THEORIES DESCRIBING AROMATIC COMPOUNDS

Traditional bonding theory, in which two nuclei are held together by the resultant attractive forces of a single pair of electrons, is inadequate to describe compounds such as benzene. Simple molecular orbital and hybridization concepts also fail to do so. Benzene's six-membered ring is usually drawn with alternating single and double C-C bonds, but in fact all of its bonds are the same length and it fails to undergo typical alkene reactions, e.g. addition by bromine or acids.

There are two independent theories explaining benzene and its relatives. The two theories have different strengths and weaknesses.

THEORY 1: VALENCE BOND OR RESONANCE (Pauling or VB)

This theory begins with line bond structures. Electrons (bonded and non-bonded) are moved (in pairs) to generate alternate electron arrangements. Molecules for which several different nearly equivalent structures can be drawn are said to be "resonance-stabilized". The molecules are said to be more stable because they are "hybrids" (resonance hybrids) of these different electron arrangements, called "contributors to the resonance hybrid" or "resonance contributors". Think of the molecule as a rhinoceros, a real molecule that is a hybrid of the mythical beasts (contributors) a unicorn and a dragon.

Some simple rules allow you to generate these alternate electron arrangements, or resonance contributors, once you have one correct structure.
1. The nuclei must be in the same place.
2. Each contributor must have the same number of electrons
3. No more than 8 electrons on elements up to F
4. In sketching one structure by modifying another, electrons may not jump - the pair must still be attached to one of the original atoms in the new contributor. Your instructor will show you some examples; the result looks like a windshield wiper.

Not every structure you can generate is equally likely. As a rule of thumb, the relative importance of a contributor to the resonance hybrid is estimated from how stable it would be if it were a real molecule. Three rules, in order of importance, will allow you to evaluate the importance of a contributor. The most important contributors have:
1. The largest number of bonds
2. The minimum dipole moment, i.e. the least separation of opposite charge and the least accumulation of like charge.
3. The charges matched to the electronegativity of the atom.

Advantages: This approach to explaining aromatic compounds can give great insight about electron distribution in a molecule without any computational equipment - a piece of paper and a pencil will suffice. It explains qualitatively why the bond lengths in benzene are all the same. The VB or resonance theory can be used on ions and acyclic molecules too, although it does not provide much insight into polyenes.

Disadvantages: The fact that we can draw several structures does not suffice as a reason for enhanced stability in these compounds. The theory also fails to predict that not all compounds with alternating single and double bonds have enhanced stability. For example: benzene (cyclohexatriene) is stabilized and unreactive; cyclooctatetraene has stability and reactivity typical of alkenes, but its di-anion is surprisingly stable. Moreover, the theory fails to explain why aromatic compounds have larger NMR chemical shifts (H-1 and C-13) than alkenes.

THEORY 2. MOLECULAR ORBITAL (Huckel or MO)

This theory begins with atomic molecular orbitals, hybridized for multiple bonding (sp^2 or sp). Huckel's simple version assumed the sigma bond network consisted of independent electron pair bonds and examined only the pi system. Molecular orbitals for the molecule were computed by allowing the p orbitals to interact wherever possible; since the orbitals are mathematical functions describing space, the interaction was computed by adding and subtracting. The computation of molecular orbitals correctly predicted that benzene

and its relatives have energies lower than corresponding alkenes, and gave a visual picture of the orbital shapes.

Molecules with stability greater than their line bonds would predict are called "aromatic" in this theory. To be stabilized and thus classified as aromatic, a molecule must:

1.   Be planar,
2.   Have a p orbital perpendicular to the plane on every atom,
3.   Be cyclic,
4.   Have $4n+2$ electrons in the ring pi system, where "n" is an integer.

Huckel found that compounds with $4n$ pi electrons have <u>higher</u> energies than the corresponding alkenes, and called them antiaromatic. Real molecules with $4n$ pi electrons, such as cyclooctatetraene, content themselves with electron distributions and reactivities that are characteristic of alkenes and have higher energies than their $4n+2$ relatives. Huckel's $4n+2$ rule does not apply to molecules with an odd number of electrons in the ring.

Advantages: This theory provides a theoretical explanation for the increased stability and decreased reactivity of aromatic compounds. The theory also explains why cyclooctatetraene is like an alkene while its di-anion is more like benzene, and why cyclobutadiene is too unstable to isolate while the more strained cyclopropanone can be readily isolated. The theory applies to ions as well. MO theory explains why the H-1 and C-13 atoms in an aromatic ($4n+2$-electron) rings have higher NMR chemical shifts than do alkene H-1 and C-13, why the NMR chemical shifts of H-1 and C-13 over an aromatic ring are exceptionally low, and why $4n$-electron rings exhibit NMR shifts in exactly the opposite direction to $4n+2$-electron rings.

Disadvantages: This theory needs a computer for calculation of the orbitals for all but the simplest molecules. The simple rules above do not apply to acyclic molecules, although the calculations can be done for them, with similar success; it is especially useful for polyenes.

Distinct patterns in the molecular orbitals arise which allow a shortcut for estimating the energies of the orbitals (and their general appearance). If the molecule is drawn as accurately as possible with a vertex pointed down, the relative energies of the orbitals correspond to the height of each of the vertices. The energy of the unbonded p orbitals is the height of the center of gravity of the polygon; the energy scale is "one bond length = 1/2 ethylene pi bond energy". The lowest energy orbital has no nodes in the "wave". The others have one more node for each step in energy, and have two perpendicular alternatives when there are two identical energies.

In their most sophisticated versions, MO and VB theory look very much alike, and a powerful computer can use modified Schrodinger atomic orbitals to calculate structure and properties of quite complex molecules <u>ab initio</u>, using the methods of quantum mechanics.