The Simple Hückel Method and its Applications: Lecture 5

Learning outcomes:

1. Understanding cyclic systems, the concept of aromaticity and antiaromaticity

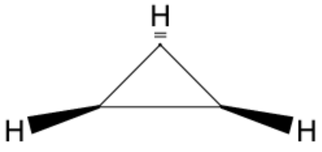
2. Understanding alternant and non-alternant hydrocarbons

7. MOs of Cyclic Conjugated Systems

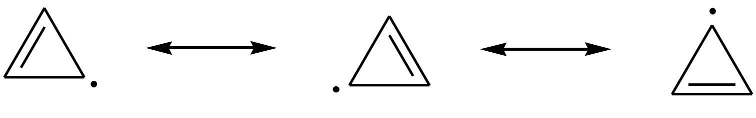
Cyclic conjugated systems are those in which all of the carbons bearing the 2*p* AOs form a ring. Here we discuss monocyclic conjugated systems in which the conjugated carbon atoms are contained in a single ring, such as cyclopropenyl, cyclobutadiene, benzene, etc. They have higher degrees of symmetry than acyclic systems, and consequently degeneracy in their orbital energies. For example, benzene has a six-fold symmetry axis (D_{6h}), whereas acyclic systems generally have no more than a two-fold (C_2) symmetry axis. One result of this is that cyclic conjugated systems typically have a number of degenerate orbitals, i.e. MOs of the same energy but having different spatial distributions of the electrons. Recall that we had learnt that a particle in a square box has a high degree of degeneracy, while the energy levels in a rectangular box are non-degenerate.

7.1 The Cyclopropenyl System

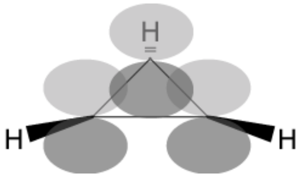
The simplest cyclic conjugated system is the three carbon atom cyclopropenyl system



According to valence bond theory, it is a resonance hybrid of three structures:



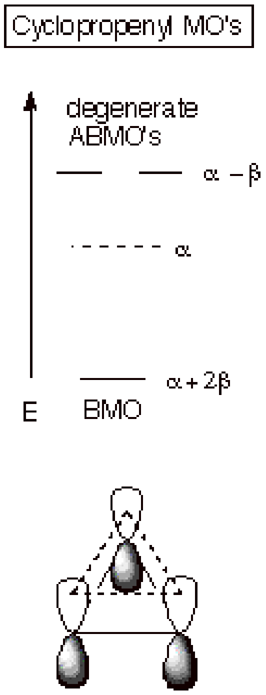
Is there a double bond and a radical that swap around in real time? No – we have π-molecular orbitals, which are delocalized over the three atoms.



Following the rules for writing the HMO determinant, we obtain:

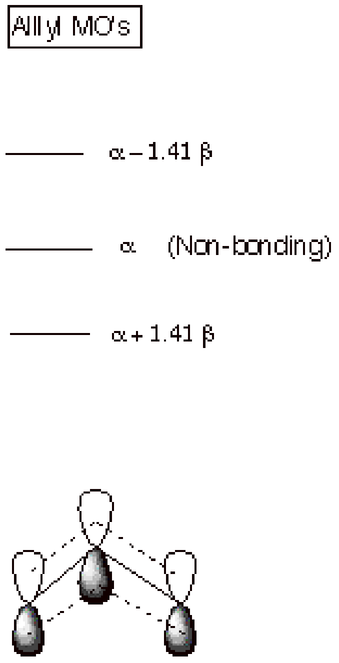
$$\begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{vmatrix} = 0$$
$$\Rightarrow x(x^2 - 1) - 1(x - 1) + 1(1 - x) = 0$$
$$\Rightarrow x^3 - 3x + 2 = 0$$
$$\Rightarrow (x - 1)(x - 1)(x + 2) = 0$$
$$\Rightarrow x = 1, 1, -2$$

Note the difference from its acyclic counterpart, the allyl system. It has one pair of degenerate MOs which are antibonding. The MOs are shown below. Note that there is one very highly bonding MO, along with the degenerate pair. In contrast to allyl, there is no nonbonding MO.



E_π(cation) = $2\alpha + 4\beta$

E_π(qnion) = $2\alpha + 2\beta$

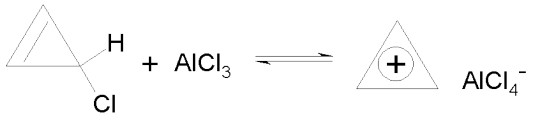


E_π(cation) = $2\alpha + 2.82\beta$

E_π(anion) = $2\alpha + 2.82\beta$

With only a single bonding MO, this conjugated system is best adapted to accommodate two electrons, i.e. as a carbocation. In the cyclopropenyl radical (three electrons), one electron is forced to occupy a high energy antibonding MO, and in the anion (four electrons), two electrons must be filled into the antibonding MOs. Recall that in the acyclic, allyl, case, the cation, radical, and anion are all relatively stable, since the electrons entering the nonbonding MO do not diminish the stabilization. The total π-electron energy of the cyclopropenyl cation is seen to be much lower than that of the allyl cation. However, the corresponding four electron anion has less stabilization than the allyl anion, and no more than a simple double bond of ethene.

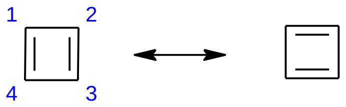
The total energy of the neutral cyclopropenyl system is $2(\alpha + 2\beta) + (\alpha - \beta) = 3\alpha + 3\beta$. The delocalization energy is therefore $3\alpha + 3\beta - (2\alpha + 2\beta) - \alpha = \beta$ w.r.t. ethylene and one extra electron. The delocalization energy for the cation is $2(\alpha + 2\beta) - (2\alpha + 2\beta) = 2\beta$, confirming its greater stability. In fact, experimentally, the cyclpropenyl cation is found to be relatively stable. It can be synthesized and isolated using the following reaction:



Its triphenyl derivative has been crystallized and its structure determined by X-ray crystallography. The C-C distances are all equal (140 pm), similar to benzene (139 pm).

7.2 Cyclobutadiene

The next higher analogue is 1,3-cyclobutadiene. It can be represented as a resonance hybrid of two equivalent structures similar to the Kekulé structures of benzene, i.e.



(1)

Its secular determinant can be written as

$$\begin{vmatrix} x & 1 & 0 & 1 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 1 & 0 & 1 & x \end{vmatrix} = 0$$

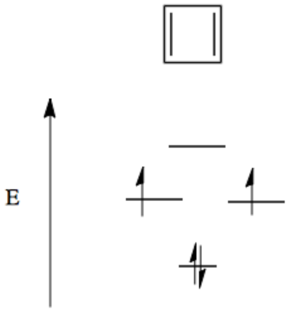
Expansion gives the polynomial

$$x^2 - 4x^2 = 0$$

giving the roots

$$x = -2, 0, 0, 2$$

Again we find that two roots are degenerate and correspond to nonbonding MOs. The energy level diagram is shown below:



Two electrons occupy the bonding orbital and the remaining two remain unpaired in the degenerate levels according to Hund's rules. In order to have all electrons in bonding orbitals to achieve stable bonding, the molecule would need to lose two electrons.

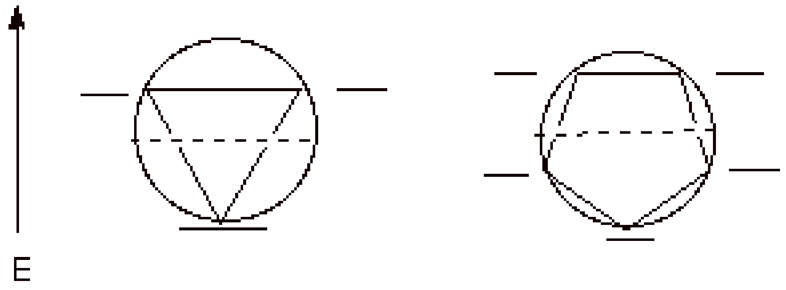
The total energy is $4\alpha + 4\beta$, which is exactly the same as that of two ethylene molecules. Hence, there is no resonance stabilization and the picture of two resonance structures is incorrect. This molecule is highly unstable, even at temperatures near absolute zero (e.g. 20 K). From this we can see that the resonance treatment of cyclobutadiene (two equivalent resonance structures) fails to agree with the MO treatment or with experiment. According to the simple HMO theory, the ground state of cyclobutadiene should be a triplet, but experimental evidence shows that it is diamagnetic in nature as it shows no ESR spectra. In fact, the molecule is not square planar, as it would have been had there been resonance stabilization. Rather, it is rectangular in shape and can be represented as a single structure, as shown in the energy level diagram. The two bond lengths are dissimilar, the two opposite single bonds having a length of 1.567 Å and the double bonds having a bond length of 1.346 Å, typical of C=C double bonds. As observed for the particle in a square box, distortion removes the degeneracy of the levels and the two electrons are now paired in the lower of the two energy levels.

This is an example of the **Jahn-Teller** effect, which essentially states that any non-linear molecule with a spatially degenerate electronic ground state will undergo a geometrical distortion that removes that degeneracy, because the distortion lowers the overall energy of the species.

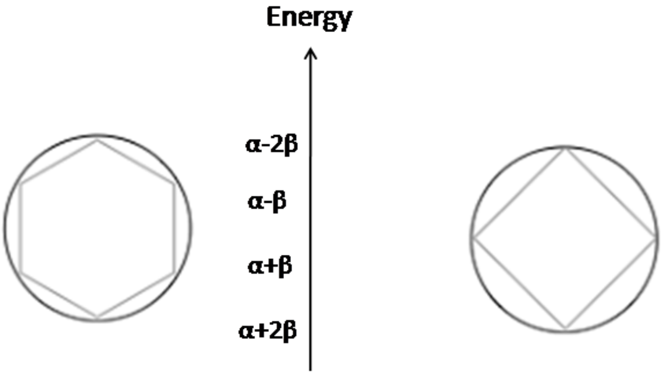
As in the case of acyclic systems, the secular determinant becomes harder to solve for five or more atoms in conjugation. Fortunately, there are certain simplifications. The first is a circle mnemonic.

7.3 Forst diagrams

A good way to obtain the energies of MOs of simple monocyclic conjugated systems is to use the circle mnemonic. Draw a circle of radius 2*β*. The centre of the circle corresponds to energy *α*. Inscribe a polygon of the appropriate number of sides inside the circle with one vertex down, corresponding to the unique, highly bonding MO, which has an energy of $\alpha + 2\beta$. The MO energies then correspond to the vertices of the polygon. Examples for the cyclopropenyl and cyclopentadienyl systems are shown below.



Simple geometrical considerations show that the degenerate energy levels of cyclopropenyl radical have an energy of $\alpha + \beta$, as already obtained. Since the third electron of the neutral radical species occupies an antibonding orbital (above the dotted line), it has a tendency to lose an electron and form a cation. On the other hand, neutral cyclopentadiene, which has five electrons, would tend to gain an additional electron, which will go to its bonding orbital, making it an anion with six electrons in its bonding orbitals. For the odd electron cycloheptatriene radical, the odd electron goes to an antibonding orbital, and so this electron is readily lost, leaving the cation, which has six electrons in three bonding orbitals. For benzene and cyclobutadiene, the Forst diagrams are shown below



It is clear that cyclobutadiene will have to lose two electrons so that both the remaining electrons are in the bonding orbital. Benzene has all its six electrons in bonding orbitals and has the highest delocalization energy equal to 2β.

We now have the basis for the Húckel rule.

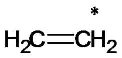
7.4. The Huckel Rule

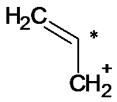
The fact that the delocalization energy of cyclic conjugated systems crucially depends on the number of electrons, even more than on the number of carbon atoms over which the electrons are potentially delocalized, gives rise to the Húckel Rule. The stability of such systems varies from the benzene standard (highly stabilized) to no stabilization whatsoever (or even destabilization). Systems which are unusually highly resonance stabilized, like benzene, the cyclopropenyl cation, the cyclopentadienyl anion, and the cycloheptatrienyl cation, are often termed aromatic. They are all planar molecules. Those which are regarded as especially unstable are often referred to as antiaromatic. Examples are cyclobutadiene and cyclooctatetraene.

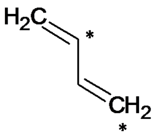
As you may recall, the cyclic systems which have special stability can be predicted by the $4n+2$ Rule, where $n = 0, 1, 2, 3, \ldots$. Therefore, monocyclic conjugated systems having 2, 6, 10, 14,… electrons are highly stabilized, but those having $4n$ electrons (4, 8, 12,,,,) are surprisingly lacking in stability, even in comparison to their acyclic counterparts. *The basis for the Huckel Rule is essentially that the bonding MOs of cyclic systems occur in a regular pattern. There is one highly bonding MO, followed by varying numbers of pairs of BMOs (zero for cyclopropenyl, cyclobutadiene; two* *for cyclopentadiene, benzene, and cycloheptatriene, etc.). There will always be 1, 3, 5, 7—BMOs, which can accommodate 2, 6, 10, 14 – electrons when completely filled.*

7.5 Alternant Hydrocarbon Systems:

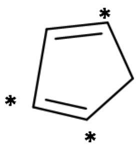
By now you must have observed that there is symmetry in the energy levels of the acyclic system. The bonding and antibonding orbitals are paired. For example, if the bonding orbital of ethylene has an energy equal to $\alpha + \beta$, its antibonding orbital has an energy $\alpha - \beta$. For butadiene, the first energy level is paired with the fourth and the second with the third. This continues for the higher homologues as well. In case of conjugated polyenes with an odd number of atoms, e.g. the allyl system, the odd energy level cannot be paired with any orbital, so it is a nonbonding orbital having energy α. Not only are the energies paired, the wave functions are also paired. Observe this for butadiene. The pairing of energy levels is also observed for cyclobutadiene. The first and fourth energy levels are paired, with energies $\alpha + 2\beta$ and $\alpha - 2\beta$, respectively, and the second and third energy levels are paired. However, the odd carbon atom systems, cyclopropenyl and cyclopentadiene, do not show this behavior. This is a property of *alternant* hydrocarbons. An alternant hydrocarbon is one in which, if we start placing stars on alternate carbons in the conjugated system, no adjacent carbons have stars on them. By this definition, all acyclic systems are alternant, even if there are an odd number of carbons (in which case they are called odd alternant), If the number of carbon atoms is even, it is an even alternant system. Examples are

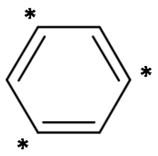






In the case of cyclic systems,





we observe that monocyclic rings with an even number of carbon atoms (cyclobutadiene, benzene) are alternant, whereas those with an odd number of carbon atoms (cyclopropene, cyclopentadiene) are not. They are called nonalternant hydrocarbons.

Thus, an alternant system is a planar conjugated π electron system which contains no odd-membered rings. They *may* have even membered rings or be purely acyclic or may contain a mixture of rings and acyclic features (e.g., styrene, i.e., vinylbenzene or the benzyl system).

Alternant systems have certain unique properties:

- *All alternant hydrocarbon systems (but not non-alternant systems) have π MOs whose energies and coefficients are paired in terms of energy and coefficients*
- *Paired* means that for every BMO there exists an ABMO, the energy of which is exactly as antibonding as the BMO is bonding. Also, the coefficients at each atom in the ABMO have the same absolute magnitude as the coefficient at that atom in the BMO, so that the electron distributions are the same. In fact, the coefficients are obtained by reversing the signs of coefficients for the starred atoms.
- *Odd alternant systems have, in addition to the paired BMOs and ABMOs, a single NBMO.*
- The charge density on each carbon atom in alternant systems is unity.

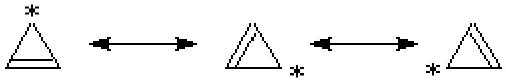
References

Lowe, J.P. Quantum Chemistry

Sample Problem 2

Compare the Hückel molecular orbital model and the valence bond model for the cyclopropenyl cation, radical, and anion, and comment on the aromatic properties of each.

In the valence bond model we can draw three resonance structures for each of these - and therefore predict no difference in energy between them - with the electrons, charges, and π bonds equally distributed over the three carbons (*i.e.*, 1/3 ⊕ on each carbon in the cation, 1/3 ⊖ on each in the anion, 1/3 π bond between each carbon):



where * = ⊕for cation
• for radical
⊖for anion

As in the previous problem (Lecture 3), the HMO model also predicts the same charge distribution:

	cation	radical	anion
electron density:	0.667	1.000	1.333
charge:	+0.333	0.000	-0.333

However, these three species show very different behavior in the π bond orders:

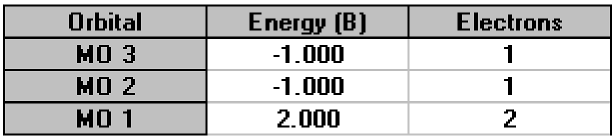
	cation	radical	anion
π bond order:	0.667	0.500	0.333

Again, as in the previous problem, these differences in π bond order reflect different stabilities for the three species - the cation being the most stable and the anion being the least. To determine their aromatic properties, one needs to compare with the total π energy of each to their open-chain counterparts (the corresponding allyl systems):

	cation	radical	anion
cyclopropenyl:	$4.000\,\beta$	$3.000\,\beta$	$2.000\,\beta$
allyl:	$2.828\,\beta$	$2.828\,\beta$	$2.828\,\beta$

Notice that the cyclopropenyl cation is more stable than the allyl cation, and is therefore aromatic. The cyclic radical is about the same stability as the open-chain, and is *non*aromatic. The cyclic anion, being less stable than the open-chain, is *anti*aromatic. This follows from the Hückel 4*n* + 2 rule: The cyclopropenyl cation has 2 π electrons [4(0) + 2] in a cyclic, planar, conjugated system and is therefore aromatic.

Also note that the HMO calculations predict that the cyclopropenyl anion is a *diradical* species (has two unpaired electrons in the two degenerate molecular orbitals), something not predicted by the valence bond model:



Orbital	Energy (B)	Electrons
MO 3	-1.000	1
MO 2	-1.000	1
MO 1	2.000	2

8. Exercises.

1. Construct a display of the MOs of benzene and fill in the appropriate number of electrons, using one canonical structure as a basis for computing the number of π electrons. Using the information that the MOs have energies $\alpha + 2\beta$, $\alpha + \beta$, $\alpha + \beta$, $\alpha - \beta$, $\alpha - \beta$, and $\alpha - 2\beta$, calculate the π electron energy of benzene and compare it with the energy of three molecules of ethene. Estimate the resonance energy (delocalization energy) of benzene as the difference in π electron energy of benzene and three ethene molecules.

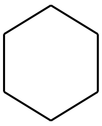
2. Construct energy level diagrams for cyclopentadiene and 1,3,5-cycloheptatriene systems and fill in the appropriate numbers of electrons for the cation and anion of each. Which species are especially stable? Do these agree with the Húckel Rule?

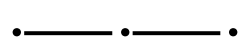
5. Explain why cyclopentadiene readily accepts an electron to become cycolpentadienide ($C_5H_5^-$, which is abbreviated Cp in organic and organometallic chemistry).

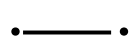
6. Predict which cyclopolyenes (C_NH_N) will be aromatic: (i) neutral, (ii) single negative charge, and (iii) single positive charge?

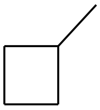
7. Using Hückel theory, determine the energies of the four π orbitals of cyclobutadiene. Show what would be the effect on the final energy level diagram of elongation of two opposite sides of the molecule.

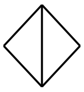
8. Indicate in the following group the alternant (A) and the nonalternant (N) hydrocarbons, as well as the even (E) and the odd (O) hydrocarbons:











9. Many aromatic hydrocarbons are colourless but their anion and cation radicals are often strongly coloured. Give a qualitative explanation for the phenomenon. (*Hint:* Consider only the π molecular orbitals).