single. Elsewhere, the vertical bonds are double and the oblique ones single. If the paths cannot be drawn, it must be a radical. The proofs of these results were elaborated by Sachs [9] and faster methods of counting the paths have been given by Gutman and Cyvin [10] and Hall [11]. Other recent developments of this approach and their application to radicals (non-Kekuléan benzenoids in their terminology) have been reviewed by Cyvin and Gutman [12]. It is much faster to test for these paths than to draw structures with individual bonds. Polyhex V in fig. 1 has three "up" atoms on the right and three "down" ones on the left, so it requires three paths between them. The ring in the centre has only two sides, so only two mutually exclusive paths through it are possible. This must be a type 2 radical.

As in this example, many of the type 2 radicals contain a feature which may be called an "isthmus". Two large type 1 components are joined by a narrower part. The path test gives a useful criterion for such polyhex. If the components have unbalanced peaks and valleys, then paths from one component must pass through the

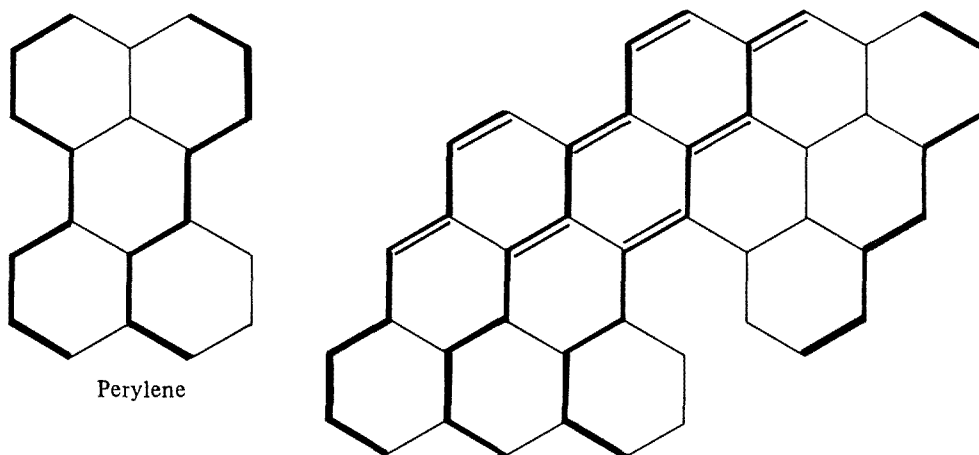


Fig. 3.

isthmus to the other component. The isthmus needs to be wide enough for all the paths that are required. Thus, perylene (IV in fig. 1) has two peaks and the isthmus between the naphthalene moieties has two verticals so that paths can be formed. One set of paths is shown in fig. 3 for the molecules IV and VII. In IV, both vertical bonds will be single in all structures, while in VII the two isthmus bonds will be double in all structures.

## 7. The excised internal structure or dibual

In a recent paper [13], a test was given using the concept of the excised internal structure which was introduced earlier by Dias (alternatively called dibual [14]). These are indicated in fig. 1 by darker lines. It was demonstrated, using many examples, that if the excised internal structure is a trimethylenemethane-related radical, then the full structure will also be a radical, and if it is a molecule, then a molecule.

Since the perimeter alone is always cyclic with an even number of C atoms, it can be numbered separately so that it has a square block in  $B$  and the rectangularity of the dibual is then a necessary and sufficient condition for that of  $B$ , so the type 1 radicals can be identified from their type 1 internal structures. Furthermore, it is easily proved, using the path idea, that if the dibual is a molecule, then each of its Kekulé structures can be extended into a structure for the polyhex, so it also must be a molecule. Similarly, if the dibual has sets  $S$  and  $T$  satisfying the Hall–Tutte test, then these can be enlarged to prove that the polyhex is also a radical.

The test fails when the dibual (excised internal structure) has unconnected parts. This occurs often for type 2 radicals when the parts are type 1 radicals. Polyhex VI in fig. 1, due to Dias [12], is an example of a  $C_{44}H_{22}$  diradical of this kind, and V and VII in fig. 1 are others. Unfortunately, the two molecules in fig. 3 also have two disconnected radical components in the dibual, e.g. perylene has two single C atoms in its dibual, so the presence of two radicals in the dibual cannot be used as a test to recognize radicals.

## 8. Type 2 diradicals

Balaban [4] has discussed what he calls  $S$ -diradicals. He cites Gutman [15] and a personal communication from Mallion as the source of the first example. Balaban explains the idea in this way:

“Dualist graphs of  $S$ -diradicals are formed from two dualist graphs of  $D$ -diradicals by fusion of a vertex; since this common vertex is an apex of a triangle, this means that the two  $D$ -diradicals share a common benzenoid ring, and this explains why a central perylene system occurs in all  $S$ -diradicals.”

The diradical V in fig. 1 is this first example. However, since the diradical VI in fig. 1 does not possess a perylene-like system, this explanation is not complete.

Another approach to the recognition of diradicals can be found using the matrix  $B$ . These diradicals have structures whose matrix  $B$  is square and, with suitable numbering, takes the form



$$B = \begin{pmatrix} C & 0 \\ F & D \end{pmatrix},$$

where  $C$  is rectangular with more rows than columns. It has an nbo which satisfies

$$u^T C = 0.$$

It follows that  $D$  is also rectangular but has more columns than rows, so it has an nbo satisfying

$$Dv = 0.$$

Thus,  $B$  has two nbo's with

$$(u^T, 0)B = 0, B \begin{pmatrix} 0 \\ v \end{pmatrix} = 0.$$

This demonstrates that the polyhex is, at least, a diradical. Thus, the structure can be divided into two components which are rectangular radicals with matrices  $C$  and  $D$ . The connection between the radicals  $F$  must involve the minority set of atoms in the first and the minority set in the second, but 0 means that the majority sets are not connected. It is readily shown that this criterion gives results identical to those of the Hall–Tutte test. The set  $S$  consists of the majority atoms of both radicals (see fig. 2).

A rapid visual test for a structure having this form of  $B$  can be given. The structure will have an isthmus connecting its two parts, and in this region it can be divided into two by a line which cuts the bonds but not the atoms. On each side will be a rectangular radical, and the cut bonds must connect atoms of the minority sets in these two. Figure 1 gives some examples of this division. When the division is not immediately apparent, as in VIII, the fastest way to determine it is to calculate one of the nbo's. It should be noted that the diradicals VI, VIII and IX do not contain a central perylene system, whereas the molecules IV and VII do! VII has an isthmus, but it connects the majority sets not the minority sets, so it is not a species of this type.

## 9. Magnetic molecules

This class of type 2 diradicals has one very interesting property. As has been shown above, each non-bonding orbital has nodes on all the atoms of its minority set and, because the radicals are joined only at these nodes, each of these orbitals becomes a non-bonding orbital of the whole structure, with vanishing coefficients on all the atoms of the other radical. (This is an example of embedding [16,17].)

An implication of this is that the exchange integral which determines the separation between the singlet and triplet states will vanish. Thus, the "excited singlet" will be degenerate with the triplet ground state. This singlet requires two determinants to describe it, so it cannot be represented by conventional Kekulé structures. In practice, spin terms may lower some components of the triplet slightly.

It follows from this that if one of these polyhex can be synthesized, it should be relatively stable in its singlet state but would acquire a strong magnetic moment and radical character in a magnetic field.

## References

- [1] A.T. Balaban, J. Brunvoll, J. Cioslowski, B. Cyvin, S. Cyvin, I. Gutman, H. Wenchen, H. Wenjie, J. Knop, M. Kovacević, W. Muller, K.S. Zymanski, R. Tosić and N. Trinajstić, *Z. Naturforsch.* 42A(1987)863,
- [2] G.G. Hall, *Proc. Roy. Soc.* A229(1955)251.
- [3] M. Gordon and W. Davison, *J. Chem. Phys.* 20(1952)428.
- [4] A.T. Balaban, *Pure Appl. Chem.* 54(1982)1075.
- [5] G.G. Hall, *Int. J. Math. Ed. Sci. Tech.* 4(1973)233.
- [6] H. Hosoya, *Croat. Chem. Acta* 59(1986)583.
- [7] P. Hall, *J. London Math. Soc.* 10(1935)26.
- [8] W. Tutte, *J. London Math. Soc.* 22(1947)107.
- [9] H. Sachs, *Combinatoria* 4(1984)89.
- [10] I. Gutman and S.J. Cyvin, *Chem. Phys. Lett.* 136(1987)137.
- [11] G.G. Hall, *Chem. Phys. Lett.* (1988).
- [12] S.J. Cyvin and I. Gutman, *Kekulé Structures in Benzenoid Hydrocarbons* (Springer-Verlag, Berlin, 1988).
- [13] J.R. Dias, *J. Mol. Struct. (Theochem)* 137(1986)137; *J. Chem. Inf. Comput. Sci.* 24(1984) 124.
- [14] G.G. Hall, *Theor. Chim. Acta* 73(1988)425.
- [15] I. Gutman, *Croat. Chem. Acta* 46(1974)209.
- [16] G.G. Hall, *Bull. Inst. Math. Appl.* 17(1979)51.
- [17] J.R. Dias, *J. Chem. Ed.* 64(1987)213.