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The Interpretation of the Stability of Aromatic Hydrocarbon Ions by Valence Bond Theory

By

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Hückel theory predicts the experimentally observed stabilities of the cyclic polyene ions $C_nH_n^-$, $C_nH_n^+$, $n = 3, 5, 7$ ($C_3H_3^+$ stable, $C_3H_3^-$ unstable, etc.) correctly. This result can also be obtained by a simple valence bond calculation which takes into account only the lowest energy resonance structures. E. g. it turns out that $C_3H_3^+$ should be a singlet ground state while $C_3H_3^-$ should be a triplet ground state. However, the stability cannot be explained by just counting the number of resonance structures.

Es wird gezeigt, daß die Stabilitätsverhältnisse der Cyclopolyenionen $C_nH_n^-$, $C_nH_n^+$, $n = 3, 5, 7$ ($C_3H_3^+$ stabil, $C_3H_3^-$ instabil, usw.), die nach der Hückeltheorie richtig erklärt werden, auch nach der VB-Methode vorhergesagt werden können. Dabei ist es ausreichend, nur die energetisch niedrigsten Resonanzstrukturen mit zu berücksichtigen. Es ergibt sich dann z. B., daß $C_3H_3^+$ einen Singulett-Grundzustand besitzt, $C_3H_3^-$ dagegen einen Triplett-Grundzustand. Die Anzahl der möglichen Resonanzstrukturen erlaubt jedoch keinen Rückschluß auf die Stabilitätsverhältnisse.

La théorie de Hückel prédit correctement les stabilités expérimentales des ions des cyclopolyènes $C_nH_n^-$, $C_nH_n^+$, $n = 3, 5, 7$ ($C_3H_3^+$ stable, $C_3H_3^-$ instable, etc.). Ce résultat peut être obtenu aussi par un simple calcul au cadre de la méthode de la mésomérie, ne comprenant que les formules de plus basse énergie. Il en résulte, par exemple, que l'état fondamental du $C_3H_3^+$ devrait être un singulet, celui de $C_3H_3^-$ un triplet. Cependant, on ne peut pas expliquer la stabilité en comptant le nombre des formules mésomères.

Although resonance is still widely used in chemistry to explain facts relating to molecular stability, there are many cases in which these explanations are misleading. A striking case of this concerns the stability of aromatic hydrocarbon ions. It is said that cyclopentadiene is a relatively strong acid because its anion is stabilized by resonance between the five structures which exist of the type I.

I

But the same argument can be used to predict the stability of $C_5H_5^+$, since there are just as many structures for the cation as for the anion, and yet the cation has never been obtained. The reverse situation occurs for the seven membered ring: the cation is stable but the anion not.

Molecular-orbital theory gives a very simple explanation of the above results. The lowest energy π-molecular orbital of a cyclic polyene is non-degenerate, and the higher ones are doubly degenerate, except for the highest, which is degenerate

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for an odd membered ring and non-degenerate for an even ring. Stability is then predicted for cyclic polyenes having $4n+2\,\pi$-electrons (Hückel's rule), since these have closed-shell structures. It follows that the ions $C_3H_3^+$, $C_5H_5^-$, $C_7H_7^+$, etc., should be stable.

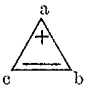
It is interesting to ask why molecular-orbital theory gives such a simple explanation but resonance theory fails to explain the facts [2]. Valence-bond theory must also explain the facts if it is applied correctly to the problem. What does one need in valence-bond theory to explain the stability of the aromatic hydrocarbon ions? Is it multiple ionic structures; is it electron interaction? In fact neither: we will show that the only thing necessary is to take account of the sign of the interaction element linking the resonance structures.

Let us first be clear on what molecular-orbital theory says: ions with $4n+2$ electrons will have closed-shell structures; those with $4n$ electrons will have open shells (be triplet-states). The stability rule just follows from the generally recognized instability of open shells. It needs to be shown that valence-bond theory says as much. We will examine the form of the interaction elements between the resonance structures for the three and five membered rings and then extend the results to higher members of the series.

Three membered ring

A wave function for the resonance structure of the positive ion having a positive charge on nucleus a is:

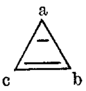
$${}^1\Psi_a^+ =$$



$$= \frac{1}{\sqrt{2\cdot 2!}}\left[\,|b\bar{c}| + |c\bar{b}|\,\right]$$

$|b\bar{c}|$ represents a Slater determinant formed of the $2p\pi$ atomic orbitals b and c, orbital b having an associated α-spin function and c a β-spin function. This represents a singlet-spin state. The two other equivalent structures are ${}^1\Psi_b^+$ and ${}^1\Psi_c^+$. For the negative ion we have a typical singlet function

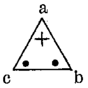
$${}^1\Psi_a^- =$$



$$= \frac{1}{\sqrt{2\cdot 4!}}\left[\,|a\bar{a}b\bar{c}| + |a\bar{a}c\bar{b}|\,\right].$$

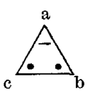
For the triplet states typical wave functions are (the dots represent unpaired electrons):

$${}^3\Psi_a^+ =$$



$$= \frac{1}{\sqrt{2!}}|bc|$$

$${}^3\Psi_a^- =$$



$$\frac{1}{\sqrt{4!}}|a\bar{a}bc|$$

We can confine our attention to just one component of the triplet ($S_z = 1$).

If we now evaluate the overlap integrals between the three structures of each type we find, to first order in S:

$$\langle {}^1\Psi_a^+ \mid {}^1\Psi_b^+ \rangle = \langle {}^3\Psi_a^- \mid {}^3\Psi_b^- \rangle = +S$$

$$\langle {}^1\Psi_a^- \mid {}^1\Psi_b^- \rangle = \langle {}^3\Psi_a^+ \mid {}^3\Psi_b^+ \rangle = -S, \text{ etc.,}$$

where S represents the overlap integral between neighbouring atomic orbitals ($S = \langle a \mid b \rangle$).

Each of the structures is normalized to first order in S, so that the overlap matrices to this order are as follows:

Singlet$^+$ and Triplet$^-$

$$\begin{array}{c} \\ \Psi_a \\ \Psi_b \\ \Psi_c \end{array} \begin{array}{c} \begin{array}{ccc} \Psi_a & \Psi_b & \Psi_c \end{array} \\ \begin{pmatrix} 1 & S & S \\ S & 1 & S \\ S & S & 1 \end{pmatrix} \end{array}$$

Singlet$^-$ and Triplet$^+$

$$\begin{array}{c} \\ \Psi_a \\ \Psi_b \\ \Psi_c \end{array} \begin{array}{c} \begin{array}{ccc} \Psi_a & \Psi_b & \Psi_c \end{array} \\ \begin{pmatrix} 1 & -S & -S \\ -S & 1 & -S \\ -S & -S & 1 \end{pmatrix} \end{array}$$

The eigenvalues of these matrices are:

$$1 + 2S,\ 1 - S,\ 1 - S \qquad\qquad 1 + S,\ 1 + S,\ 1 - 2S$$

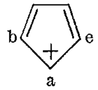
To interpret stability we need to evaluate the eigenvalues of the Hamiltonian matrix, but qualitatively one can see what will happen from the overlap matrices. A positive overlap integral between two structures corresponds to a stabilizing (negative energy) term in the Hamiltonian matrix. The Hamiltonian matrix element will be roughly proportional to the overlap matrix element. As far as the diagonal Hamiltonian matrix elements are concerned: the terms which are independent of overlap in the overlap matrix correspond to Coulomb interactions in the Hamiltonian matrix and these are independent of electron spins. The diagonal exchange terms in the Hamiltonian matrix which will be different for singlet and triplet states, are of order S^2. If overlap is small the eigenvalues of the Hamiltonian matrix are dominated by the off-diagonal terms of order S rather than by the diagonal terms of order S^2, since because of the degeneracy of the resonance structures the off-diagonal terms of order S contribute to order S in the eigenvalues of the Hamiltonian [*1*].

From the above statements we conclude that the resonance stabilization of the lowest state from the singlet$^+$ and triplet$^-$ states will be proportional to S. From this we conclude that for the cation the singlet state will be more stable than the triplet, and for the anion the triplet will be more stable than the singlet. In other words the ground state of $C_3H_3^+$ is a closed shell, that for $C_3H_3^-$ is an open shell: this is identical with the molecular orbital conclusion.

Five membered ring

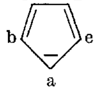
Typical singlet state functions for the positive and negative ions respectively are:

$${}^1\Psi_a^+ =$$



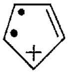
$$= \frac{1}{2\cdot\sqrt{4!}}\left[|b\bar{c}d\bar{e}| + |c\bar{b}d\bar{e}| + |b\bar{c}e\bar{d}| + |c\bar{b}e\bar{d}|\right]$$

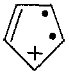
$${}^1\Psi_a^- =$$



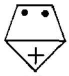
$$= \frac{1}{2\cdot\sqrt{6!}}\left[|a\bar{a}b\bar{c}d\bar{e}| + |a\bar{a}c\bar{b}d\bar{e}| + |a\bar{a}b\bar{c}e\bar{d}| + |a\bar{a}c\bar{b}e\bar{d}|\right].$$

The rule for constructing the wave functions is that if there is a bond (singlet state) between two atoms the wave function must change sign on exchanging the spins of the two electrons forming the bond. For example ${}^1\Psi_a^+$ must change sign on replacing $b\bar{c}$ by $\bar{b}c$ and vice-versa. For the triplet state the function must be unchanged on exchanging electron spins of the two unpaired electrons. For the five membered ring there is more than one triplet state. Each of the following structures represents a triplet state of the positive ion:


II


III


IV


V

but only three of these are independent. We will take IV to represent the most stable triplet. It has one short bond like II and III which will give it stability; and the unpaired electrons are far apart, which will give it less instability than II and III. Our wave functions for typical resonance structuring of the ions are then:

$$
{}^3\Psi_a^+ = \frac{1}{\sqrt{2\cdot 4\,!}}\,[\,|bc\bar{d}e| + |bd\bar{c}e|\,]
$$

$$
{}^3\Psi_a^- = \frac{1}{\sqrt{2\cdot 6\,!}}\,[\,|a\bar{a}bc\bar{d}e| + |a\bar{a}bd\bar{c}e|\,].
$$

The overlap integrals between these resonance structures are then to first order in overlap:

$$
\langle\, {}^1\Psi_a^+ \mid {}^1\Psi_b^+ \,\rangle = \langle\, {}^3\Psi_a^- \mid {}^3\Psi_b^- \,\rangle = -S/2
$$

$$
\langle\, {}^1\Psi_a^- \mid {}^1\Psi_b^- \,\rangle = \langle\, {}^3\Psi_a^+ \mid {}^3\Psi_b^+ \,\rangle = +S/2.
$$

The overlap integrals between two structures in which the charges are not on neighbouring atoms can be taken to be zero. The overlap matrices are then as follows:

Singlet$^+$ and Triplet$^-$

$$
\begin{array}{c|ccccc}
 & \Psi_a & \Psi_b & \Psi_c & \Psi_d & \Psi_e \\
\Psi_a & 1 & -S/2 & 0 & 0 & -S/2 \\
\Psi_b & -S/2 & 1 & -S/2 & 0 & 0 \\
\Psi_c & 0 & -S/2 & 1 & -S/2 & 0 \\
\Psi_d & 0 & 0 & -S/2 & 1 & -S/2 \\
\Psi_e & -S/2 & 0 & 0 & -S/2 & 1
\end{array}
$$

Singlet$^-$ and Triplet$^+$

$$
\begin{array}{c|ccccc}
 & \Psi_a & \Psi_b & \Psi_c & \Psi_d & \Psi_e \\
\Psi_a & 1 & S/2 & 0 & 0 & S/2 \\
\Psi_b & S/2 & 1 & S/2 & 0 & 0 \\
\Psi_c & 0 & S/2 & 1 & S/2 & 0 \\
\Psi_d & 0 & 0 & S/2 & 1 & S/2 \\
\Psi_e & S/2 & 0 & 0 & S/2 & 1
\end{array}
$$

The eigenvalues of these matrices are:

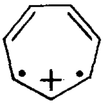
$1 + 0.81\,S$, $1 + 0.81\,S$, $1 - 0.31\,S$, $1 - 0.31\,S$, $1 - S$

$1 + S$, $1 + 0.31\,S$, $1 + 0.31\,S$, $1 - 0.81\,S$, $1 - 0.81\,S$

For the five membered ring we see that the negative ion should have a closed shell ground state and the positive ion an open shell ground state.

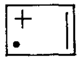
Seven membered ring

It can be shown that the seven membered ring is analogous to the three membered, if the lowest triplet state is built up from structures in which there are two conjugated double bonds and the unpaired electrons are on next nearest neighbours:



The resonance ocurring in the ions discussed above, and the ions of other non-alternant hydrocarbons, is different from that encountered for the alternants. For ions such as allyl or triphenylmethyl one can only draw perfect pairing structures having short bonds which have the charge residing on alternant atoms; for example

$$a = b - c^{+} \text{ and } a^{+} - b = c$$

The interactions between these structures now depend either on the overlap between orbitals a and c or the square of overlap between neighbouring orbitals. The interaction between different structures is therefore a less important stabilizing feature than it is for the non-alternants. For the radical ions of the even alternants (e.g. ), there is again interaction of order S between the structures, but in these cases the eigenvalues of the overlap matrix are obtained in pairs $1 \pm kS$, so that the signs of the overlap integrals are unimportant as far as energy is concerned.

The lesson to be learnt from this paper is that although one cannot explain the stability of hydrocarbon ions simply by examining the *number* of resonance structures, a valence bond treatment which takes into account only the lowest energy structures will probably be sufficient to give agreement with experiment.

Literature

[1] Eyring, H., J. Walter and G. E. Kimball: Quantum Chemistry, pp. 143—151. New York: John Wiley and Sons 1944.

[2] Staab, H. A.: Einführung in die theoretische organische Chemie, pp. 123—133 Weinheim: Verlag Chemie 1960.

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