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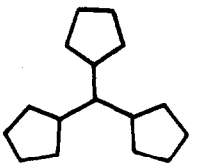
Degeneracies in Molecular Graph Spectra

T.P.Radhakrishnan
School of Chemistry, University of Hyderabad
Hyderabad - 500 134, India

Abstract : Unusual degeneracies of the Hückel π- molecular orbitals in some molecular frameworks is explained on the basis of the molecular graph decomposition.

π-orbital degeneracies higher than those predicted on the basis of the molecular point group in certain special molecular frameworks has been analysed in a recent Letter[1]. Here we delineate the origin of these unusual degeneracies; we note that, these degeneracies in the eigenvalue spectrum arise due to the particular molecular graph connectivity and will be seen only at the simple Hückel level of theory.

We consider graphs **1** and **2** as prototypes for the following discussion. As usual[2] the connectivity of the vertices represent the



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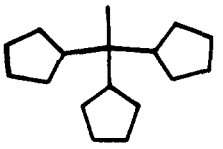

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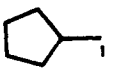
carbon $2p_z$-orbital adjacencies for the Hückel treatment (usual HMO treatment is not applicable to **2**; it is considered here only for the graph theoretical discussion). Both graphs show 5-fold degeneracy in the eigenvalues 0.618 and -1.618 on diagonalization of the unweighted adjacency matrix. If **r** represents the number of rings around the central atom, both have (2r-1)-fold degeneracy as pointed out for **1** and several similar systems in Ref.1. However it may be noted that non-bonding orbitals do not contribute to the (2r-1) value as mentioned in Ref.1. Further, the application of the proof given in Ref.1 to systems



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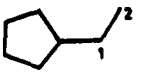

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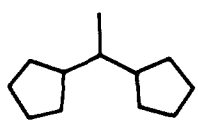
like **2** (and **5**, here as well as in Ref.1) is not clear. On the contrary, the approach of Dias[3], incrementing the degeneracies of a chosen eigenvalue (in this case, 0.618 or equivalently -1.618) by adding rings (5-rings) to an initial graph (**3** or **4**) leading to the required graph (**1** or **2**) suggests a more general basis for the formulation, 2r-1.

3 and **4** have a non-degenerate level at 0.618 which corresponds to one of the degenerate pair at 0.618 in the 5-ring that was left unperturbed by the substitution. Addition of another 5-ring at vertex 1 (a nodal vertex for this eigenvalue) of **3** or **4** adds two levels of eigenvalue 0.618. If thus r-1 rings are added around the central vertex, the final degeneracy of the eigenvalue 0.618 is 1+2(r-1) = 2r-1. This explains the (2r-1)-fold degeneracy of both **1** and **2**. Same approach can be extended to all other systems treated in Ref.1.

However, this approach raises two important questions. First, what is the basis for the propagation of these degeneracies? Second, does the addition of a similar ring (5-ring) at any of the nodal verices (1 or 2) corresponding to a particular eigenvalue (0.618) of a perturbed ring (**4**) lead to similar propagation of its degeneracy ? If not why ? **5** has 3-fold and **6** only 2-fold degeneracy in the eigenvalue 0.618; so the answer to the second question is in the negative.



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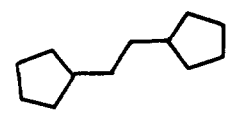

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Inspection of several graphs shows that when an n-ring (with sufficient symmetry to have a 2-fold degenerate level) is attached to a vertex which is already directly connected to a similar n-ring, the degeneracy of the relevant level increases by 2; if connected to a different vertex, degeneracy increases by one only. The reason for this becomes transparent, if one looks at the resolution of the secular polynomial of the graph into the secular polynomials of its subgraphs according to Heilbronner's procedure[4]. The following relation was presented by Heilbronner for the secular polynomial, $P_G(x)$ of acyclic graphs and cyclic graphs with no fused rings (x is a dummy variable)

$$P_G(x) = P_{G-e}(x) - P_{G-(e)}(x)$$

where G, G-e and G-(e) represent respectively the graph, its subgraph with one edge, e deleted and the subgraph with the vertices connected by e and their incident edges deleted. Gutman et. al.[5] have shown that a similar relationship holds for the acyclic polynomial of any graph. From this we infer that the Heilbronner relation can be generalised to all graph decompositions in which the number of cycles in G and G-e are the same. Hence it may be applied to the graphs considered here.

If G-e and G-(e) are n- and m-fold degenerate respectively in the eigenvalue λ^*, then

$$P_{G-e}(x) = (x - \lambda^*)^n.P_1(x); \qquad P_{G-(e)}(x) = (x - \lambda^*)^m.P_2(x)$$

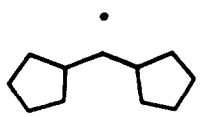
Hence, for the case $n \leqslant m$,

$$P_G(x) = (x - \lambda^*)^n.[P_1(x) - (x - \lambda^*)^{m-n}.P_2(x)]$$

Therefore it is seen that G will be n (or m) -fold degenerate in λ^* if $n \leqslant m$ (or $m \leqslant n$). The case of **5** and **6** can be illustrated as follows.

$$P_5(x) = P_7(x) - P_8(x); \qquad P_6(x) = P_9(x) - P_8(x)$$

where **7**, **8** and **9** are the appropriate subgraphs. **5** is 3-fold degenerate



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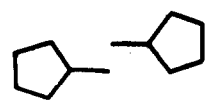

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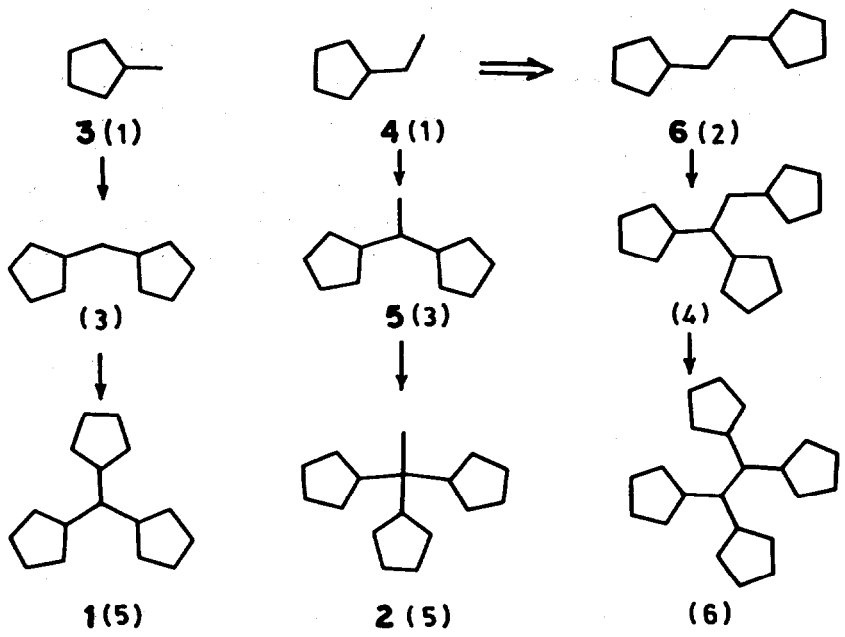
in the eigenvalue 0.618, since **7** is 3-fold and **8** is 4-fold degenerate respectively in the same eigenvalue. **6** is only 2-fold degenerate, since **9** also has only 2-fold degeneracy. (Note, trivially, that a graph will be (n+m)-fold degenerate in a particular eigenvalue, if it has two disconnected components of degeneracy n and m in the same eigenvalue).

Thus the answer to the questions above, may be summarized as shown in Scheme 1. For each graph, the number in parenthesis indicates the degeneracy of the eigenvalue 0.618. The single arrows represent the Dias-type propagation of graphs where the degeneracy increases by 2 and the double-line arrow indicates the case where it increases by 1.

In conclusion, it is seen that degeneracies in molecular graph spectra can be propagated by appropriate extension of the molecular



Scheme 1.

framework, and the basis for it can be understood in terms of the Heilbronner graph decomposition formula.

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References and Notes :

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