Chemistry 433, "Computational Chemistry", Prof. Rainer Glaser

HMO Problems I.

(1) Draw the MOs of fulvene using the information given on the following page.

(2) Consider ethene. Construct the interaction matrix and solve the problem on paper. Give the MOs and their energies.

(3) Consider the allyl system. Construct the interaction matrix and solve the problem on paper. Give the MOs and their energies. What are the overall energies of the allyl cation, the allyl radical, and of the allyl anion?

(4) Consider methylenecyclopropane. Construct the interaction matrix, formulate the characteristic polynominal for x. The solutions for x are 2.1700, 0.311, -1.000, and -1.4812. Give the MOs explicit and make sketches of these MOS.

Fulvene

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*********************************************************
*              Hueckel Molecular Orbital Program        *
*            Rainer Glaser, UMC, January 21, 1991       *
*       Written for but not limited to 30 carbon atoms  *
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Title: fulvene

HMO Connectivity Matrix:
  0.  1.  0.  0.  0.  0.
  1.  0.  1.  0.  0.  1.
  0.  1.  0.  1.  0.  0.
  0.  0.  1.  0.  1.  0.
  0.  0.  0.  1.  0.  1.
  0.  1.  0.  0.  1.  0.

The MO energies (Beta units) in line 1
The MO coefficient vectors follow
    1      2      3      4      5      6
  2.115  1.000  0.618 -0.254 -1.618 -1.861

  0.247 -0.500  0.000  0.749  0.000  0.357
  0.523 -0.500  0.000 -0.190  0.000 -0.664
  0.429  0.000 -0.602 -0.351 -0.372  0.439
  0.385  0.500 -0.372  0.280  0.602 -0.153
  0.385  0.500  0.372  0.280 -0.602 -0.153
  0.429  0.000  0.602 -0.351  0.372  0.439

The squared MO coefficient vectors are
    1      2      3      4      5      6
  0.061  0.250  0.000  0.562  0.000  0.127
  0.273  0.250  0.000  0.036  0.000  0.440
  0.184  0.000  0.362  0.123  0.138  0.193
  0.148  0.250  0.138  0.078  0.362  0.024
  0.148  0.250  0.138  0.078  0.362  0.024
  0.184  0.000  0.362  0.123  0.138  0.193

Charge:   0    Number of Electrons:  6
Doubly occ. MOs:   3   Singly occ. MOs:   0

Ground State Energy:   6 alpha + 7.466 Beta
The ground state electron configuration is:
 2 2 2 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0

Bond  1- 2 has pi-bond order:   0.759
Bond  2- 3 has pi-bond order:   0.449
Bond  2- 6 has pi-bond order:   0.449
Bond  3- 4 has pi-bond order:   0.778
Bond  4- 5 has pi-bond order:   0.520
Bond  5- 6 has pi-bond order:   0.778

Atom  1 has pi-density:   0.622
Atom  2 has pi-density:   1.047
Atom  3 has pi-density:   1.092
Atom  4 has pi-density:   1.073
Atom  5 has pi-density:   1.073
Atom  6 has pi-density:   1.092
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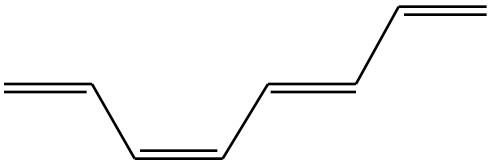
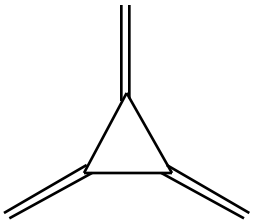
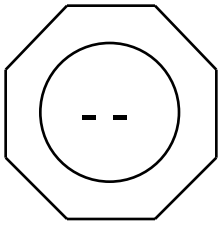
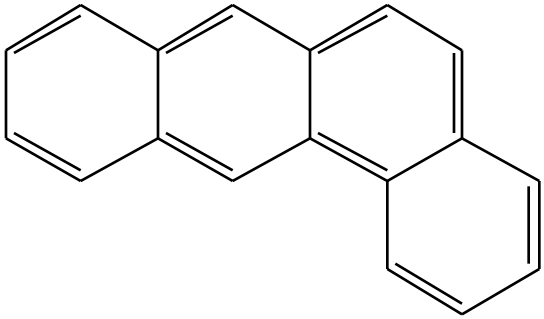
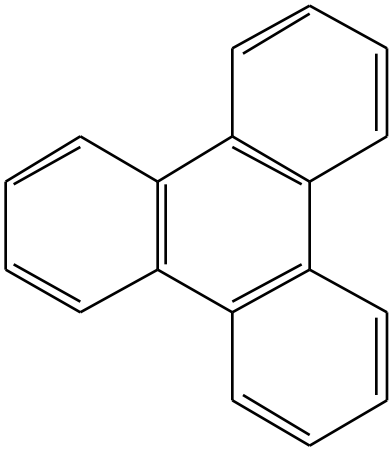
HMO Problem II. Which of the following π-systems are alternant or non-alternant?

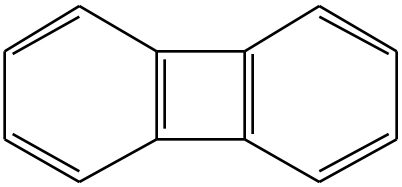


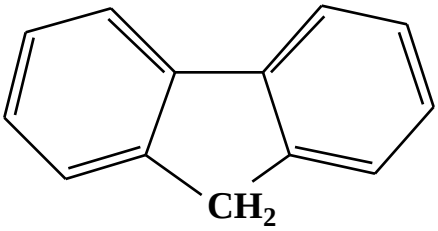


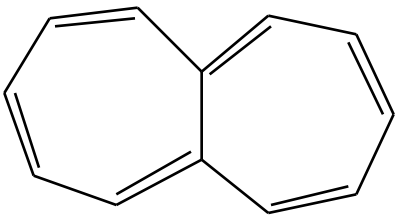






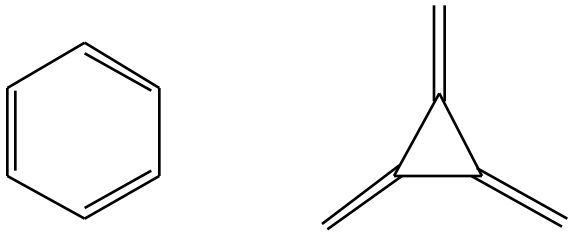






HMO Problems III.

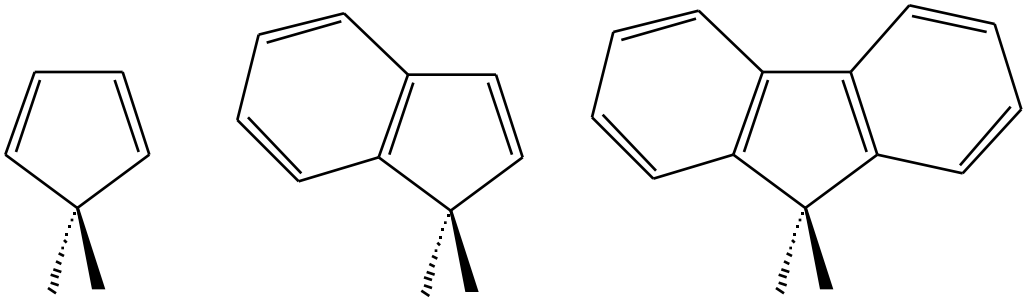
(1) Let's consider the two C_6H_6 systems benzene and trimethylenecyclo-propane.



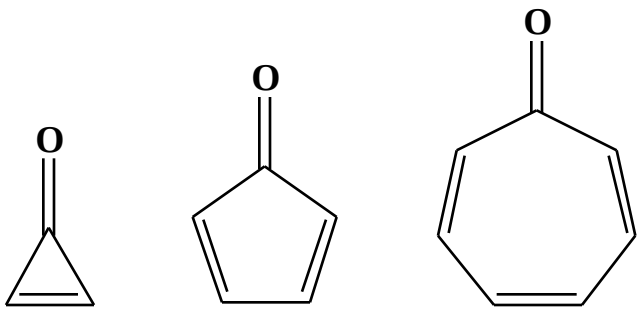
(a) Write down the connectivity matrices for these systems. (b) Solve the HMO problem on a computer. (c) Sketch the molecular orbitals and draw energy level diagrams. (d) Determine the charge distributions. (e) Which molecule is more stable? By how much? (f) Predict the site of electrophilic attack.

(2) Consider the polyenes $H_2C=CH-(CH=CH)_n-CH=CH_2$ for n=0 to n=5. Perform HMO calculations on all of these systems. Explain why the UV/Vis absorption moves to longer wave lengths with increasing chain length. Use the departmental Macintosh to draw a diagram of the HOMO and of the LUMO energy levels as a function of chain length.

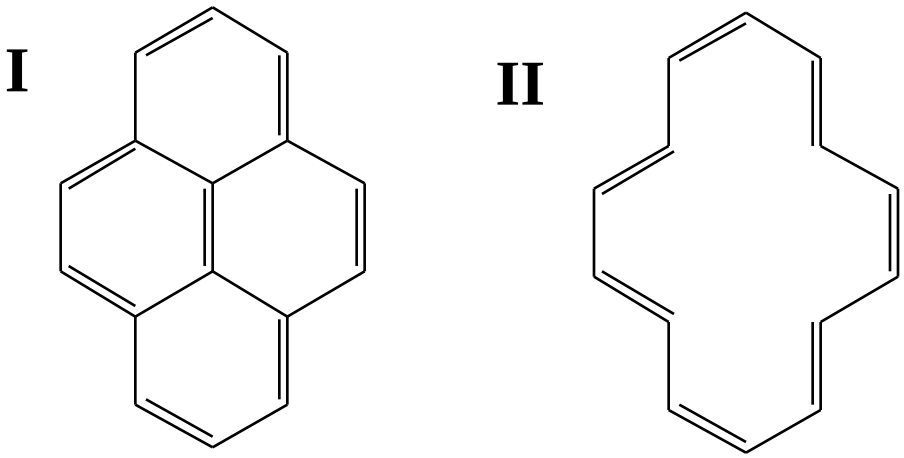
(3) The acidities of cyclopentadiene, indene, and fluorene are quite different. Give the order of their acidities and explain this ordering with HMO theory.



(4) Explain the following observation using MO concepts but without carrying out any computations. Cyclopropenone and tropone are stable molecules which do not show the typical ketone properties. On the other hand, the cyclopentadienone is rather unstable (dimerizes fast).

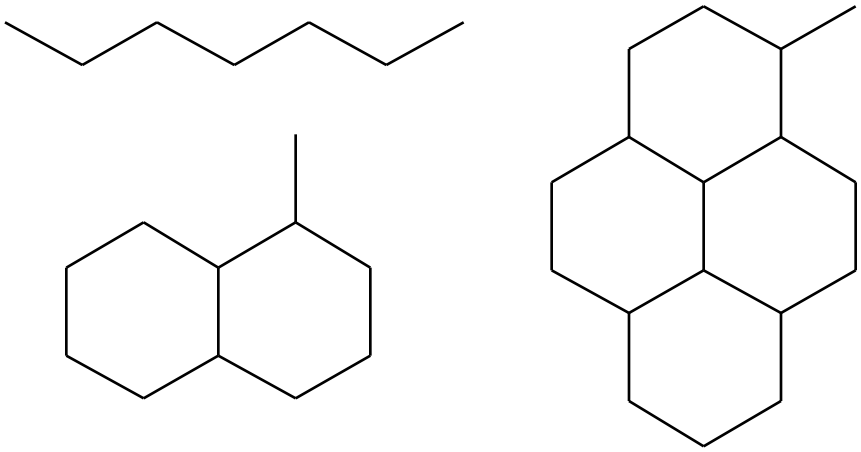


(5) Consider the molecules shown.

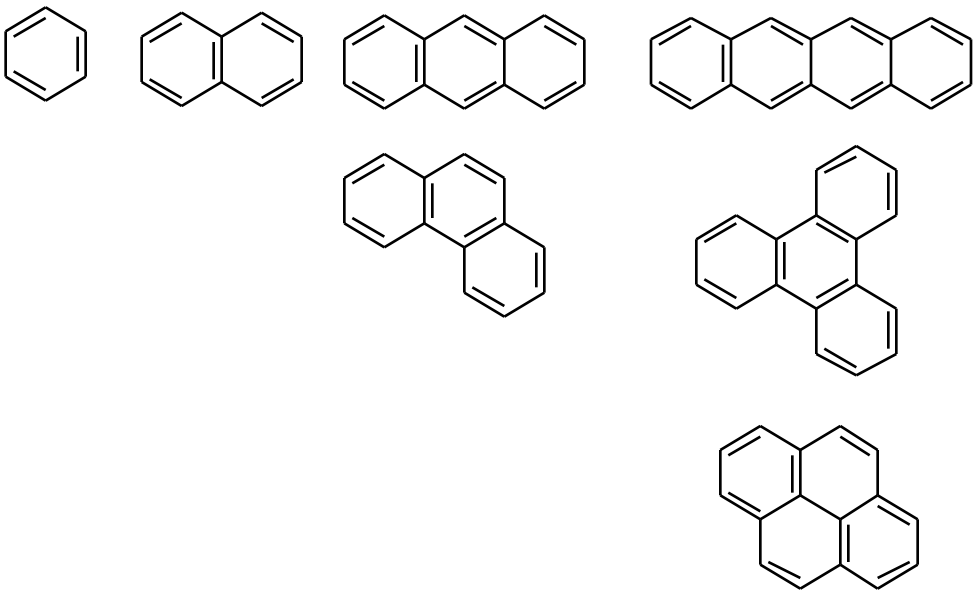


Are they aromatic or not? Draw the energy level diagrams. How do they differ? Are these alternant or non-alternant hydrocarbons. Are there any non-bonding orbitals?

(6) The following hydrocarbons are alternant. Determine the non-bonding orbital coefficients for each using pen and paper only.

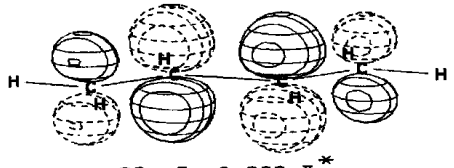


(7) Compare and contrast electron densities, bond orders, and resonance energies of the following molecules. Consider effects of molecular size and consider effects of isomerism.

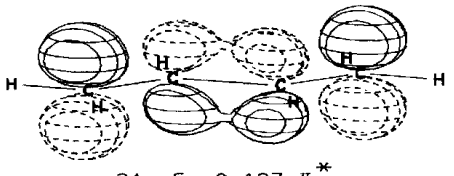


Butadiene

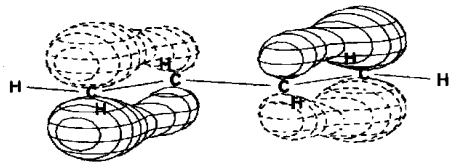
	ψ_1	ψ_2	ψ_3	ψ_4
c_1	0·3717	0·6015	0·6015;	0·3717
c_2	0·6015	0·3717	−0·3717	−0·6015
c_3	0·6015	−0·3717	−0·3717	0·6015
c_4	0·3717	−0·6015	0·6015	−0·3717
Symmetry about mirror plane	*S*	*A*	*S*	*A*



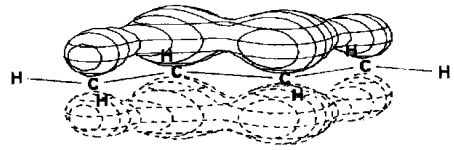
$2B_g$ E= 0.283 π^*_4



$2A_u$ E= 0.127 π^*_3



$1B_g$ E=-0.358 π_2



$1A_u$ E=-0.477 π_1