Electronic Configurations of some Organic Molecules

This material is more or less lifted from the classic organic text, *Organic Chemistry*, by Morrison and Boyd. It illustrates dramatically how much we have gained in sophistication over the term.

Let us look at the electronic configurations of some familiar molecules. The shapes and relative stabilities of the various molecular orbitals are calculated by quantum mechanics, and we shall simply use the results of these calculations. We picture the nuclei in place, with the molecular orbitals mapped out about them, and we feed electrons into the orbitals. In doing this we follow the same rules that we followed in arriving at the electronic configurations of atoms. There can be only two electrons -- and of opposite spin -- in each orbital, with orbitals of lower energy being filled up first. If there are orbitals of equal energy, each gets an electron before any one of them gets a pair of electrons. We shall limit our attention to orbitals containing \( \pi \) electrons, since these electrons will be the ones of chief interest to us.

For the \( \pi \) electrons of ethylene, there are two molecular orbitals since there are two linear combinations of the two component \( p \) orbitals. The broken line in the figure indicates the non-bonding energy level; below it lies the bonding orbital, \( \pi \), and above it lies the antibonding orbital, \( \pi^* \).

Normally, a molecule exists in the state of lowest energy, the *ground state*. But, as we have seen absorption of light of the right frequency (in the ultraviolet region) raises a molecule to an *excited state*, a state of higher energy. In the ground state of ethylene, we see, both \( \pi \) electrons are in the \( \pi \) orbital; this configuration is specified as \( \pi^2 \), where the superscript tells the number of electrons in that orbital. In the excited state, one electron is the \( \pi \) orbital and the other -- still of opposite spin -- is in the \( \pi^* \) orbital. This configuration, \( \pi \pi^* \), is naturally the less stable, since only one electron helps to hold those atoms together, while the other tends to force them apart.

For 1,3 butadiene, with four component \( p \) orbitals, there are four molecular orbitals for \( \pi \) electrons. The ground state has the configuration \( \psi_1^2 \psi_2^2 \); that is, there are two electron in each of the bonding orbitals, \( \psi_1 \) and \( \psi_2 \). The higher of these, \( \psi_2 \), resembles two isolated \( \pi \) orbitals, although it is of somewhat lower energy. Orbital \( \psi_1 \) encompasses all four carbons; this delocalization provides the net stabilization of the conjugated system. Absorption of light of the right
frequency raises one electron to $\psi_3$.

$$\psi_1^2 \psi_2^2 \rightarrow \psi_1^2 \psi_2 \psi_3$$

Next, let us look at the allyl system: cation, free radical and anion.

\[
\text{CH}_2\text{CCH}_2 \quad \text{CH}_2\text{CCH}_2 \quad \text{CH}_2\text{CCH}_2
\]

Allyl cation    Allyl radical    Allyl anion

Regardless of the number of $\pi$ electrons, there are three component $p$ orbitals, one on each carbon, and they give rise to three molecular orbitals, $\psi_1$, $\psi_2$ and $\psi_3$. As shown in the figure below, $\psi_1$ is bonding and $\psi_3$ is antibonding. Orbital $\psi_2$ encompasses only the end carbons (there is a node at the middle carbon) and is of the same energy as an isolated $p$ orbital; it is therefore non-bonding.
The allyl cation has $\pi$ electrons only in the bonding orbital. The free radical has one electron in the non-bonding orbital as well, and the anion has two in the non-bonding orbital. The bonding orbital $\psi_1$ encompasses all three carbons, and is more stable than a localized $\pi$ orbital involving only two carbons; it is this delocalization that gives allylic particles their special stability. We see the symmetry we have attributed to allylic particles on the basis of the resonance theory; the two ends of each of these molecules are equivalent.

Finally, let us look at benzene. There are six combinations of the six component $p$ orbitals, and hence six molecular orbitals. Of these, we shall consider only three combinations, which correspond to the three most stable molecular orbitals, all bonding orbitals. Each contains a pair of electrons. The lowest orbital, $\psi_1$, encompasses all six carbons. Orbitals $\psi_2$ and $\psi_3$ are of different shape, but
equal energy; together they provide -- as does \( \psi_1 \) -- equal electron density at all six carbons.

The net result, then, is a highly symmetrical molecule with considerable delocalization of \( \pi \) electrons. But this is only part of the story; in the next section we shall look more closely at just what makes benzene such a special kind of molecule.

**Aromatic character. The Hückel 4n + 2 rule**

An aromatic molecule is flat, with cyclic clouds of delocalized \( \pi \) electrons above and below the plane of the molecule. We have just seen, for benzene, the molecular orbitals that permit this delocalization. But delocalization alone is not enough. For that special degree of stability we call *aromaticity*, the number of \( \pi \) electrons must confirm to Hückel’s rule: *there must be a total of* \((4n + 2)\) \( \pi \) electrons.
There is evidence of special stability associated with the magic numbers of 2, 6 and 10 \( \pi \) electrons, that is, with systems where \( n \) is 0, 1 and 2 respectively.

Hückel was a pioneer in the field of molecular orbital theory. He developed the LCAO method in a particularly simple form, one that has proved enormously successful in dealing with organic molecules. Hückel proposed the \( 4n + 2 \) rule in 1931. It has been tested in many ways since then, and it works. Now, what is the theoretical basis for this rule?

Let us begin with the cyclopentadienyl system. Five \( sp^2 \)-hybridized carbons have five component \( p \) orbitals, which give rise to five molecular orbitals. At the lowest energy level there is a single molecular orbital. Above this, the orbitals appear as degenerate pairs, that is, pairs of orbitals of equal energy. The lowest degenerate pair is bonding, the higher ones are antibonding.

The cyclopentadienyl cation has four electrons. Two of these go into the lower orbital. Of the other two electrons, one goes into each orbital of the lower degenerate pair. The cyclopentadienyl free radical has one more electron, which fills one orbital of the pair. The anion has still another electron, and with this we fill the remaining orbital of the pair. The six \( \pi \) electrons of the cyclopentadienyl anion are just enough to fill all the bonding orbitals. Fewer than six leaves bonding orbitals unfilled; more than six, and electrons would have to go into antibonding orbitals. Six \( \pi \) electrons give maximum bonding and hence maximum stability.

The figure shows the molecular orbitals for rings containing five, six and seven \( sp^2 \)-hybridized carbons. We see the same pattern for all of them: a single orbital at the lowest level, and above it a series of degenerate pairs. It takes \( (4n + 2) \pi \) electrons to fill a set of these bonding orbitals: 2 electrons for the lowest orbital, and 4 each of \( n \) degenerate pairs. Such an electron configuration has been likened to the rare-gas configuration of an atom, with its closed shell. It is the filling of these molecular orbital shells that makes these molecules aromatic.

In the MathCad calculations, we saw that the cyclopropenyl cation is unusually stable: 20 kcal/mol more stable even than the allyl cation. In contrast, the cyclopropenyl free radical and anion are not unusually stable; indeed, the anion seems to be particularly unstable. The cation has the Hückel number of two \( \pi \) electrons (\( n \) is zero) and is aromatic. Here, too, aromaticity results from the filling
up of a molecular orbital shell.

In the allyl system, the third and fourth electrons go into a non-bonding orbital, whereas here they go into antibonding orbitals. As a result, the cyclopropenyl free radical and anion are less stable than their open-chain counterparts. For the cyclopropenyl anion in particular, with two electrons in antibonding orbitals, simple calculations indicate no net stabilization due to delocalization, that is, zero resonance energy. Some calculations indicate that the molecule is actually less stable than if there were no conjugation at all. Such cyclic molecules, in which delocalization actually leads to destabilization, are not just non-aromatic; they are antiaromatic.

A mnemonic device has been discovered which correctly gives the HMO energies. One inscribes a regular polygon of $n_c$ sides in a circle of radius $2|\beta|$, putting an apex at the bottom of the circle. If a vertical scale of energy is set up with energy $\alpha$ coinciding with the center of the circle, then each polygon vertex is located at one of the HMO energies. This construct gives both the correct degeneracies and the correct spacings of the Hückel levels of the ring hydrocarbon $C_{n}H_{n}$.
Mnemonic device for HMO energies of monocyclic planar hydrocarbons.

The levels shown are for cyclobutadiene and benzene. The radius of the circle is $\beta$ and the center of the circle is located $\alpha$ below the ionization energy.

Consider the Hückel energy levels for the monocyclic polyene $C_nH_n$. The lowest subshell consists of a nondegenerate level and holds 2 electrons. Each of the remaining low-lying subshells consists of a doubly degenerate level and holds 4 electrons. (If $n_c$ is even, the highest $\pi$ energy level is nondegenerate, but this level is not occupied in the ground state.) To have a stable filled-subshell $\pi$-electron configuration, the number of $\pi$ electrons must satisfy

$$n_\pi = 4m + 2$$

$m = 0, 1, 2 \ldots$

This is Hückel’s $4m + 2$ rule, which ascribes extra stability to monocyclic conjugated systems that satisfy it. With $4m + 1$ or $4m - 1$ $\pi$ electrons, the compound is a free radical. With $4m$ $\pi$ electrons, there are two electrons in a subshell that can hold four electrons, and Hund’s rule predicts a triplet (diradical) ground state.

Benzene satisfies the $4m + 2$ rule. The cyclopentadienyl radical $C_5H_5$ is one electron short of satisfying it; the cyclopentadienyl anion $C_5H_5^-$ satisfies the $4m + 2$ rule; the cation $C_5H_5^+$ is predicted to have a triplet ground state and be highly
reactive. These predictions are all borne out; $\text{C}_5\text{H}_5^-$ is found to be considerably more stable than either $\text{C}_5\text{H}_5^+$ or $\text{C}_5\text{H}_5$. (The ground-state pi-electron configuration of $\text{C}_5\text{H}_5$ is of the form $a^2e^3$; the equivalence of holes and electrons shows this configuration to be equivalent to an $e^1$ configuration, which gives an orbitally degenerate level; thus, the Jahn-Teller theorem predicts that $\text{C}_5\text{H}_5$ is distorted from a regular pentagon.) Similarly, $\text{C}_7\text{H}_7^+$ should be more stable than $\text{C}_7\text{H}_7$ or $\text{C}_7\text{H}_7^-$ as is verified experimentally; e.g., the salt $\text{C}_7\text{H}^+\text{Br}^-$ is readily prepared.

Cyclobutadiene is predicted to be a diradical. After many unsuccessful efforts, cyclobutadiene has apparently been isolated by the pyrolysis of $\text{C}_4\text{H}_4\text{Fe(CO)}_3$ followed by quenching of the reaction mixture to $-196^\circ\text{C}$; $\text{C}_4\text{H}_4$ is evolved when the condensate is warmed to $-100^\circ\text{C}$. HMO theory predicts planar cyclooctatetraene (COT) a diradical; experimentally, $\text{C}_8\text{H}_8$ has a nonplanar “tub” structure, with alternating single and double bonds. Because of nonplanarity, the amount of conjugation between the double bonds is slight, and the delocalization energy (this term is defined later in this section) is small. The dianion $\text{C}_8\text{H}_8^{2-}$ satisfies the $4m + 2$ rule; the salt $[\text{K}_2]^{++}[\text{C}_8\text{H}_8]^{-2}$ has been prepared and the evidence is that $\text{C}_8\text{H}_8^{-2}$ is planar. In fact, the $\text{C}_8\text{H}_8^-$ ion is stable and is known to be planar.