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On some problems in the theorems of alternant hydrocarbons

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A number of theorems of alternant hydrocarbons presented by Dewar are proved to be wrong. A statement of the related theorem instead of Dewar's is presented.

Key words: Alternant hydrocarbons

The HMO behavior of alternant hydrocarbons (AH) was early studied in detail [1-3]. In 1969, Dewar [4] presented a series of theorems to summarize the HMO theory of AH. However, it is found that some of the theorems do not hold. The main problem arises from the number and composition of nonbonding MOs (NBMOs) stated in

Theorem 6.7. *An* AH *with n starred atoms and m unstarred atoms has* $n-m$ NBMOs, *composed entirely of* AOs *of starred atoms.*

Contradictions of the number of NBMOs to the theory are found in many cases, e.g. in cyclobutadiene, in which $n-m=0$, but there are two NBMOs. They can be chosen in mutually paired or self-paired forms. In the mutually paired form, each NBMO of cyclobutadiene involves the AOs of all four carbon atoms. In the self-paired form, one of the NBMOs consists of the AOs of only the starred atoms, while the other consists of those of the unstarred atoms. Both cases are in disagreement with Dewar's theory 6.7.

Some of Dewar's theorems are corollaries of theorem 6.7. They are theorem 6.1c about the number and the composition of the NBMOs of odd AH, theorem 6.8

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about the number of unpaired π-electrons, and theorems 6.9 and 6.10 about the stability of non-Kekulé AH. Since theorem 6.7 does not hold, they lose their foundation and are also false.

We are presenting the following theorem instead of Dewar's theorem 6.7.

Theorem. *The rank of the* HMO *matrix for an* AH *with n starred and m unstarred atoms* $(n \geq m)$ *is an even number,* $2r$, *resulting in* $n+m-2r$ NBMOs, *which can be linearly combined into* $n-r$ NBMOs *composed entirely of* AOs *of starred atoms and* $m-r$ NBMOs *composed of* AOs *of unstarred atoms; they can also be linearly combined into* $n-m$ *self-paired* NBMOs *composed entirely of* AOs *of starred atoms and* $2(m-r)$ *mutually paired* NBMOs.

Proof. The starred atoms are numbered $1, \ldots, n$, and the unstarred atoms $n+1, \ldots, n+m$. If C is an NBMO,

$$HC = \begin{pmatrix} 0_{n\times n} & R_{n\times m} \\ R^T_{m\times n} & 0_{m\times m} \end{pmatrix} \begin{pmatrix} C^*_{n\times 1} \\ C^0_{m\times 1} \end{pmatrix} = 0, \quad (1)$$

where H is the HMO matrix, C^* and C^0 are the sets of coefficients of AOs of starred and unstarred atoms, respectively. The rank of block R is denoted by r. The rank of R^T is also r, since transposing a matrix does not change the rank. As a result, the rank of H is $2r$. $C^0=0$ and

$$R^TC^*=0 \quad (2)$$

with $C^* \neq 0$ satisfy Eq. (1). A set of homogeneous linear equations, e.g. Eq. 2, should have $n-r$ linearly independent solutions, where n and r are the number of columns and the rank of the coefficient matrix. The solutions of Eq. 2 correspond to $n-r$ NBMOs composed entirely of AOs of starred atoms. Similarly, $C^*=0$ and $RC^0=0$ with $C^0 \neq 0$ result in $m-r$ linearly independent solutions corresponding to $m-r$ NBMOs composed entirely of AOs of unstarred atoms. The total number is $(n-r)+(m-r)=n+m-2r$. They are all self-paired.

We can choose $m-r$ NBMOs with $C^0=0$ and $m-r$ NBMOs with $C^*=0$ to perform the following linear combinations

$$\frac{1}{\sqrt{2}}\begin{pmatrix} C^* \\ 0 \end{pmatrix} \pm \frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ C^0 \end{pmatrix},$$

resulting in $2(m-r)$ mutually paired NBMOs. The remaining $n-m$ NBMOs are thus composed entirely of AOs of starred atoms, q.e.d.

For the number of NBMOs, six of the nine examples in Table 1 are in contradiction to Dewar's theorem 6.7, while all of them are in agreement with the presented theorem. For example, let us examine the case of 2,3,5-trimethylene-hexatriene, III. The atoms are numbered as

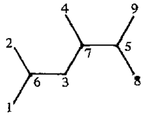
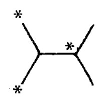


Table 1. HMO results for AHs

AH	n	m	$n-m$	r	Number of NBMOs
I	3	3	0	2	2
II	2	2	0	1	2
III	5	4	1	3	3
IV	3	3	0	2	2
V	4	2	2	2	2
VI	5	3	2	3	2
VII	4	4	0	3	2
VIII	6	3	3	3	3
IX	5	4	1	3	3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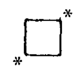
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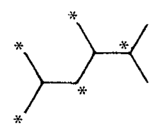
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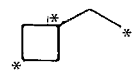
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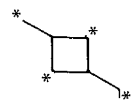
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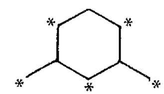
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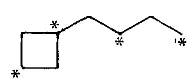
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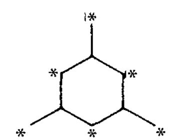
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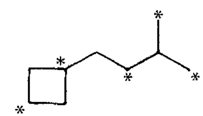
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Table 2. NBMOs of 2,3,5-trimethylene-hexatriene

	Starred atoms					Unstarred atoms			
MO	c_1	c_2	c_3	c_4	c_5	c_6	c_7	c_8	c_9
ϕ_1	0.577	0	−0.577	−0.577	0	0	0	0	0
ϕ_2	0.577	−0.577	0	−0.577	0	0	0	0	0
ϕ_3	0	0	0	0	0	0	0	0.707	−0.707
ϕ_4	0.408	−0.408	0	−0.408	0	0	0	0.5	−0.5
ϕ_5	0.408	−0.408	0	−0.408	0	0	0	−0.5	0.5

The block R in its HMO matrix is

$$R=\begin{pmatrix} 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 1 & 1 & 1 \end{pmatrix},$$

whose rank is obviously equal to 3. So the number of NBMOs is $n+m-2r=5+4-2\times 3=3$.

As to the coefficients, let us examine the data listed in Table 2. There are three linearly independent NBMOs. We can choose a set of self-paired NBMOs including ϕ_1, ϕ_2, and ϕ_3, or alternatively choose ϕ_1, ϕ_4, and ϕ_5, where

$$\phi_4=2^{-1/2}(\phi_2+\phi_3),$$
$$\phi_5=2^{-1/2}(\phi_2-\phi_3)$$

are mutually paired: the coefficients of the AOs are numerically the same for both MOs, but the signs of the coefficients of the unstarred set are reversed in going from ϕ_4 to ϕ_5.

According to the presented theorem, the NBMO set may be $n-m=1$ self-paired NBMO composed entirely of AOs of the starred atoms and $2(m-r)=2$ mutually paired NBMOs, or alternatively $n-r=2$ NBMOs composed entirely of AOs of starred atoms and $m-r=1$ NBMO composed entirely of AOs of unstarred atoms. This is in agreement with the fact listed in Table 2, while Dewar's theorem 6.7 is not.

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