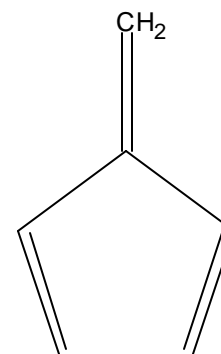


ASSIGNMENT 4 SOLUTIONS

1. The structure is of the molecule fulvene. Construct the determinant for a Huckel calculation for this molecule.

The rules for Huckel theory are that we have an α term for each carbon, and a β term for each pair of directly bonded carbons. If carbon 6 is the exocyclic carbon, and it is bonded to carbon 5, then the determinant is as follows. We define x as $(\alpha - E)/\beta$, to keep things tidy.

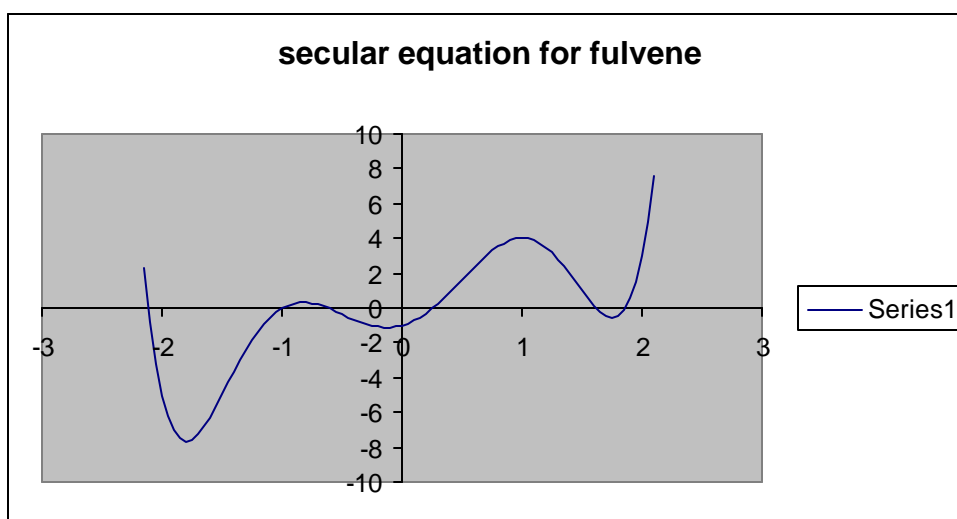
$$\begin{vmatrix} x & 1 & 0 & 0 & 1 & 0 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 1 & 0 & 0 & 1 & x & 1 \\ 0 & 0 & 0 & 0 & 1 & x \end{vmatrix}$$



2. The determinant reduces to the secular equation

$$x^6 - 6x^4 + 8x^2 + 2x - 1 = 0$$

where $x = (\alpha - E)/\beta$. Calculate the six roots of this equation to 3 decimal places. One way to do this is to plot the function on a spreadsheet, and look for the x values at which the function is zero.



The more exact roots are -2.1149, -1.0000, -0.6180, 0.2541, 1.6180, 1.8608.

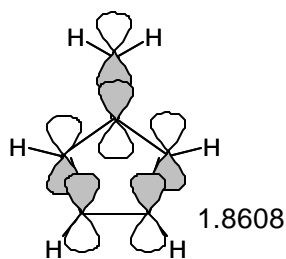
3. The coefficients for the molecular orbitals are given below. Carbon 6 is the CH₂ carbon, and it is attached to carbon 5.

	C1	C2	C3	C4	C5	C6
a	-0.439	0.153	0.153	-0.439	0.664	-0.356
b	0.601	0.372	-0.372	-0.601	0	0
c	0.429	0.385	0.385	0.429	0.523	0.247
d	-0.350	0.279	0.279	-0.350	-0.190	0.749
e	0	0.5	0.5	0	-0.5	-0.5
f	-0.372	0.601	-0.601	0.372	0	0

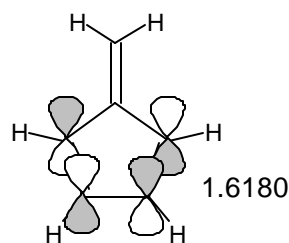
Associate each of these MO's with an energy from question 2, and explain your reasoning.

The roots, and the associated MO's are given below.

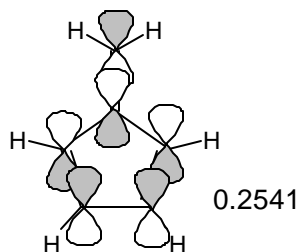
Huckel MO's for Fulvene



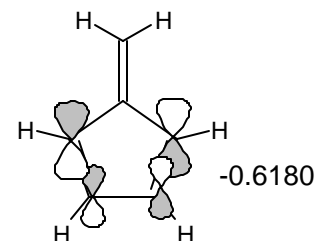
three nodes



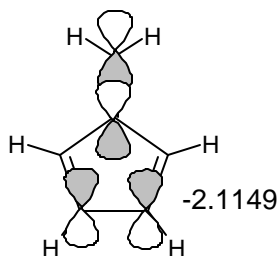
two nodes



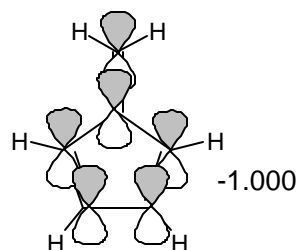
two nodes



one node



one node



no nodes

3. (continued) In assigning the order of the orbital energies, the main problem is deciding between the two orbitals with one node, and the two with two nodes. The no-node orbital is always the lowest, and the orbital with the most nodes will be highest. One way to rationalize the two orbitals with the same number of nodes is to look at how much the two parts of the orbital are "pushed together" toward the node. The more antibonding-type overlap, the higher the energy. Another way of looking at it is to consider that the orbitals are the result of an interaction between an isolated carbon atom and the cyclopentadiene orbitals. For cyclopentadiene, the two orbitals with one node are degenerate (recall inscribing the ring in a circle). This orbital has an energy of -0.618 in cyclopentadiene, and the energy is not changed in fulvene. One of these orbitals has a node through what we call carbon 5, and the other does not. When carbon 6 is brought close, there is a strong bonding interaction along the 5-6 bond, so that orbital is stabilized. The diagram shows that it is almost two isolated double bonds, so its energy is close to -2.0. The orbital with a node through carbon 5 is not affected by this interaction. Again, for the two-node orbitals, one is a pure cyclopentadiene orbital, (energy 1.618, from inscribing the ring in a circle).

4. Calculate the bond order for each bond, if there are two electrons in each of the three lowest energy MO's.

The equation for bond order between carbon i and carbon j in Huckel theory is given by the following equation. The number n_k is the number of electrons in orbital k .

$$\text{bond order} = \sum_{\substack{k \text{ running over} \\ \text{occupied orbitals}}} n_k c_{ik} c_{jk}$$

For example, between carbon 1 and carbon 2, orbitals c , e , and b are occupied by the six valence electrons.

$$\text{Bond order} = 2 [0.429*0.385 + 0.0*0.500 + 0.601*0.372] = 0.778$$

For the others, remember that the signs must be included.

Bond orders for fulvene	
C1-C2	0.778
C2-C3	0.520
C3-C4	0.778
C4-C5	0.449
C5-C1	0.449
C5-C6	0.758