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Conference Paper

## Graph-theoretical Search for Benzenoid Polymers with Zero Energy Gap<sup>\*,\*\*</sup>

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Recently structural features which characterize the energy gap in polymeric conjugated hydrocarbons within the framework of the simple Hückel MO theory have been specified using graph-theoretical methods. It has been shown that molecules of interest as potential units in polymers with zero energy gap have to satisfy certain structural conditions which relate the number of selected »excited« valence structures to that of the Kekulé structures for the system. As in the previous work we consider units separated by essentially single bonds.

Here we elaborate on the search for *benzenoid systems* which can satisfy the requirement. A necessary condition that a system may have zero energy gap is that the repeating benzenoid unit has a non-prime number ( $K$ ) of Kekulé valence structures. Then  $K$  could be factored:  $K_1 \cdot K_2 \dots K_m$ . (Generally, there are more factorizations of  $K$  and our procedure needs to be carried out over all of them). Fragments  $F_i$  that have the number of Kekulé structures given by  $K_i$  are recognized, and we try to superimpose all of them over the skeleton of monomer unit. (Our procedure needs to be carried out for all possible fragmentations corresponding to a given factorization). If it is possible to cover the monomer unit with all the fragments leaving at least two positions available for linking the units in polymer form, then the energy gap of such a polymer is zero.

In a number of examples it is illustrated how the actual search is performed. A list of benzenoid systems of interest as units in a polymer with zero energy gap is given. The search is quite efficient and speedy.

### INTRODUCTION

The number of possible species of interest in a certain domain, be it a new synthetic drug or a polymer of prescribed physical and chemical properties, is frequently so enormous that a systematic examination of every structure is prohibitive. One needs to develop a strategy to apply to the

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individual situations some kind of screening of structures which will hopefully eliminate the most undesirable but include those that should be examined.

For the purpose of the screening, even rather elementary theoretical models can provide a useful tool, since limitations of these may well be understood on selected structures and thus allow some generalizations when more complex systems are treated.

Particularly here we have in mind the simple Hückel MO method which has been found useful in specific applications. Since the scheme correctly accounts for the connectivity of a system the validity of many conclusions based on HMO is not so surprising.

We may specifically quote the so called NBMO's, the presence of which in some cases is indicative of molecular instability and the lack of aromatic nature.<sup>1</sup> In consideration of conductivity in polymeric conjugated hydrocarbons one of its influencing factors is the magnitude of the energy gap  $\Delta E$  (i. e., the energy difference between the highest filled and the lowest empty bands) which could be related to the determinants of the adjacency matrices of the molecular graph of the monomer unit.<sup>2</sup> Bochvar and Stankevich<sup>3</sup> have shown, that in the case when the monomer units are linked only through single bonds the width and the position of electronic bands is determined with the matrix  $T(k)$  for  $k = 0$  and  $k = \pi$ . These matrices are obtained from the adjacency matrices by insertion of a link between the vertices which are connecting neighboring units, with the proviso that their weights are  $+1$  and  $-1$ , respectively.

The condition for zero energy gap is that  $\det T(0)$  or  $\det T(\pi)$  is zero. The problem is reduced to the examination of the determinants for any acceptable pair of vertices of a given system. As it has already been pointed out<sup>2</sup> application of the described procedure, although elegant, simple and practical on a small sample, nevertheless becomes lengthy when applied to larger monomer units, because the number of combinatorial possibilities grows with the increase in the size of the molecule. It has even been indicated<sup>2</sup> that instead of evaluating the determinants one can in the case of benzenoid systems derive valid conclusions by examining valence structures, in particular the so called »excited« valence structures in which coupling between  $\pi$  electrons which are not adjacent is allowed. It has been found that<sup>2</sup> a system has zero energy gap if the number of singly »excited« valence structures which can be written for a *selected pair of sites* acting as terminals of the so called »long« bond is equal to the number of classical Kekulé-type valence structures for the system.

Applying the above search for potential systems of interest in the semi-conductivity of polymers one has succeeded only in replacing a more lengthy numerical calculation by a pictorial structure examination, since again the answer depends on verification of the condition for any pair of atoms linking the units in the polymer. Clearly, the pictorial approach provides a simpler search, but the ultimate efficiency can be increased if we could say something about the repeating unit without full examination of all pairs of sites that are available. Such a procedure for finding systems with zero energy gap will be described in the next section. However, graph-theoretical approach suffers from all well known deficiencies of simple HMO. Therefore, it is impossible to treat the problem of gap opening and associated bond alternation of systems having zero energy gap in the original Hückel band structure.<sup>4</sup>

If all pairs of linking sites in the benzenoid monomer unit are examined, generally the polymeric systems with non-zero energy gap are formed. However, the differences between the number of classical Kekulé structures ( $K$ ) and the number of »excited« valence structures of monomer ( $K_{\text{excited}}$ ) is easy to calculate and as it was shown in reference 5, this quantity parallels the magnitude of the energy gap of the system.

Our present and previous work<sup>2,5</sup> in this field is an attempt along the line of explaining »the fact that while all the semiconducting macromolecular systems have in their structure . . . single and multiple bonds, yet the inverse is not true«. We are looking at the structure of the monomer as being an important factor in the conductivity of polymer<sup>7</sup>, more precisely at the topological part of such a dependence. The energy gap of polymers was extensively studied by Tyutyulkov, Polansky et al, including also topological considerations.<sup>8,9</sup>

#### OUTLINE OF THE METHOD

Let us illustrate the approach on the case of anthracene unit. As has been shown in the preceding paper<sup>2</sup> among 12 acceptable pairs of sites for linking anthracene units in a polymer the pair 5, 10 leads to  $\det T(0) = 0$ . As has been argued, since  $\det T(0)$  and  $\det T(\pi)$  is given by a square of a sum, the determinant can only be zero if the sum is zero itself. This further leads to a requirement that in the sum we have the same number of positive and negative contributions which then are equivalent to demanding that the structure has an equal number of Kekulé valence structures and »excited« structures with a selected »long« bond (to terminate at the chosen pair of vertices for a linking site). The situation is illustrated in Figure 1 for anthracene. This is a summary of the scheme as so far developed in reference 2.

Figure 1 allows an alternative interpretation, which, as will be seen, leads to a considerable improvement in efficiency of the search for potentially interesting monomer units among benzenoid conjugated hydrocarbons. Observe, that formally the »long« bond fragments the structure of anthracene into two benzene units.

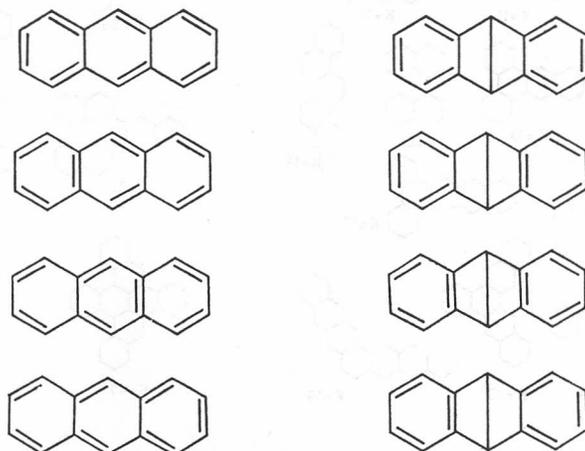


Figure 1. The four Kekulé structures of anthracene and the four »excited« structures involving a »long« bond across 5, 10 positions.

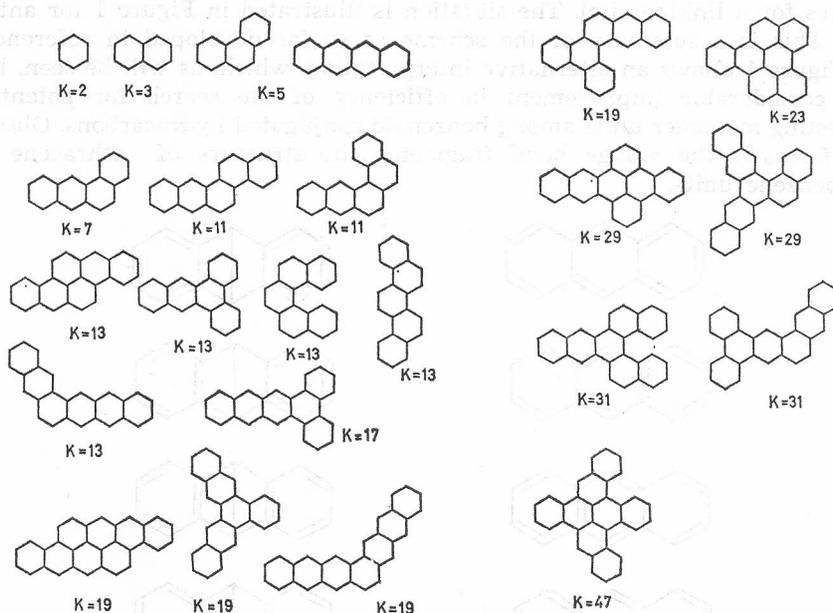
This is perhaps most apparent if one erases the »long« bond together with its adjacent single bonds. The benzene fragments have the same number of Kekulé structures as the parent anthracene, i. e.  $2 \cdot 2 = 4$ .

The analysis can now proceed via *factorization* of the number  $K$  (Kekulé structures for a system). Only those fragments  $F_1, F_2, \dots, F_m$  are of interest for which holds  $K = K_1 \cdot K_2 \cdot \dots \cdot K_m$ . This viewing permits immediately selection of fragments to be screened, the fragments being those whose number of valence structures appears as a factor in factorization of  $K$ .

We will illustrate the application of such a scheme with a number of examples which will show the great efficiency of the approach. Namely, it is generally quite simple to select acceptable fragments among all molecules with a given number of Kekulé valence structures. The fragments have to be compatible with the underlying connectivity of the parent structure, and very few molecules among those which have the same number of Kekulé valence structures will satisfy this condition. Perhaps the spirit of this new view of the condition is well explained by the conclusion that follows immediately from the above discussion: benzenoid hydrocarbons which have for the number of Kekulé valence structures a *prime* number cannot contribute to a zero energy gap polymer. In Table I we list several benzenoid systems with a prime number of Kekulé valence structures.

TABLE I

Some Benzenoid Systems with a Prime Number of Kekulé Valence Structures



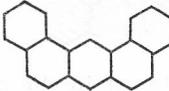
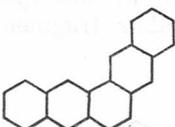
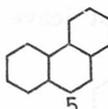
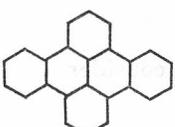
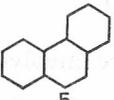
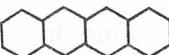
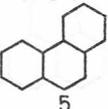
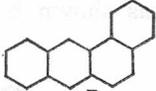
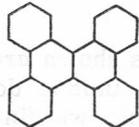
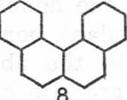
These, of course, can be fragments in other larger units, but themselves are immediately disqualified from further analysis as monomer units.

As one sees, the structures include benzene, naphthalene and phenanthrene — the structures that we have previously individually considered and which required 25 pair testings.

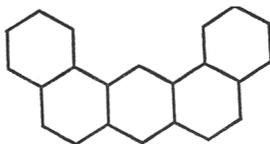
Now, by a single theorem, these and many others are simply eliminated from further study.

In Table II we give a number of benzenoid systems with a number of Kekulé valence structures and their factorization.

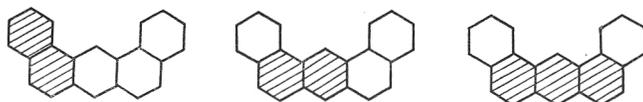
TABLE II  
Some Benzenoid Systems and Their Factorizations

Molecule	Factors	Fragments to be considered and their number of Kekulé structures
	2·2·3 4·3 6·2	 2  3
	2·5	 2  5
	2·2·5 2·10 4·5	 2  5  5
	2·5	 2  5
	2·7	 2  7
	2·2·3·4 2·4·3 3·8 4·6	 2  3  4  8

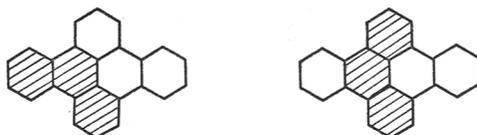
Let us discuss few examples in some details. Take for instance dibenzanthracene:



It has 12 Kekulé valence structures and as possible factorization we have  $2 \cdot 2 \cdot 3$ ;  $2 \cdot 6$ ; and  $3 \cdot 4$ . The possible fragments are benzene (2), naphthalene (3), anthracene (4), other structures like pyrene (6) or pentacene (6) need not be considered since they cannot overlap the molecular skeleton of dibenzanthracene. However, by superimposing structures of naphthalene or anthracene over the skeleton of dibenzanthracene no position for the other fragment(s) is available



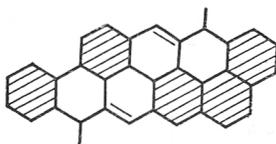
Hence, dibenzanthracene is not a unit of potential interest in the zero energy gap polymers search. Similarly in dibenzpyrene, one of the fragments has to be phenanthrene with five Kekulé structures, but its inscription on the molecular skeleton does not leave a position for other fragment required by the factorization



Finally, as a somewhat more involved case one can consider



which has 20 Kekulé valence structures. After screening possible fragments corresponding to factorization  $2 \cdot 10$  (no acceptable case) we come to factorization  $2 \cdot 2 \cdot 5$  which, as shown below, is apparently compatible with the structure



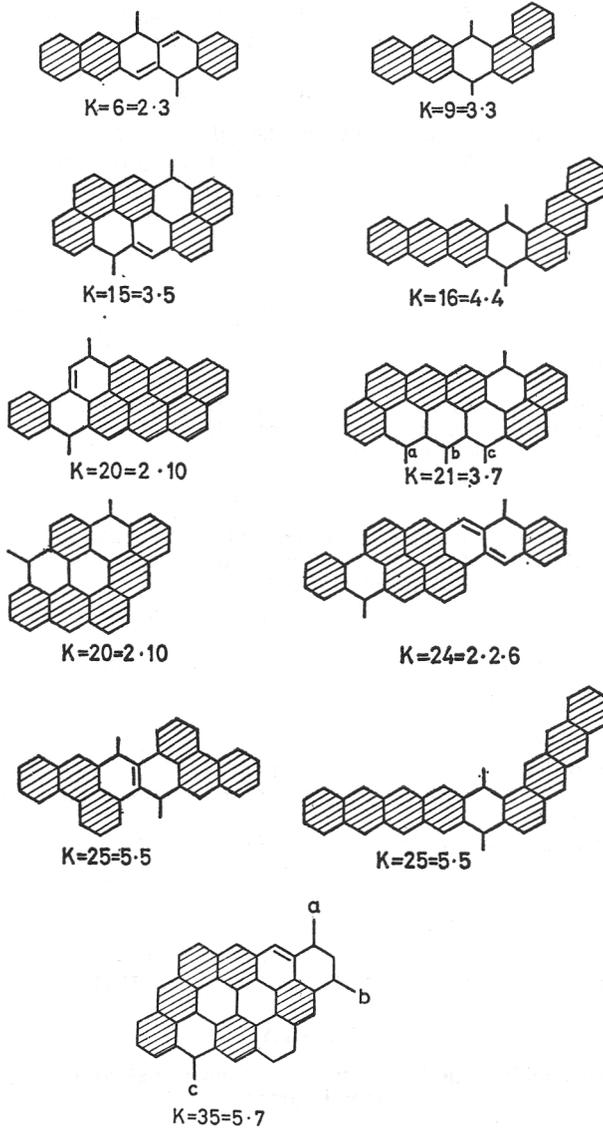
However, a closer look shows that the double bonds as shown *are* part of a larger fragment, i.e., are not pendant bonds with a unique double bond character assignment. So again in the above example we find that the conditions having zero energy gap are also not met.

## ZERO ENERGY GAP POLYMERS WITH BENZENOID MONOMER UNITS

In Table III we list several benzenoid systems which are found to satisfy the conditions set forward for zero energy polymers. Pentacene (after anthra-

TABLE III

*Some Benzenoid Systems Serving as the Building Blocks for Zero Energy Gap Polymers*



a,b,c... are alternative sites

cene) and benzotetracene are among the smallest. In the first case  $K = 6$ , hence only naphthalene and benzene can appear as fragments, and as shown in the Table III, they are consistent with the connectivity of the parent structure. In the second case the only fragments permissible are naphthalene units, and they again can be combined as shown in the Table III. In other examples phenanthrene, anthracene, benzantracene, tetracene, pyrene etc. appear. It appears that certain structures are more likely to satisfy the structural conditions than others. Thus angularly fused polyacenes, and certain reticular structures appear more frequently than other types.

#### CONCLUDING REMARKS

The previous paper<sup>2</sup> suggested a useful approach which can quickly identify a polymer with  $\Delta E = 0$ . The present work produces a further improvement in the search for such substances with no apparent limitations on the size of the units examined. If one combines such a search with an efficient procedure for evaluation of Kekulé valence structures<sup>10</sup> (which is not a trivial matter for larger systems) a rather ambitious and fairly complete screening can be effected in rather short time. Further generalization of the scheme may be of interest, such as the extension of the analysis to include non-benzenoid systems.

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#### SAŽETAK

**Traženje benzenoidnih polimera sa nultim energetske rascjepom pomoću teorije grafova**

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Strukturni faktori koji karakteriziraju pi-elektronski energijski rascjep polimernih konjugiranih ugljikovodika, u okviru jednostavne Hückelove MO-teorije, nedavno su specificirani upotrebom postupaka teorije grafova.

Na nizu primjera ilustrirano je kako se vrši stvarno traženje. Dana je lista benzenoidnih sustava koji su od interesa kao jedinice za polimere s nultim energijskim rascjepom. Traženje je efikasno i brzo jer je potrebno samo prebrojavanje Kekuléovih valentnih i srodnih struktura promatranog monomera.

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