

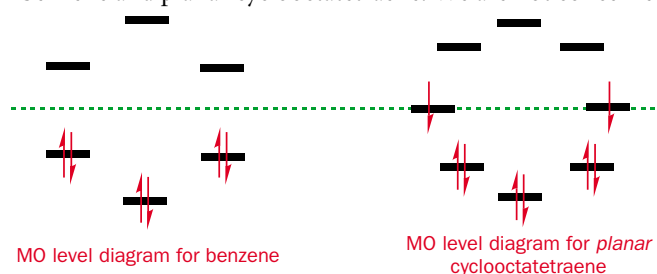
Notes on these energy level diagrams:

- This method predicts the energy levels for the molecular orbitals of planar, monocyclic, arrangements of identical atoms (usually all C) only
- The dashed line represents an energy level α and in each case the circle radius is 2β
- There is always one single molecular orbital lower in energy than all the others (at energy $\alpha + 2\beta$). This is because there is always one molecular orbital where all the p orbitals combine in-phase
- If there are an even number of atoms, there is also a single molecular orbital highest in energy; otherwise there will be a pair of degenerate molecular orbitals highest in energy
- All the molecular orbitals come in degenerate pairs except the one lowest in energy and, for even-numbered systems, the one highest in energy

Now we can begin to put all the pieces together and make sense of what we know so far. Let us compare the energy level diagrams for benzene and planar cyclooctatetraene. We are not concerned with the actual shapes of the molecular orbitals involved, just the energies of them.

Benzene has six π electrons, which means that all its bonding molecular orbitals are fully occupied giving a closed shell structure. COT, on the other hand, has eight electrons. Six of these fill up the

bonding molecular orbitals but there are two electrons left. These must go into the degenerate pair of nonbonding orbitals. Hund's rule (Chapter 4) would suggest one in each. Therefore this planar structure for COT would not have the closed shell structure that benzene has—it must either lose or gain two electrons in order to have a closed shell structure with all the electrons in bonding orbitals. This is exactly what we have already seen—both the dianion and dication are planar, allowing delocalization all over the ring, whereas neutral COT adopts a nonplanar tub shape with localized bonds.



Of course, this isn't the molecular orbital energy level diagram for real cyclooctatetraene since COT is not planar but tub-shaped.

This is not a strict definition of aromaticity. It is actually very difficult to give a concise definition. Hückel's rule is certainly a good guide but also important is the extra stability of the compound (shown, for example, in resistance to changes to its π system) and low reactivity towards electrophiles. Perhaps the best indication as to whether or not a compound is aromatic is the proton NMR spectrum. The protons attached to an aromatic ring are further downfield than would otherwise be expected (Chapter 11).

Hückel's rule tells us if compounds are aromatic

Using this simple method to work out the energy level diagrams for other rings, we find that there is always a single low-energy bonding orbital (composed of all p orbitals combining in-phase) and then pairs of degenerate orbitals. Since the single orbital will hold two electrons when full and the degenerate pairs four, we shall have a closed shell of electrons in these π orbitals only when they contain $2 + 4n$ electrons (n is an integer 0, 1, 2, etc.). This is the basis of Hückel's rule.

● Hückel's rule

Planar, fully conjugated, monocyclic systems with $(4n + 2)$ π electrons have a closed shell of electrons all in bonding orbitals and are exceptionally stable. Such systems are said to be **aromatic**.

Analogous systems with $4n$ π electrons are described as anti-aromatic

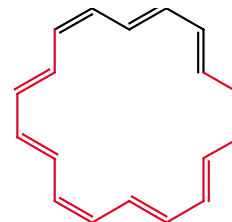
Annulenes (meaning ring alkenes) are compounds with alternating double and single bonds. The number in brackets tells us how many carbon atoms there are in the ring. Using this nomenclature, you could call benzene [6]annulene and cyclooctatetraene [8]annulene—but don't.



all-*cis*-[10]annulene

That the π system is fully conjugated and planar are important conditions for aromaticity. The next $(4n + 2)$ number after six is ten so we might expect this cyclic alkene to be aromatic.

If this annulene with five *cis* double bonds were planar, each internal angle would be 144° . Since a normal double bond has bond angles of 120° , this would be far from ideal. This compound can be made but it does *not* adopt a planar conformation and therefore is not aromatic even though it has ten π electrons. By contrast, [18]annulene, which is also a $(4n + 2)$ π electron system ($n = 4$), does adopt a planar conformation and *is* aromatic (as shown by proton



[18]annulene