CHEMISTRY 3BB3 1999/2000

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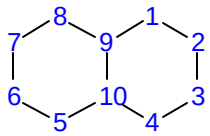
SOLUTIONS TO ASSIGNMENT 5



1. For naphthalene (numbering scheme shown above), set up the Hückel matrix, using $b = 1$ and $x = (a - l)/b$.

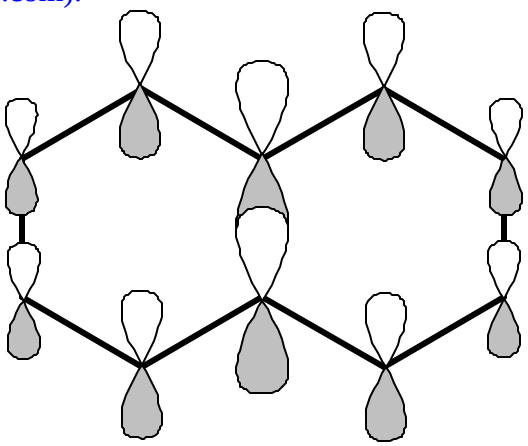
There are x's down the main diagonal, and 1 for any element where the two carbons are connected.

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

2. Using Maple (or something else) obtain the eigenvalues and eigenvectors of the Hückel matrix. Use the matrix from question 1, and set x=0, since all the eigenvalues are usually relative to a in Hückel theory. With some fiddling, (exporting the output as a text file, editing the text file) you should be able to get the numbers into a spreadsheet for further calculations.

Carbon	E	-2.3028	-1.6180	-1.3028	-1.0000	-0.6180	0.6180	1.0000	1.3028	1.6180	2.3028
1		-0.301	-0.263	0.400	0.000	0.425	0.425	0.000	-0.400	0.263	0.301
2		0.231	0.425	-0.174	0.408	-0.263	0.263	-0.408	-0.174	0.425	0.231
3		-0.231	-0.425	-0.174	-0.408	-0.263	-0.263	-0.408	0.174	0.425	0.231
4		0.301	0.263	0.400	0.000	0.425	-0.425	0.000	0.400	0.263	0.301
5		0.301	-0.263	0.400	0.000	-0.425	0.425	0.000	0.400	-0.263	0.301
6		-0.231	0.425	-0.174	-0.408	0.263	0.263	-0.408	0.174	-0.425	0.231
7		0.231	-0.425	-0.174	0.408	0.263	-0.263	-0.408	-0.174	-0.425	0.231
8		-0.301	0.263	0.400	0.000	-0.425	-0.425	0.000	-0.400	-0.263	0.301
9		0.461	0.000	-0.347	-0.408	0.000	0.000	0.408	-0.347	0.000	0.461
10		-0.461	0.000	-0.347	0.408	0.000	0.000	0.408	0.347	0.000	0.461

Lowest energy MO (no nodes) (drawn with Chemsketch, free over the net from acdlabs.com).



3. Calculate the total π electron energy, and compare it to the energy of five isolated double bonds.

Total π electron energy is just the sum of the individual orbital energies, times the number of electrons in each orbital. In this case,

Energy = 2(2.3028+1.6180+1.3028+1+0.6180) = 13.6832

(remember β is negative, so positive eigenvalues mean lower energies. This should also be obvious from the node patterns.)

Each doubly occupied isolated double bond has an energy of 2, so the energy of 5 double bonds is 10, in this system of units.

4. There are four unique types of bond in naphthalene - calculate the bond order for each of them.

The formula for bond order in Hückel theory is

$$\text{bond order } (i,k) = \sum_{k}^{occupied} n_k c_{ik} c_{jk}$$

where n_k is the number of electrons in orbital k, and c_{ik} is the coefficient of atom i in orbital k.

The four different bonds are 1-2 (0.7246 π bond order), 2-3 (0.6032 π bond order), 1-9 (0.5547 π bond order) and 9-10 (0.5182 π bond order).

5. For the radical anion, estimate the unpaired electron density at the three different types of carbon. Remember that the π electron charge is given by the following equation.

$$\text{charge on atom } i = \sum_{k}^{\substack{occupied \\ MO's}} n_k c_{ik}^2$$

Because naphthalene is an alternant hydrocarbon, each carbon has no net charge in the neutral molecule (*i.e.* each carbon will have a charge of 2, according to the formula, for the neutral molecule). This should be an easy thing to verify. Therefore, the unpaired density is just the square of the coefficient of the singly

occupied orbital. For carbon 1, this is 0.1801, for carbon 2, it is 0.0691, and for carbon 9, it is zero.