

Chem 260 Laboratory 3

This lab explores orbital symmetry in the “Particle on a Ring”, which may be thought of as the particle in a 1-D Box (Lab 1) with the ends joined together. The model is applied to the π -electron system of benzene and a large cyclic polyene.

PARTICLE ON A RING – π ORBITALS IN BENZENE

1. Start HyperChem Lite and draw the benzene molecule. For a “resonant bond” structure instead of alternating single and double bonds draw the carbon ring and then double click (left mouse button) with the drawing tool. Build/Add Hydrogens, Model Build.
2. Optimize the structure using Molecular Mechanics.
3. Open a log file with File/Start Log. Choose a suitable file name and set the directory to your local drive (e.g. C:\TEMP\CHEM 260). If you leave the default file name (chem.log) it will be overwritten the next time a log is started. In the same Start Log window set the Extended Hückel Print Level to 1 (default is 0).
4. Perform a single point EHT calculation. Look at the log file. It is a simple text file, so you can read it with Notepad, WordPad, or Word.
5. Notice how only atomic orbitals involved in bonding are included in the EHT calculation. Each of the six carbons contributes one s and three p orbitals. These are $2s$ and $2p$ orbitals – the “core” $1s$ orbitals are ignored. On the other hand, the $1s$ orbitals of the H atoms **must** be considered. In all, 30 orbitals ($6H + 4 \times 6C$) are included. Similarly there are 30 electrons which, in the unexcited molecule, pair up to fill the 15 orbitals of lowest energy. This is evident from the HyperChem Compute Orbitals/Labels display.
6. The column of numbers under each molecular orbital number and eigenvalue in the EHT log represents the coefficients of the atomic orbitals in the linear combination which makes up the molecular orbital. For example,

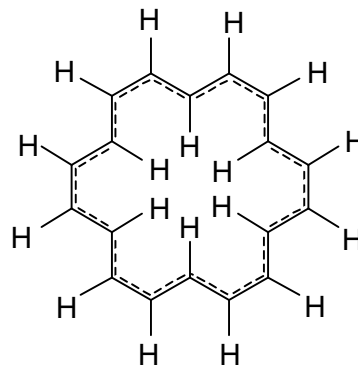
$$\begin{aligned} \Psi_1 = & -0.28352\phi(C_1 2s) - 0.00418\phi(C_1 2p_x) - 0.00241\phi(C_1 2p_y) \\ & + (-0.28352)\phi(C_2 2s) - 0.00418\phi(C_2 2p_x) - 0.00241\phi(C_2 2p_y) \\ & + \dots \end{aligned}$$

The **square** of the orbital coefficient indicates the relative contribution of each atomic orbital (i.e. probability that the electron will be there).

7. In this lab we are only interested in the molecular orbitals constructed from the carbon p_z atomic orbitals. Find them. Notice how they do not mix with the other atomic orbitals. This is because of their symmetry – the nodal plane in the plane of the molecule. Record the molecular orbital numbers of the π orbitals. There should be 6 of them (one for each atomic orbital).
8. Use the HyperChem Orbitals display to view the π molecular orbitals one at a time. Cut and paste the orbitals into your report (remember to Edit/Setup Image to metafile, not bitmap). Arrange the orbital pictures in your report according to energy (highest at top of page). Pasting pictures into different cells of a table is a good way to arrange them.
9. Stop logging and shut your log file viewer.

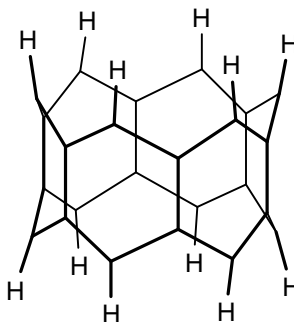
PARTICLE ON A RING – CYCLIC POLYENES

10. Find the file coronene.hin (on the network drive or on the HyperChem CD in \Samples\Aromatic) and copy it to your local hard drive. Open the file in HyperChem and delete the middle hexagon. Use Build/Add Hydrogens so that what remains is the planar 18 carbon cyclic polyene. Do not use the Model Build command or you will get something else (see the optional exercise below). Save your cyclic polyene structure with a *different* filename than coronene.
11. Optimize the structure. Open a log file and perform a single-point EHT calculation. There should be 90 molecular orbitals.
12. Just as you did for benzene, look only at the orbitals which have π symmetry. What number molecular orbital is the lowest energy π orbital?
13. Look at the next two π orbitals. Notice the degeneracy. How many nodal planes are there (don't count the one in the plane of the molecule that is common to all the π orbitals). How many nodes are there if you count them by moving around the ring?
14. Notice how the orbitals occur in pairs, except for the lowest and highest energy ones. Why are these two unique? How do the number of nodes relate to the orbital energies (qualitatively)?
15. Find the π orbitals with 3 nodal planes (6 nodal points around the ring). Paste these orbital plots into your report. Notice how the degenerate orbitals have somewhat different shapes but *the number of nodes is the same*.



JUST FOR FUN (OPTIONAL)

16. Use the Build/Model Build command. Do you get a “belt-like” structure? By deleting six pairs of H's and replacing them with carbon atoms which complete aromatic rings you can create this aromatic belt.



Synthesizing molecular scale “machine parts” is a current hot research area.