Hyperconjugation and stability in cyclohexadiene

We have seen that MO theory can explain the stabilization of conjugated dienes; the electrons occupy lower energy levels than they would in isolated dienes. For example, 1,3-hexadiene is about 20 kJ/mol more stable than 1,4- or 1,5-hexadiene.[*] We call this the "resonance energy." 1,4- and 1,5-hexadiene don't have any; their enthalpy of hydrogenation is the same as that of two moles of 1-hexene.

We expect the same thing to be true for 1,3-cyclohexadiene compared to 1,4-cyclohexadiene. But the hard facts contradict us: 1,3- and 1,4-cyclohexadiene are about equally stabilized relative to a hypothetical isolated cyclohexadiene, by about 10 kJ/mol.

Why is this? Why doesn't 1,3-cyclohexadiene have the same resonance energy as open-chain 1,3-hexadiene? Why is 1,4-cyclohexadiene stabilized, but open-chain 1,4-hexadiene is not? And why do they have the same resonance energy? After all, only 1,3-cyclohexadiene can have resonance, right?

In order to explain this, we have to appeal to a concept called "hyperconjugation" by organic chemists, and "perturbation theory" by everybody else. This is firmly rooted in the molecular-orbital theory of bonding.

It turns out that we can construct molecular orbitals by taking a subset of the molecule, and allowing neighboring atomic orbitals or bonds interact with that subset. Resonance energy is firmly based in extended π-molecular orbital systems; in order to perturb π-orbitals, neighboring orbitals must have the same symmetry: one plus-phase and one minus-phase lobe, above and below the plane of the π-system.

In cyclohexadienes, it turns out that a combination of C-H σ-bond orbitals can have the same symmetry as a p atomic orbital. These are bonding orbitals, and so they are occupied.

When two neighboring orbitals or orbital systems perturb each other, one is pushed up in energy and the other down. If only one is occupied, the result is stabilization of the molecule as a whole because the electrons go into the lower-energy of the two new orbitals. But if both orbitals are occupied, the result can be a net destabilization since some of the electrons are raised in energy.

We can use perturbation theory to explain why it is that 1,4-cyclohexadiene is stabilized (compared to what we would expect) and why it is that 1,3-cyclohexadiene is destabilized. As shown by the numbers above, this is not a very big effect; it is equal to about ½ the resonance energy of a pair of conjugated double bonds. But it is significant.

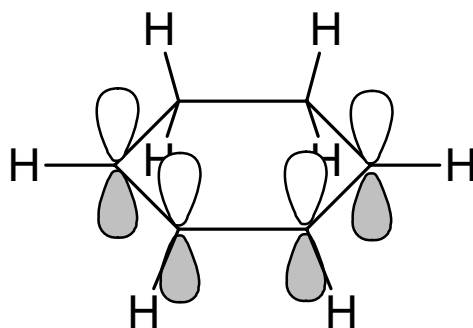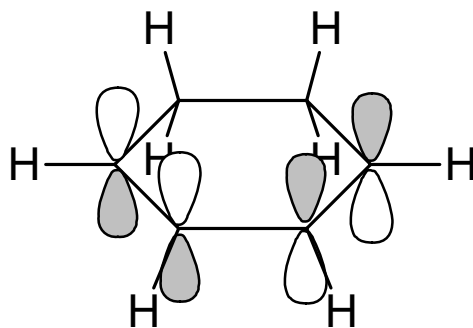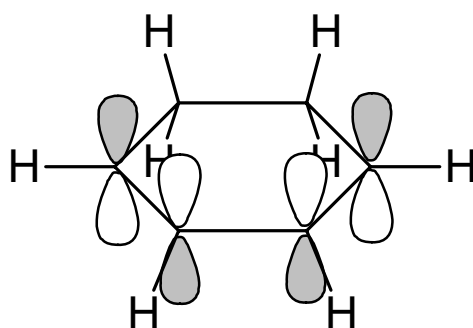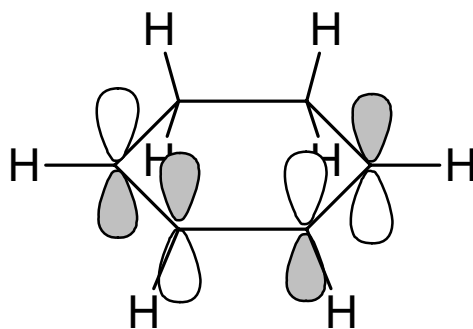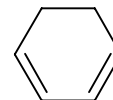**1,3-hexadiene**: both of the occupied π-MOs are able to interact with the C-H bond on the CH_2 groups in the ring. This raises the energy of all four π-electrons. It also lowers the energy of the CH_2 σ-bonds, but apparently the effect is not as large. So hyperconjugation *destabilizes* 1,3-cyclohexadiene relative to its unperturbed energy.

1,4-hexadiene: only one of the occupied π-MOs is able to interact with the C-H bonds on the CH_2 groups, and so only one pair of π-electrons is raised in energy. The other stays the same. But the CH_2 groups can also combine with an unoccupied π-MO; this lowers the energy of the σ-bond electrons without raising the energy of any other electrons, and so hyperconjugation *stabilizes* 1,4-hexadiene.
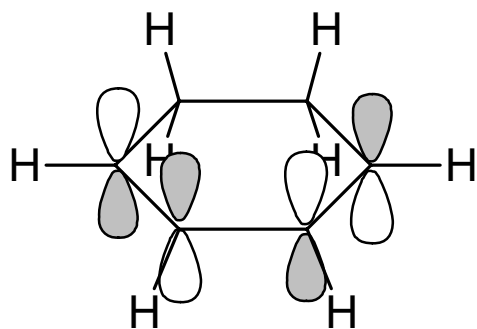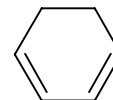
On the following pages, you can compare the hypothetically unperturbed π-orbitals of the two cyclohexadienes with their actual π-molecular orbitals.

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[*] "Resonance energy" is defined as the difference between the hydrogenation enthalpy of a diene and twice that of the corresponding mono-ene. For example, hexadiene is compared to hexene, and cyclohexadiene to cyclohexene.
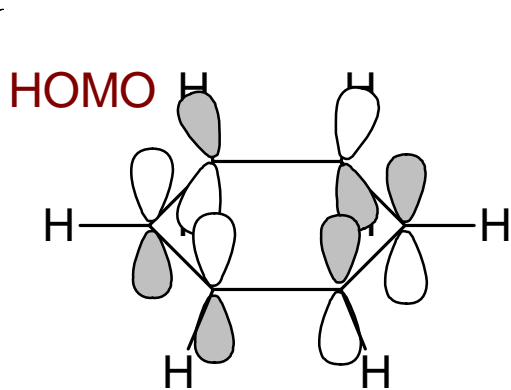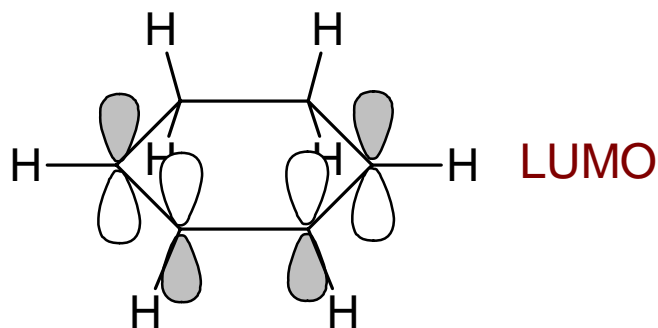
π−Molecular Orbitals of 1,3-cyclohexadiene (hypothetically)
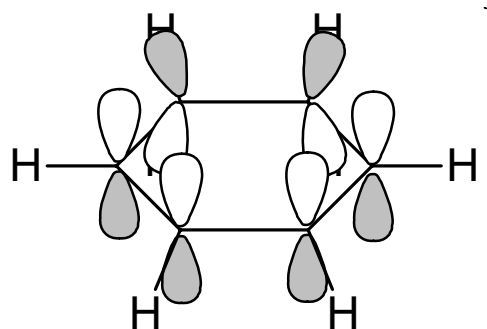before interacting with the C-H bonds on C5 and C6

LUMO

HOMO
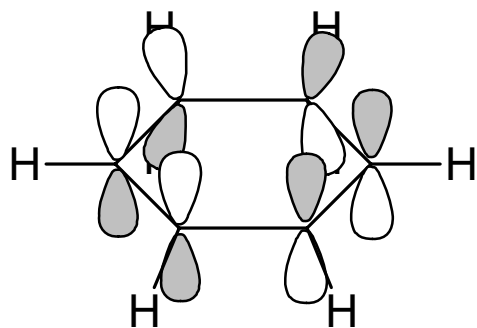
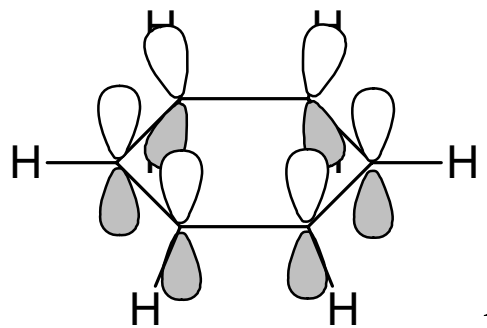π−Molecular Orbitals of 1,3-cyclohexadiene

LUMO

HOMO

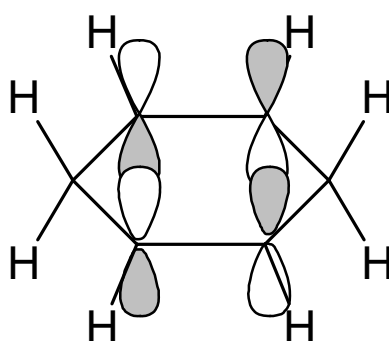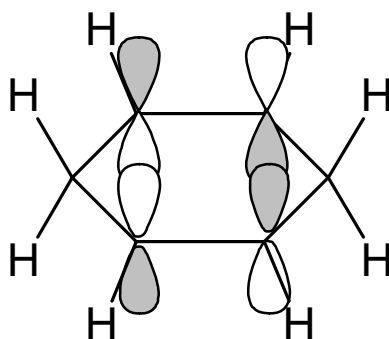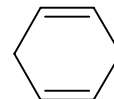combinations of the next lowest-energy diene π-orbital with the C-H bonds on C5 and C6

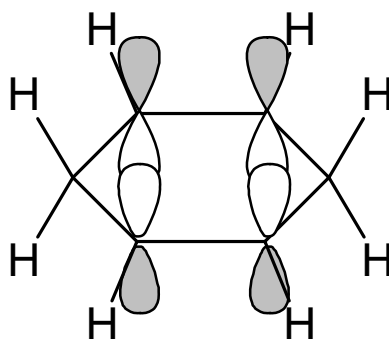combinations of the lowest-energy diene π-orbital with the C-H bonds on C5 and C6

All combination MOs are occupied; there is stabilization, but not as much as in an open-chain diene.
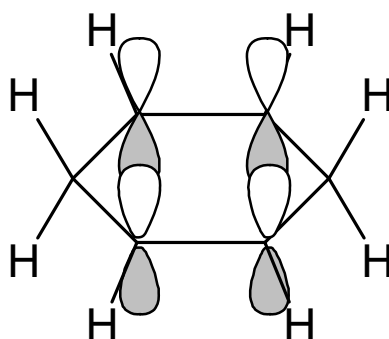
π−Molecular Orbitals of 1,4-cyclohexadiene (hypothetically)
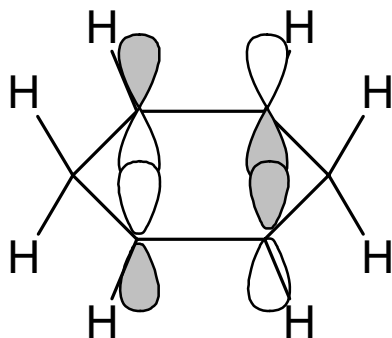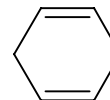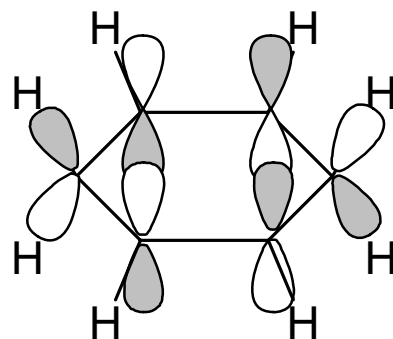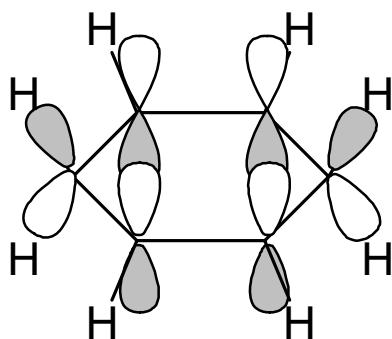before interacting with the C-H bonds on C3 and C6

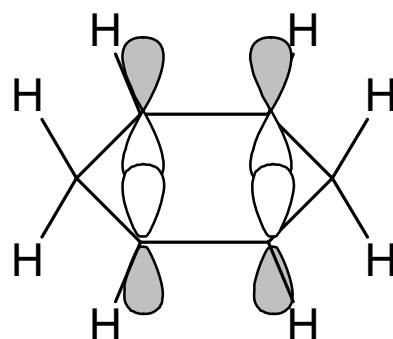

LUMO

HOMO

π−Molecular Orbitals of 1,4-cyclohexadiene
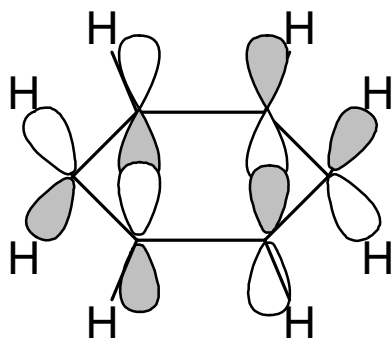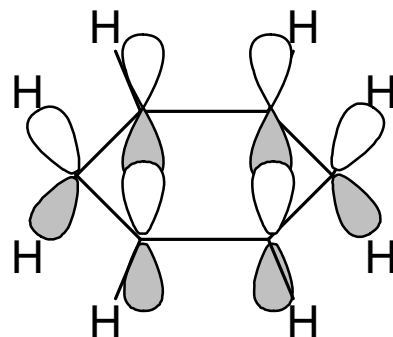
Compare to the "unperturbed" π-MOs

LUMO

HOMO

the HOMO of the π-system is unchanged

combinations of the lowest-energy diene π-orbital with the C-H bonds on C3 and C6

the LUMO of the π-system stabilizes the occupied C-H bonding orbitals

compound	resonance energy (kJ/mol)	resonance energy (kcal/mol)
E-1,3-hexadiene	-22	-5.23
Z-1,3-hexadiene	-19	-4.52
Z-1,4-hexadiene	0	0.02
E-1,4-hexadiene	0	0.03
1,5-hexadiene	2	0.48
E,E-2,4-hexadiene	-21	-4.96
E,Z-2,4-hexadiene	-20	-4.73
Z,Z-2,4-hexadiene	-19	-4.49
E-1,3,5-hexatriene	-33	-7.89
Z-1,3,5-hexatriene	-31	-7.41
1,3-cyclohexadiene	-10	-2.36
1,4-cyclohexadiene	-10	-2.33
benzene	-150	-35.93