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Graph Theoretical Derivation of Pauling Bond Orders

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A method of evaluating Pauling bond orders of conjugated hydrocarbons is outlined. It is based on the reduction of a molecular graph by excising the bond in question and other bonds for which a unique assignment of bond character is possible. The method is general and applicable to alternant and non-alternant systems as well as to cata- and pericondensed hydrocarbons.

INTRODUCTION

It was pointed some time ago by Ruedenberg¹ that a quite general accounting of the basic properties of bonds in conjugated systems can be given in terms of topological orbitals. These are defined as eigenfunctions of the adjacency matrix of the molecular graph² and are essentially equivalent to eigenfunctions of an effective one-electron hamiltonian in the tight-binding approximation, such as Hückel MO's. A useful physical interpretation of these topological orbitals follows from the fact that, on the average, the long-range contributions to forces between electrons and nuclei cancel those between electrons themselves so that only short-range forces are significant for the effective hamiltonian. If the short-range forces are dominant in the effective potential, then one can expect that the topology of the molecule will determine the forms of the molecular orbitals.¹ This has in fact been found to be the case.³ Hence molecular bond orders are, in one way or another, an expression of the molecular topology.^{1,4}

Various properties of bond orders based on molecular orbitals have been fully investigated.⁵ Particularly intriguing is the relationship between Coulson's bond orders and Pauling's bond orders. In discussing these two quantities, Ruedenberg³ arrived at modified bond orders in which the contribution of each MO is weighted by the reciprocal of the corresponding eigenvalue. Subsequent numerical results^{6,7} have shown that such a procedure gives bond orders identical to the Pauling bond orders computed from resonance structures. This equivalence is evidence of the intimate relationship between MO theory and VB theory. Dewar and Longuet-Higgins⁸ have shown that for a class of benzenoid hydrocarbons the determinant of the adjacency matrix of the molecular graph is related to the number of Kekulé structures for the system.

Recent studies in resonance theory⁹ and graph theory of conjugated hydrocarbons¹⁰ have revived interest in molecular topology and its potential in characterising molecular properties. Pauling bond orders and the number of

Kekulé resonance forms are important information required in such topological considerations. In addition, apparently unrelated problems may have the same or similar combinatorial origin and consequences. The determination of the possible configurations of a polymer chain is such an example.¹¹ Therefore the search for alternative and more efficient ways to evaluate bond orders and enumerate canonical structures is of considerable importance. In this paper we are concerned primarily with use of graph theoretical reasoning in deriving Pauling bond orders.

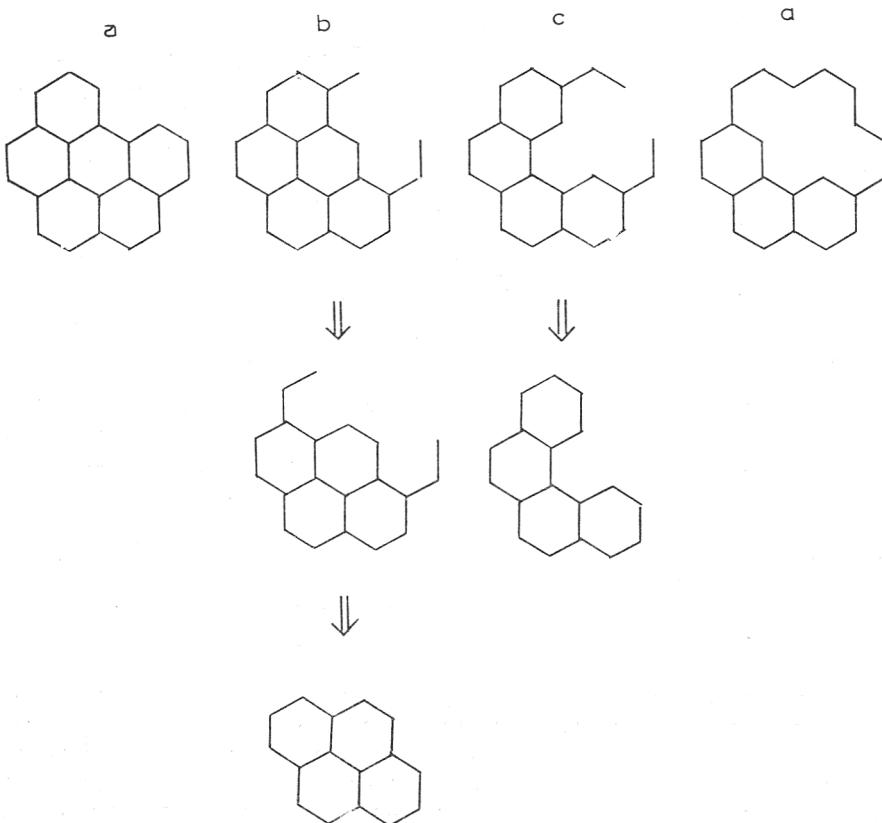
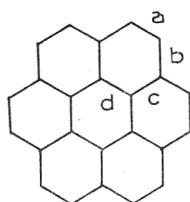
OUTLINE OF THE APPROACH

Pauling bond orders¹² are given as a ratio of the number of Kekulé structures having a double bond between adjacent carbons i, j , designated as $D(i, j)$, and the total number of Kekulé structures N . Hence to derive them we have to find the number of forms with a double bond at (i, j) and we have to know N . Determination of bond orders is therefore closely related to the problem of determining the number of canonical structures of a molecule. However, one need not to resort to the straightforward but tedious listing of all Kekulé structures. Recently Herndon¹³ suggested a graph theoretical technique which produces Pauling bond orders from coefficients assigned to vertices of a molecular graph in which a single *vertex* has been removed. The coefficients are identical to the components of the unnormalized eigenvector of the non-bonding HMO of the graph with the excised vertex. Such coefficients can be simply derived.¹⁴ Another graph theoretical algorithm for the enumeration of Kekulé structures and evaluation of Pauling bond orders was suggested by Cvetković and Gutman.¹⁵ They obtained the desired $D(i, j)$ values from the number of Kekulé structures of the molecule obtained by deletion of the non bonding HMO of the graph with the excised vertex. Such coefficiented cata-condensed conjugated systems, including non-alternants.

We consider here an alternative approach in which one examines a subgraph which is obtained from the molecular graph by excising the *bond* in question together with its adjacent bonds. The search for the double bond count $D(i, j)$ is reduced — as will be seen — to evaluation of the number of Kekulé forms for several smaller subgraphs of the initial structure. The basis of the method is the fact that the search for $D(i, j)$ is equivalent to the counting of all possible distributions of single and double bonds constrained to preserve (i, j) as a fixed double bond. Consequently all adjacent bonds have to be single. The double bond and adjacent single bonds remain constant in all permitted Kekulé structures and can therefore be deleted. Thus, the double bond count $D(i, j)$ is given by the number of ways of distributing double and single bonds in the subgraph arrived at by excising the considered bond and all its immediate neighboring bonds. This has also been recognized by Cvetković and Gutman¹⁵ and forms the basis of their approach. However, to obtain the number of Kekulé structures in a general situation one has also to consider the possibility that selected bonds in subgraphs may also become single. This will bring in additional subgraphs for examination, a complexity which does not appear in cata-condensed systems. We will illustrate the approach on coronene (Table I). The four non-equivalent bonds of coronene are designated

TABLE I

Derived subgraphs for determining $D(i,j)$ values for the four nonequivalent CC bonds of coronene. Each subgraph is obtained by excising the bond in question and adjacent bonds. In the case of bond b and c a further reduction was possible using rules (1)–(4) described in the text.



as a, b, c, and d. Assuming each of them in turn to be a double bond and subsequently erasing them together with adjacent bonds we obtain the four graphs shown in Table I. The resulting graphs can be further simplified, in many instances considerably. The simplification can be accomplished by the following rules:

- Rule 1: An even number of unbranched acyclic bonds can be deleted as they do not affect the distribution of double bonds at the branching site.
- Rule 2: A single exocyclic bond (or an odd number of exocyclic bonds, if not already reduced by Rule 1) can be deleted together with adjacent ring bonds, as it has to be double in all Kekulé structures.
- Rule 3: The number of Kekulé forms of a disconnected subgraph is given by the product of the numbers of structures of each separated fragment.
- Rule 4: Benzenoid fragments joined by a single edge or an odd number of bonds can be separated by erasing connecting bonds, since these cannot affect the distribution of single and double bonds within the fragments.

Additional rules can be formulated for a more general situation. For instance the fragments mentioned in Rule 4 may represent any conjugated system which has a Kekulé type structural formula. By successive application of the above rules, one may arrive at a subgraph for which no classical Kekulé structure is possible. The corresponding bond order is zero and so is the partial contribution of that graph to the overall count of Kekulé forms. Acyclic fragments have either one Kekulé form or none. This can be always found by applying rule 1, which for the former case will reduce the molecular graph to a single edge (ethylene).

In Table II we illustrate the method on phenanthrene and triphenylene. In most cases, the $D(i, j)$ are obtained in a single reduction step. The number of Kekulé forms of a molecule can be obtained if all bond orders are known by dividing the sum of $D(i, j)$ over all bonds by the total number of double bonds in a molecule. For instance the sum of all $D(i, j)$ is 35 for phenanthrene and there are 7 double bonds in each Kekulé structure, hence the number of different Kekulé structures is $35/7 = 5$. It is possible to obtain the number of Kekulé structures of a molecule more efficiently by considering a single edge of a graph and assuming it to be alternatively a single and a double bond. Subsequent analysis of the subgraphs obtained by erasure of all bonds for which an assignment of the bond character is unique leads to the answer. The method is described fully elsewhere.¹⁶ We will illustrate this on 1,12-benzperylene and bridged phenanthrene (Table III) which are obtained as subgraphs in the degradation of coronene. We are at liberty to select any bond to derive the number of Kekulé structures. The procedure is more efficient, however, if a peripheral bond is selected first. This leads to fewer subgraphs for analysis. A given bond is single or double in the different structures, so if we determine the number of structures in which the particular bond is single and is double separately their sum gives the total number of structures. The number of Kekulé structures which arise when the selected bond is assumed to be double is given by corresponding $D(i, j)$ as has already been discussed. Their determination can be simplified by implementing rules (1)—(4). A deter-

TABLE II

Derived subgraphs for bonds in phenanthrene and triphenylene respectively. The simplifications obtained using rules (1)–(4) described in the text are indicated for each case above the double arrow. The last column gives the number of Kekulé structures when the selected bond is assumed double, i.e., D(i,j) values.

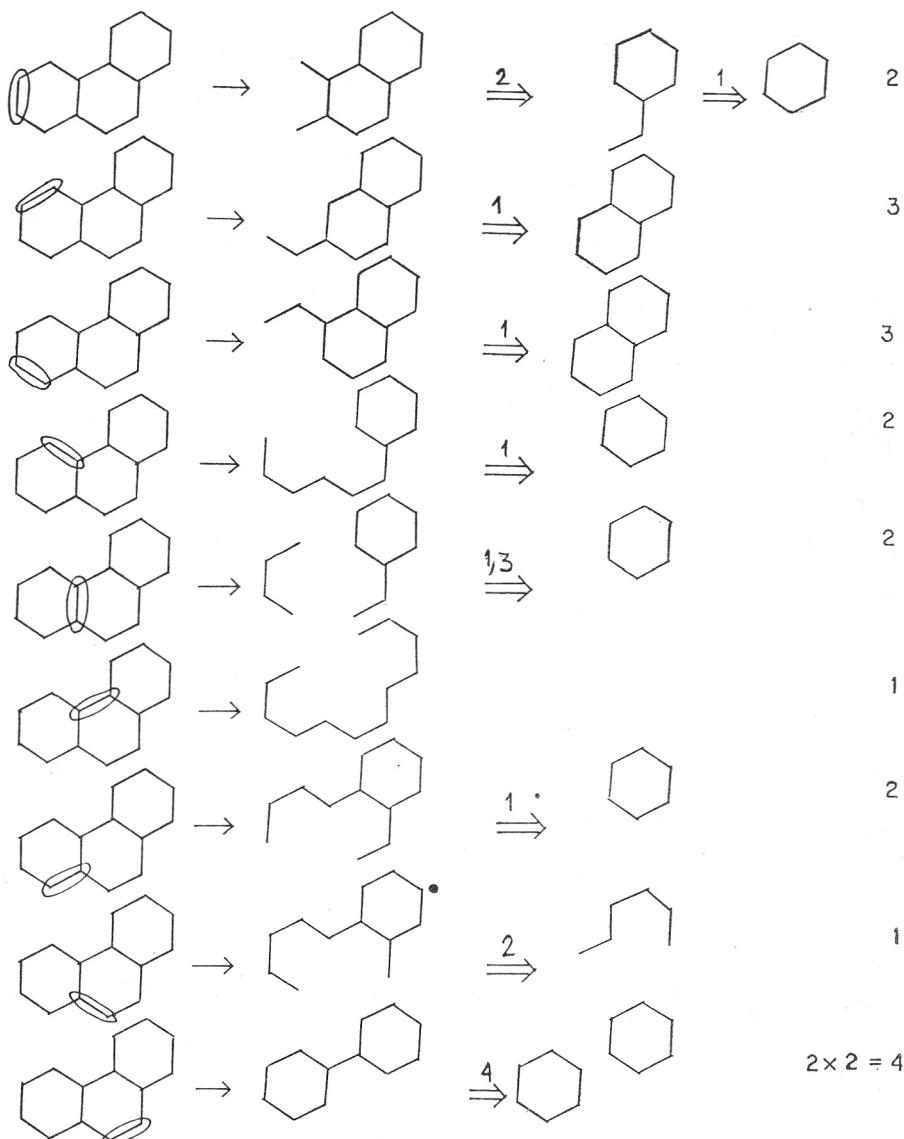


TABLE II — cont'd.

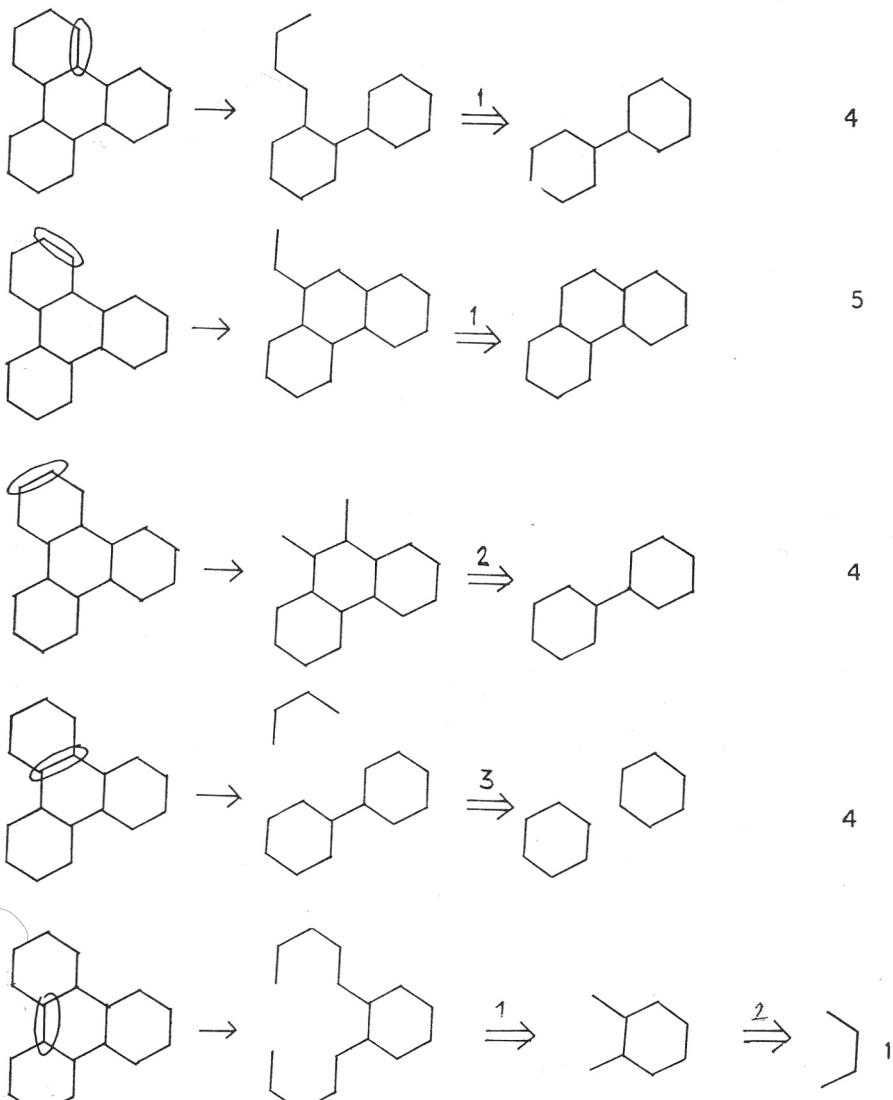
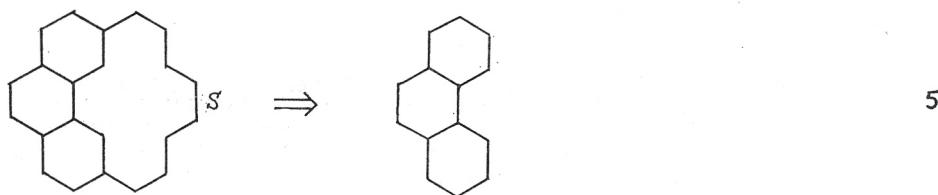
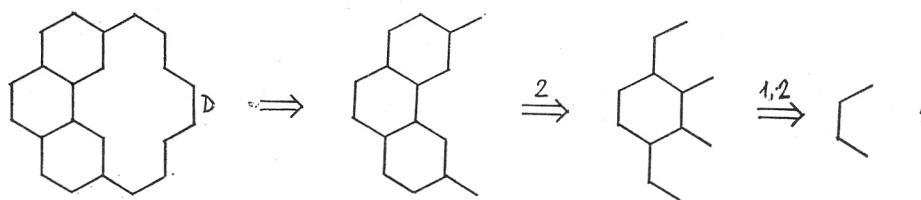
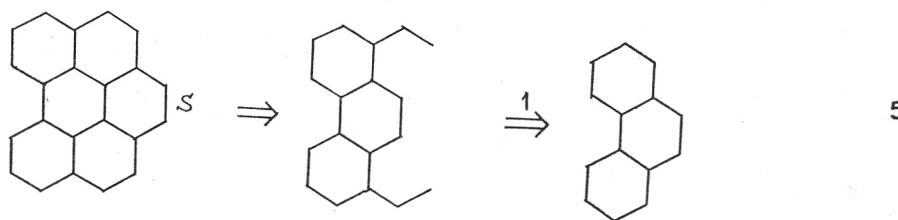
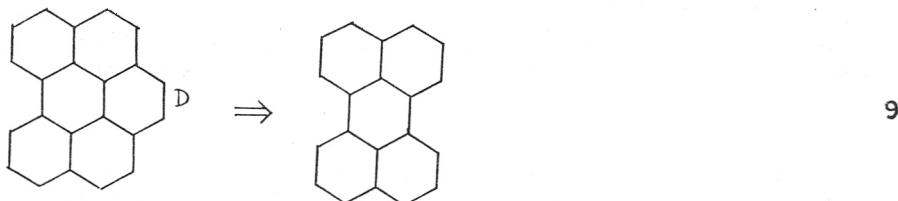


TABLE III

An illustration of the evaluation of the number of Kekulé structures for 1,12-benz-perylene and bridged phenanthrene. An exposed peripheral bond was assumed to be double (D) and single (S) alternatively. The rules (1)—(4) were applied to reduce the intermediate subgraphs to simple molecular form.



mination of the corresponding number of structures with a single bond at the selected location, *i.e.*, finding the corresponding $S(i, j)$ values, proceeds in a similar fashion. Exposed peripheral single bonds necessarily have two adjacent double bonds at each end, and these have several neighboring single bonds. All bonds for which an assignment is thus determined cannot be changed in type — as this would ultimately require a change of the assignment of the initially selected bond — hence, all these bonds can be deleted from the molecular graph. The process quickly produces smaller molecular skeletons with known number of Kekulé forms.

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SAŽETAK

Određivanje Paulingova reda veze teorijom crteža

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U radu je opisano određivanje Paulingova reda veza za konjugirane ugljikovodike. Postupak se osniva na smanjenju molekulnog crteža isključivanjem veze koja se razmatra i susjednih veza kojima se može jednoznačno pridružiti kratnost veze. Pristup je općenit i jednakovo važi za tzv. izmjenične i neizmjenične sustave kao i lančano (kata) ili rubno (peri) sažete ugljikovodike.

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