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Calculation of the Non-Bonding Molecular Orbitals in the Hückel Theory

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A method is given to obtain all NBMO's for both alternant and nonalternant aromatic hydrocarbons. In addition few theorems are derived which can be used to deduce some (or all) of the NBMO's directly from the graph of the molecule.

INTRODUCTION

Hückel molecular theory is one of the simplest semiempirical approaches to the study of electronic structure of large organic molecules. However, even this theory becomes more and more cumbersome when applied to large systems. If the number of carbon atoms exceeds 5, and there is no symmetry which would reduce the Hückel matrix, one can practically not avoid the use of a computer. On the other hand, we are always interested in the solution of the Hückel problem as a whole. The stability of the molecule, charge densities, reactivities, dipole moments *etc.* are usualy quantities which we would like to infer from those solutions. From this point of view, non-bonding molecular orbitals (NBMO's) are of particular interest. In even alternant hydrocarbons the existence of such an orbital implies a triplet ground state and instability of the molecule. Moreover, within the theory given by Fukui *et al.*,[1,2] electrons occupying NBMO's are responsible for chemical reactivity.

The aim of this paper is to describe a general method to obtain all NBMO's for both, alternant and nonalternant hydrocarbons.

Basic Algoritm for Evaluation of the NBMO's

Each carbon atom in an aromatic hydrocarbon can be linked either to one, two or three neighbouring carbon atoms (Fig. 1a, 1b and 1c, respectively). These three possibilities correspond to three types of conditions imposed by that atom to the NBMO coefficients. From the Hückel equation one can easily infer the following rules:

1) If the atom 1 is linked solely to the atom 2, then the NBMO coefficient at the atom 2 vanishes, *i. e.* $c_2 = 0$ (Fig. 1a). We will say that atom 1 is in an *a*-position.

2) If the atom 1 is linked to two atoms 2 and 3 (Fig. 1b), the sum of NBMO coefficients at these atoms vanishes, *i. e.* $c_2 + c_3 = 0$. Such a position we will define as *b*-position.

3) If the atom 1 is linked to three atoms then the sum of NBMO coefficients at these atoms vanishes, *i. e.* $c_2 + c_3 + c_4 = 0$ (Fig. 1c). We call such

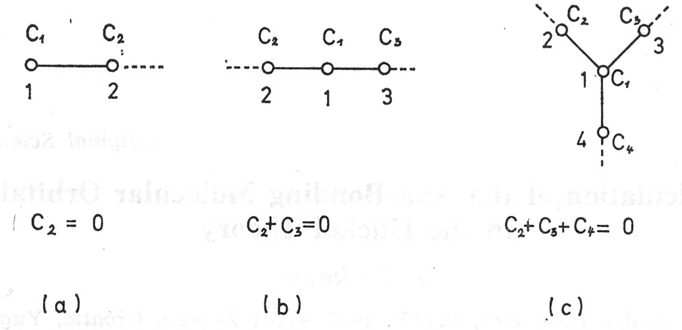


Fig. 1

a position a c-position. We notice that the above rules are generalizations of analogous rules for alternant hydrocarbons[3-5].

Now, each carbon atom gives rise to one condition of the above type. We end up with *n* conditions for *n* NBMO coefficients. Each condition is represented by a homogeneous equation in one, two or three unknowns. These equations have either only trivial solution, which means that there is no NBMO, or they have non-trivial solutions, each corresponding to one NBMO. However, it is not necessary to write down these equations in order to obtain the NBMO's. The whole calculation can be performed using the graph of the molecule. The following example (Fig. 2.) illustrates this procedure.

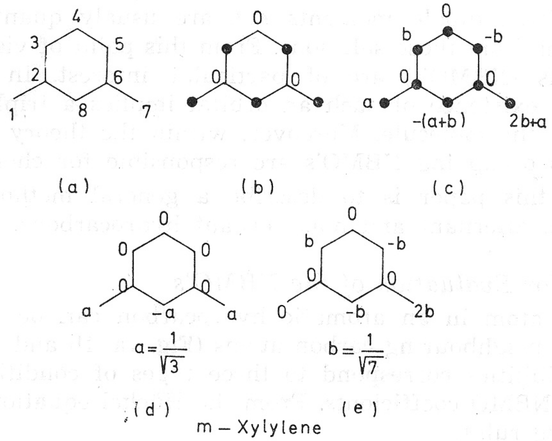


Fig. 2

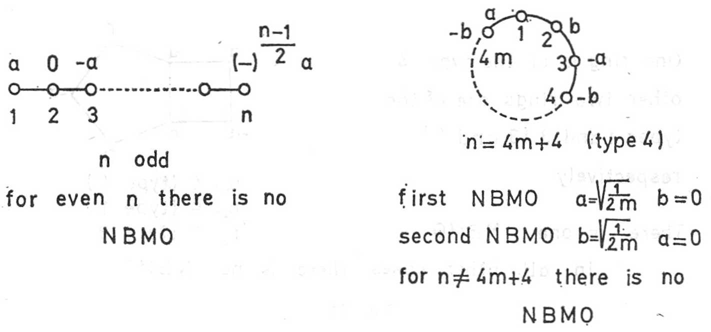
We look *e. g.* for all NBMO's (if any) of *m*-xylylene (Fig. 2a). Conditions imposed by atoms 1 and 7, which occupy *a*-positions, give NBMO coefficients at atoms 2 and 6 to be equal to zero. Atoms 3 and 5 (*b*-position) give the value of the NBMO coefficients at atom 4 equal to zero (since $c_4 = - c_2 = 0$ by 3, and $c_4 = - c_6 = 0$ by 5). At the same time condition 8 is fulfilled ($c_2 + c_6 = 0$ condition 8). In order to indicate that all these conditions have been taken into account we mark corresponding atoms with dots (Fig. 2b).

Now we arbitrarily put the value of the NBMO coefficient at atom 1 to be a and at atom 3 to be b. By 4 we have $c_5 = -b$, 2 implies $c_8 = -(a+b)$ and 6 implies $c_7 = a + 2b$. All conditions are now fulfilled, and since there are two independent parameters left, a and b, two NBMO's do exist (Fig. 2c) The first we can choose by putting $b = 0$, and the second by putting $a = 0$ (Fig. 2d and 2e). Normalisation conditions yield in the first case $a = 1/\sqrt{3}$ and in the second $b = 1/\sqrt{7}$. The two NBMO's are not orthogonal, but can easily be made to be so.

NBMO's for some Special Classes of Molecules

The above procedure can be applied to each Hückel type molecule and it automatically yields all NBMO's. However, some special classes of molecules might be of particular interest. First we will give two examples, linear and cyclic polyenes, where the number of NBMO's is already well known.

1) Linear polyenes (chain, Fig. 3a). If the linear polyene has an even number of atoms, there is no NBMO, if the number of atoms is odd, there is one and only one NBMO. Condition 1 implies $c_2 = 0$, this implies $c_4 = 0$ *etc.* Now assume the NBMO coefficient at atom 1 to be a. This implies $c_3 = -a$, hence $c_5 = a$ *etc.* If the number of atoms is even, we end with $c_{n-1} = \pm a$ and hence (condition n) $a = 0$, *i. e.* there is no NBMO. If the number is odd we have $c_n = \pm a$, all conditions being fulfilled and there is one NBMO (Fig. 3a).



(a) (b)

Fig. 3a and 3b

2) Cyclic polyenes (ring, Fig. 3b). If the number of atoms in a cyclic polyene is $4m + 4$, there are two NBMO's, otherwise there is no NBMO. We start by putting $c_1 = a$, hence $c_3 = -a$, $c_5 = a, \ldots$ If the number of atoms is odd, we end up with $c_2 = \pm a$. Now we go on in the same direction, *i. e.* $c_4 = \mp a$, $c_6 = \pm a$ and finally we hawe $c_3 = a$, which implies $a = 0$. There is no NBMO. Assume now the number of atoms to be even. The same procedure yields $c_3 = -a$, $c_5 = a, \ldots$ and finally $c_1 = \pm a$, the sign of a being positive if there are $4m + 4$ atoms in the ring and negative if there are $4m + 2$ atoms. The latter case means $a = 0$. Similarly we can put $c_2 = b$ which implies

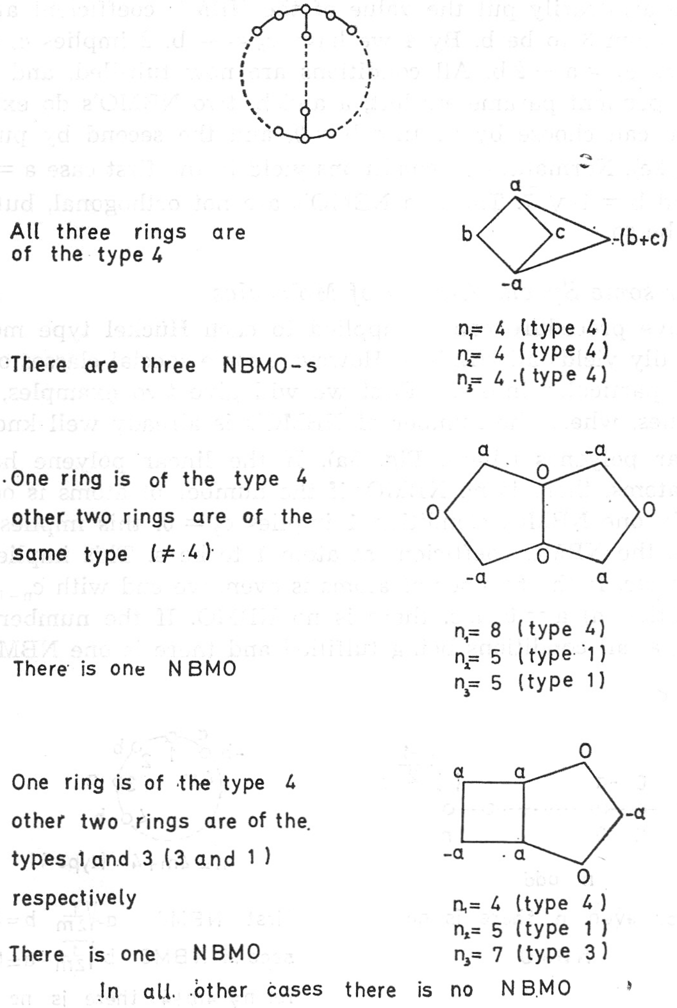


Fig. 3c

$c_4 = -b$, $c_6 = b, \ldots, c_2 = \pm b$. Hence if there are 4m + 4 atoms in the ring there are two NBMO's, and all other cases there is no NBMO (Fig. 3b).

3) Bicyclic systems (Fig. 3c). Bicyclic systems have either three, one or no NBMO. We shall notice first that a bicyclic system consists of three rings, the number of atoms in these rings being n_1, n_2 and n_3, respectively. One can formulate the necessary and sufficient conditions for a bicyclic system to have NBMO's in terms of these numbers. Let us define four types of rings, type 1 consisting of 4m + 1, type 2 of 4m + 2, type 3 of 4m + 3 and type 4 of 4m + 4 atoms in a ring (here m = 0, 1, 2, . . .). We give now, without proof which can be derived on the base of rules 1—3 (Fig. 1.), the following conclusions: In order that a bicyclic system has NBMO, there must be at least one ring of the type 4.

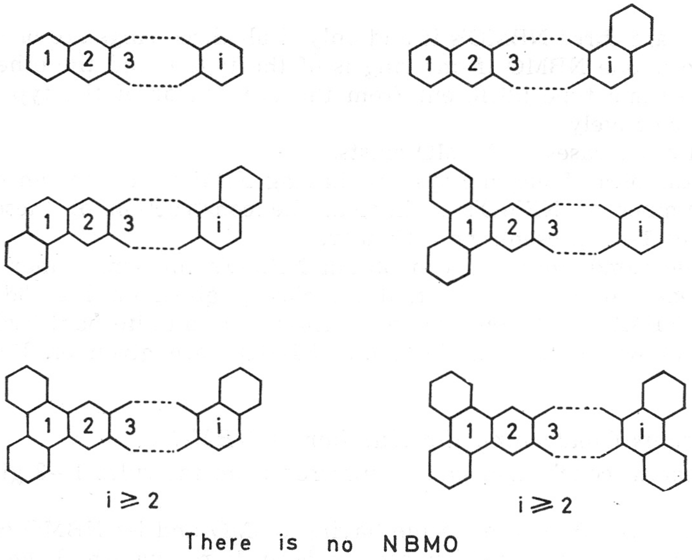


Fig. 3d

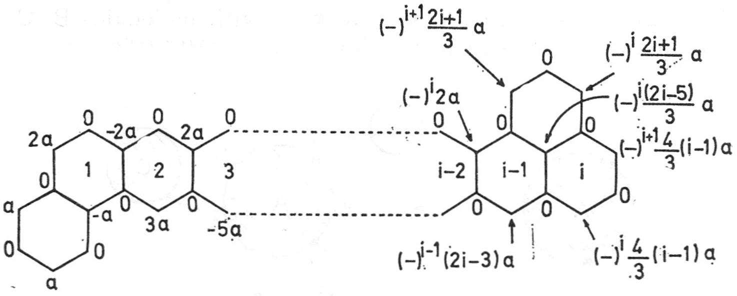
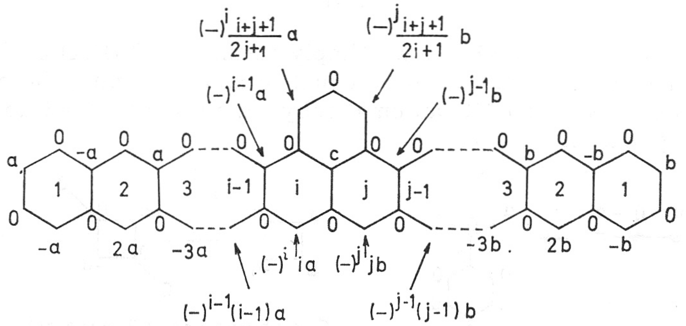


Fig. 3e



here $(-)^{i}(2i+1)\,a+(-)^{j}\,(2j+1)\,b=0$

and $c=(-)^{i+1}\,i\,a+(-)^{j+1}\,j\,b=(-)^{j}\,\frac{i-j}{2i+1}\,b=(-)^{i}\frac{j-i}{2j+1}\,a$

Fig. 3f

a) There are three NBMO's if and only if all three rings are of the type 4.

b) There is one NBMO if one ring is of the type 4 and the other two are either of the same type (different from the type 4), or of the types 1 and 3 (3 and 1), respectively.

c) In all other cases no NBMO exists.

Some examples of bicyclic systems having NBMO's are shown on Fig. 3c. Once the number of NBMO's is known, the construction of these orbitals, applying rules 1—3, presents no difficulty.

Along the same lines one can obtain NBMO's for some other classes of molecules. One can show, *e. g.*, that all classes given on Fig. 3d. have no NBMO. The NBMO coefficients for some classes of odd alternant hydrocarbons (which are known to have at least one NBMO[6]) are given on Fig. 3e. and Fig. 3f.

Some Theorems Concerning the Number of NBMO's

Some general conclusions can be inferred from the rules 1—3 given above (Fig. 1.).

Theorem 1: Let A be a molecule having NBMO and let NBMO coefficients at atoms x, y, z, u, v... (which occupy *b*-positions) vanish. Each composed molecule A′ = A + B + C + ... which can be obtained by joining molecule A at some (or all) of the atoms x, y, z, u, v... with molecules B, C, ... (or by joining these atoms inbetween) has at least one NBMO (Fig. 4a).

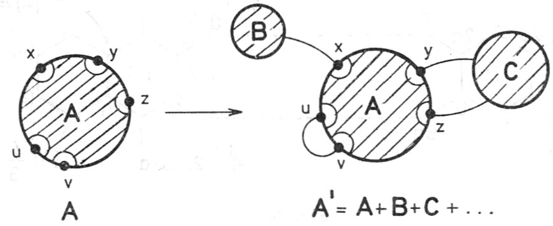


Fig. 4a

In order to obtain this NBMO we simply assume all NBMO coefficients at atoms of the molecules B, C, ... to be equal to zero, retaining the old NBMO at the molecule A. Such NBMO automatically satisfies rules 1—3 above. Some examples are given on Fig. 4b.

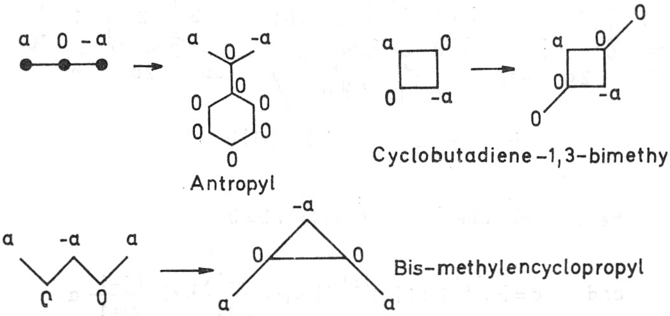


Fig. 4b

If two or more component molecules possess NBMO's, one can infer the existence of more than one NBMO (Fig. 4c).

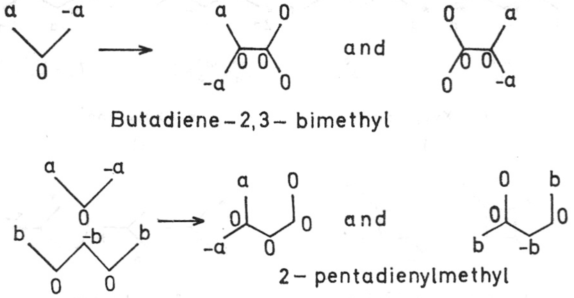


Fig. 4c

Some further specifications can be made when a component molecule is an odd alternant hydrocarbon. It is well known that such molecules have at least one NBMO with vanishing coefficients at nonstarred atoms.[6] Hence, and from theorem 1 we obtain:

Theorem 2a: If there is a component molecule which is an odd alternant hydrocarbon, and if this molecule is joined to the rest of the molecule at nonstarred *b*-positions only, then the composed molecule has at least one NBMO. This NBMO is the same as the NBMO of the component molecule.

Let us illustrate this on *m*-xylylene (Fig. 2.). One can immediately recognize two odd alternant hydrocarbon components of this molecule joined to the rest of the molecule at nonstarred *b*-positions only (Fig. 5a). Hence there are at least two NBMO's. We actually know that there are exactly two (Fig. 2d and 2e). In fact there are two more odd alternant hydrocarbon components which give rise to NBMO's (Fig. 5b). However, each of those components contains starred atoms still covered by one or the other of the components on Fig. 5a. Hence the corresponding NBMO's of Fig. 5b are linear combinations of NBMO's associated with Fig. 5a.

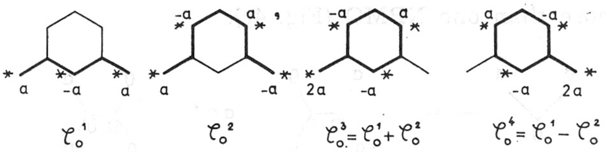
Some other examples of the application of theorem 2a are shown on Fig. 5c—5j. The structure which is a linear combination of the others is given in brackets.

One can derive a similar theorem for the case of even alternant hydrocarbon components. As shown by Coulson and Longuet-Higgins,[6] if two MO's of an even alternant hydrocarbon form a pair, they are given by

$$\varphi_i^+ = \overset{*}{\underset{r}{\Sigma}} c_{ir}\,\chi_r + \overset{o}{\underset{s}{\Sigma}} c_{is}\,\chi_s$$

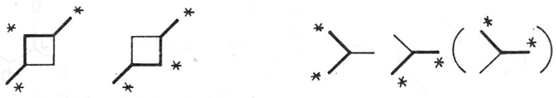
$$\varphi_i^- = \overset{*}{\underset{r}{\Sigma}} c_{ir}\,\chi_r - \overset{o}{\underset{s}{\Sigma}} c_{is}\,\chi_s$$

where r refers to starred and s to nonstarred atoms, φ_i^+ being the first and φ_i^- the second MO. Now, if two NBMO's form a pair they can be chosen in the form



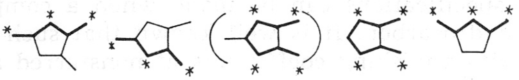
m – Xylylene
(a)

m – Xylylene
(b)



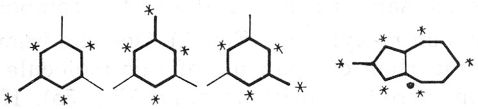
Cyclobutadiene-1,3-bimethyl
(c)

2-Allylmethyl
(d)



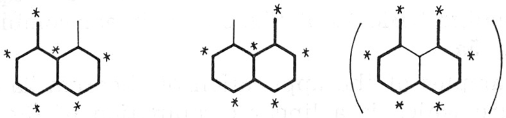
Fulvene-2,3-bimethyl
(e)

1,2-and 1,3-Bis-methylene-cyclopentenyl
(f)

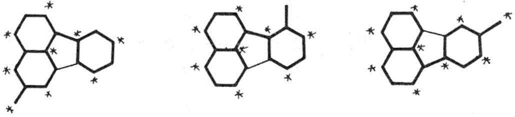


Benzene-1,3,5-tris-methyl
(g)

2-Azulenylmethyl
(h)



1,8-Naphtho-quinodimethane
(i)



2-, 7- and 8-Fluoranthylmethyl
(j)

Fig. 5

$$\varphi_o^+ = \sum_{r}^{*} c_{ir}\,\chi_r$$

$$\varphi_o^- = \sum_{s}^{o} c_{is}\,\chi_s$$

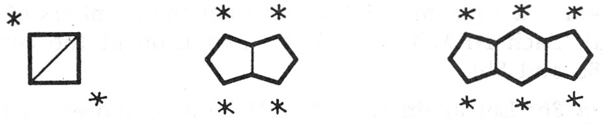
i. e. NBMO φ_o^+ has vanishing amplitudes at all nonstarred atoms, and NBMO φ_o^- at all starred. If we join such a molecule to other molecules at nonstarred *b*-positions only, there is a NBMO φ_o^+ having vanishing amplitudes at all such positions and according to theorem 1 the composed molecule has at least one NBMO. The same holds for starred positions. Hence:

Theorem 2b: If there is a component molecule which is an even alternant hydrocarbon having at least one NBMO, and if this component molecule is joined to the rest of the molecule at nonstarred (starred) *b*-positions only, then the composed molecule has at least one NBMO. This NBMO is the same as the NBMO of the component molecule.

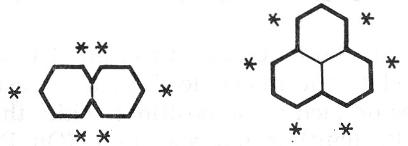
Some examples of the application of theorem 2b are given on Fig. 6.

Theorems 2a and 2b give sufficient conditions that a composed molecule has NBMO. However, these conditions are not necessary, *i. e.* there are molecules having NBMO and which have no component alternant hydrocarbon of the type specified in theorems 2a and 2b (see Fig. 7.).

The following two theorems give necessary and sufficient conditions for obtaining the number of NBMO's and NBMO coefficients of the composed molecule, once the number of NBMO's and NBMO coefficients of the component molecule are known.

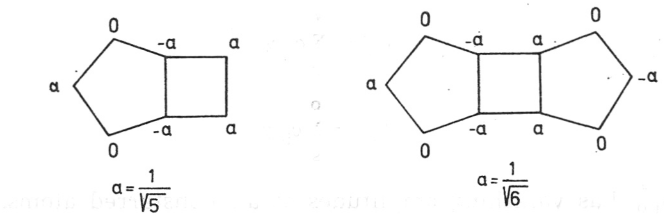


Bicyclobutadiene (a) Pentalene (b) S-Indocen (c)



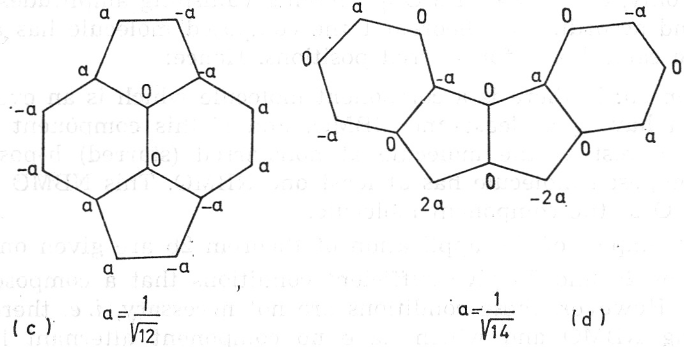
Heptalene (d) Phenolenyl (e)

Fig. 6



Bicyclo(0.2.3) heptatrienyl (a)

Bicyclopentadienylene (b)



Pyrocylene

1,2,5,6-Dibenz-pentalene

Fig. 7

Theorem 3a: Let A′ = A + B be a composed molecule and let B be joined to A at atom x which assumes either *a*- or *b*-position. If B is an even numbered chain or a 4m + 2 ring (m = 1, 2,3, . . .) then the numbers of NBMO's in A′ and A are equal. Each NBMO of A′ is an extension of the corresponding NBMO in A (Fig. 8a and 8b).

Theorem 3b: Let again A′ = A + B be a composed molecule and let B be joined to A at atom x (in either *a*- or *b*-position). Let further A* be a molecule which we obtain by removing atom x from a molecule A. If B is an odd numbered chain then the numbers of NBMO's in A′ and A* are equal, each NBMO of A′ being an extension of the corresponding NBMO in A*. If B is a 4m + 4 type ring, then the number of NBMO's in A′ is by one higher then the number of NBMO's in A*. The extra orbital corresponds to the ring, while other orbitals in A′ are extensions of the corresponding orbitals in A* (Fig. 8c and 8d).

We notice that in both cases (theorem 3a and 3b), component B is allowed to be joined to the molecule A at any position (*a*- and *b*-positions cover all possible cases of such a composition), while the nature of the molecule A (alternant or nonalternant) is not specified. (On Fig. 8. is given only the case when atom x occupies *b*-position in the molecule A. The case when x occupies *a*-position is analogous).

Both theorems can be proved by inspection. E. g. let us take the case of an even chain joined to the molecule A at *b*-position (Fig. 8a). Assume first molecule A to have an NBMO. There is an NBMO coefficient a at atom x and NBMO coefficients b and — b on neighbouring atoms (rule 2, Fig. 1b). If we

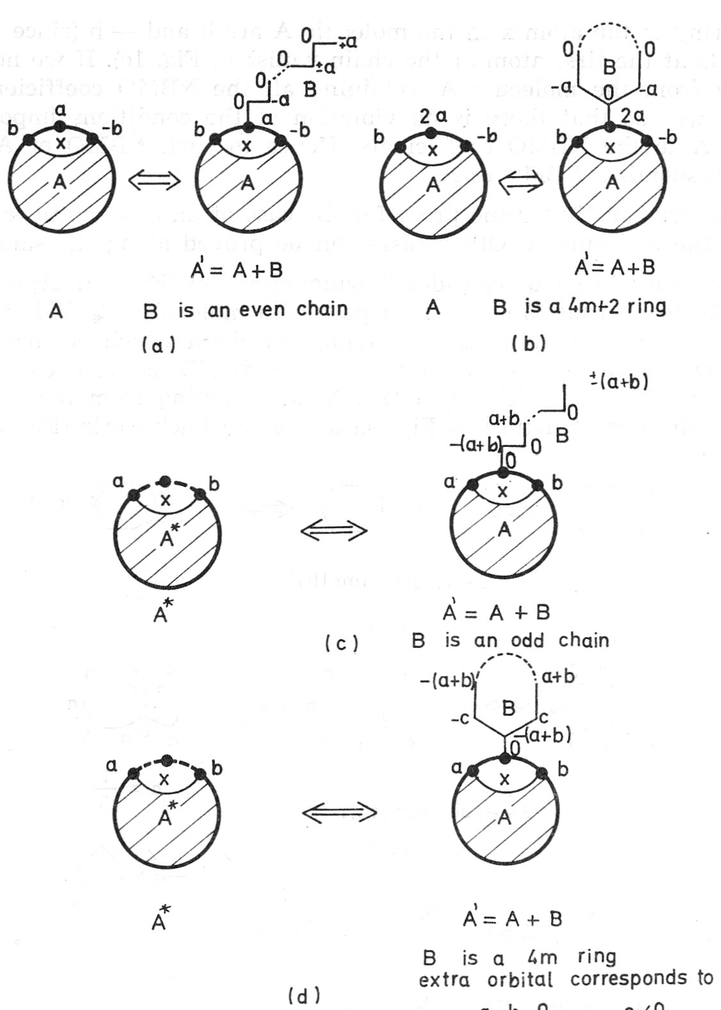
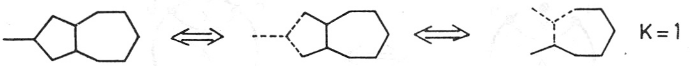


Fig. 8

now join an even chain at the atom x and retain old NBMO coefficients at all atoms of the molecule A, we have (rule 3, Fig. 1c) NBMO coefficient zero at the first atom of the chain, NBMO coefficient — a at the second atom *etc.* We end with the last atom in the chain where the NBMO coefficient assumes the value $(-)^{n/2}$ a, n being the number of atoms in the chain. Conditions imposed by all atoms in A′ are now satisfied and hence each NBMO of A induces an associated NBMO of A′ which is an extension of the first one. Conversely, let the molecule A′ = A + B have NBMO. The NBMO coefficients at the (n — 1)-th atom of the chain vanishes by virtue of the condition imposed by the last atom in the chain. Similarly the NBMO coefficients at the (n — 3)-th atom vanishes etc. We end with the first atom in the chain where the NBMO coefficient vanishes as well. Now, assume the NBMO coefficient at atom x to have the value a. The NBMO coefficients at the two atoms neighbouring to the atom x in the molecule A are b and — b (since the NBMO coefficients at the first atom of the chain vanishes, Fig. 1c). If we now remove the chain from the molecule A, retaining all the NBMO coefficients at this molecule, we see that there is no violation of the conditions imposed by all atoms of A to the NBMO coefficients. Hence to each NBMO of $A' = A + B$ there corresponds a NBMO of A.

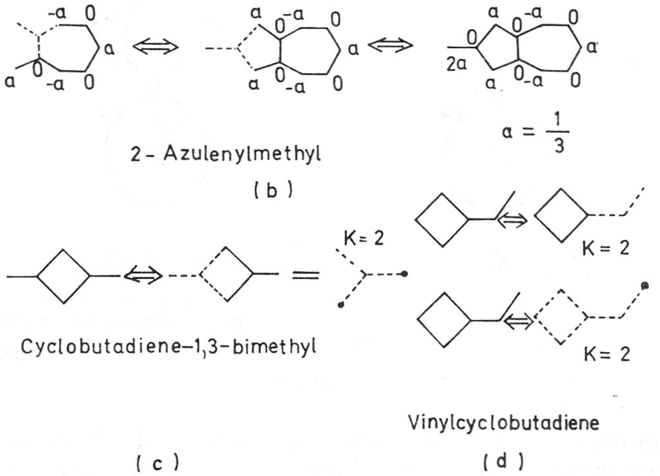
The above constitutes the proof for the case of an even numbered chain B joined to the molecule A. Other cases can be proved along the same lines.

As an example let us consider 2-azulenylmethyl (Fig. 9a). Applying twice theorem 3b (each time we remove a part of a molecule which is represented by dotted lines) we obtain the odd numbered chain which is known to have one NBMO. Hence 2-azulenylmethyl has one NBMO as well. One can easily write down NBMO coefficients of this NBMO starting from the NBMO coefficients of the last structure in Fig. 9a and going backwards (Fig. 9b).



2 - Azulenylmethyl

(a)



2 - Azulenylmethyl

(b)

Cyclobutadiene–1,3–bimethyl

Vinylcyclobutadiene

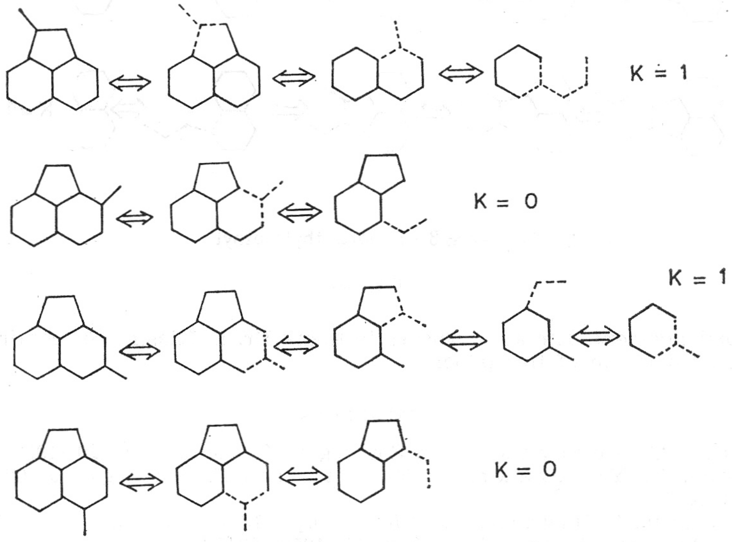
(c) (d)

Fig. 9

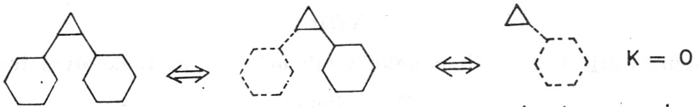
Another example is shown on Fig. 9c. The final structure consists of two separate atoms, and to each atom (which is an odd numbered chain having only one atom) corresponds one NBMO. Hence cyclobutadiene-1,3-bimethyl has two NBMO's. The number of NBMO's in vinylcyclobutadiene (Fig. 9d) can be obtained by two alternant ways. We can apply theorem 3a and remove an even chain (upper part of Fig. 9d). The final structure is a $4m + 4$ ring which is known to have two NBMO's. Alternatively we can (by theorem 3b) remove a $4m + 4$ ring and the atom by which this ring is connected to the rest of the molecule (lower part of Fig. 9d). The final structure consists of an atom, which yields one NBMO while the removed 4m + 4 ring gives another NBMO. Obviously, the number of NBMO's obtained by two alternant ways must be the same.

Some further examples how to obtain NBMO's are given on Fig. 10. In the case of 2- and 4-acenaphthylenylmethyl (Fig. 10a) the final structure is a bicyclic system having no ring of the type 4 and thus no NBMO (the numbers of atoms in three rings are 5, 6, and 9 *i. e.* types 1, 2 and 1, respectively). In the case of 1- and 3-fluoranthylmethyl (Fig. 10d) the final structure is a tricyclic system which (as can be shown applying rules 1—3) has no NBMO. Other cases are trivial.

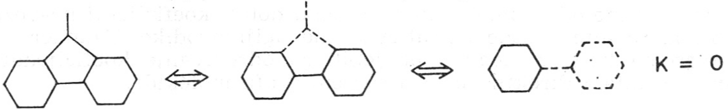
If we are interested in NBMO coefficients we can write down these coefficients for the last structure and then go backwards (as in the case of 2-azulenylmethyl Fig. 9b), doing it for each NBMO separately. However, in most cases one can apply either theorem 2a or theorem 2b and then write down NBMO coefficients. For alternant hydrocarbons this presents no difficulty.



1—, 3—, 4-and5— Acenaphthylenylmethyl
(a)

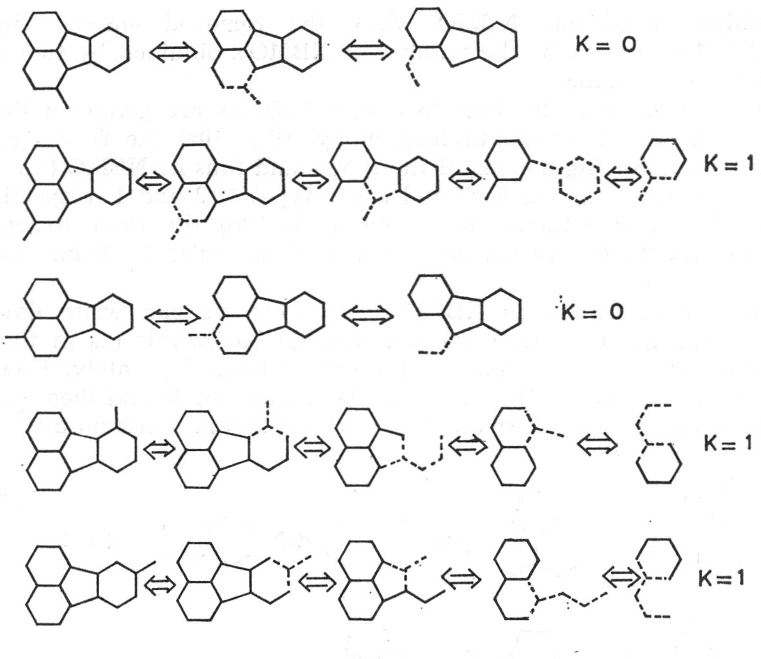


(b) 1,2—Diphenylcyclopropenyl



(c) Dibenz — fulvene

Fig. 10a—10c



1-, 2-, 3-, 7-and 8- Fluoranthylmethyl

Fig. 10d

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REFERENCES

1. K. Fukui, T. Yonezawa, and Shingu, *J. Chem. Phys.* **20** (1952) 722.
2. K. Fukui, T. Yonezawa, C. Nagata, and H. Shingu, *J. Chem. Phys.* **22** (1954) 1433.
3. H. C. Longuet-Higgins, *J. Chem. Phys.* **18** (1950) 265.
4. M. J. S. Dewar, *J. Am. Chem. Soc.* **74** (1952) 3345.
5. E. Heilbronner and H. Bock, *Das HMO-Modell und seine Anwendung,* Verlag Chemie, Weinheim 1968.
6. C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* **A 192** (1947) 16.

IZVOD

Izračunavanje ne-veznih molekularnih orbitala u Hückelovoj teoriji

T. Živković

Razvijena je metoda pomoću koje se mogu dobiti koeficijenti ne-veznih molekularnih orbitala za alternantne i nealternantne ugljikovodike. Također je predloženo nekoliko teorema koji se mogu upotrijebiti za određivanje koeficijenata ne-veznih molekularnih orbitala direktno promatranjem grafa molekule.

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