

**CHEMISTRY 412/512**

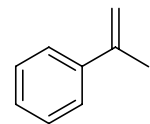
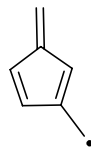
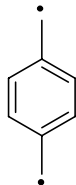
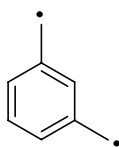
MIDTERM # 2

April 02, 2007

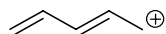
Name .....

The total number of points in this midterm is 45. The total exam time is 90 min (1.5 h).

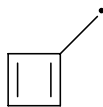
1. (4 pts) Classify each of the following radicals or biradicals as an even alternant, odd alternant or nonalternant hydrocarbon structure.



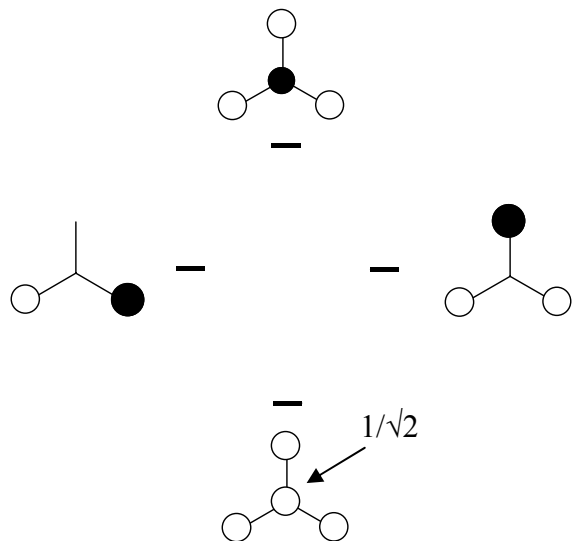
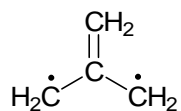
2. (6 pts) Consider the pentadienyl cation. Use the sine methodology to derive qualitatively the shapes of the MOs and order them by increasing energy. Derive the actual coefficients for the nonbonding molecular orbital (NBMO).



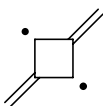
3. (3 pts) The cyclobutadienylmethyl radical (shown below) is an odd alternant species. Derive the coefficients of its nonbonding MO (NBMO) and use the values to determine the odd electron density at particular positions (Taking into account the fact that the odd electron resides in the NBMO, so for each position  $i$  we will have  $\rho_{\text{odd electron}} = C_i^2$ ). Provide appropriate resonance structures that lead to an equivalent conclusion about the distribution of the odd electron. Rationalize the result on the basis of the aromaticity/antiaromaticity concept.



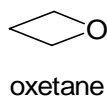
4. (6 pts) The qualitative MOs of trimethylenemethane are shown below. Derive the actual coefficients at each atomic center, for each MO.



5. (6 pts) Write the secular determinants for the following systems:



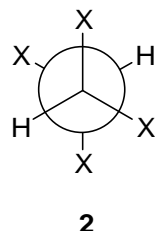
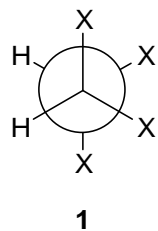
6. (4 pts) Although cyclobutane exists in a bent conformation, its oxygen analog, oxetane, is planar. Suggest an explanation.



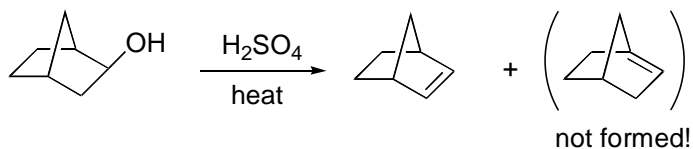
7. (4 pts) The strain energy of spiro[3.3]heptane (62.5 kcal/mol, see structure below!) is considerably greater than the doubled strain energy of cyclopropane (2 x 27.5 kcal/mol). Explain!



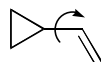
8. (4 pts) 1,1,2,2-Tetrahaloethanes exist in two distinct conformations: *gauche* (**1**) and *anti* (**2**). Experiments have shown that 1,1,2,2-tetrafluoroethane exists predominantly in the *anti* conformation, while 1,1,2,2-tetrachloroethane and 1,1,2,2-tetrabromoethane prefer the *gauche* conformation. Provide a brief rationalization for this phenomenon.



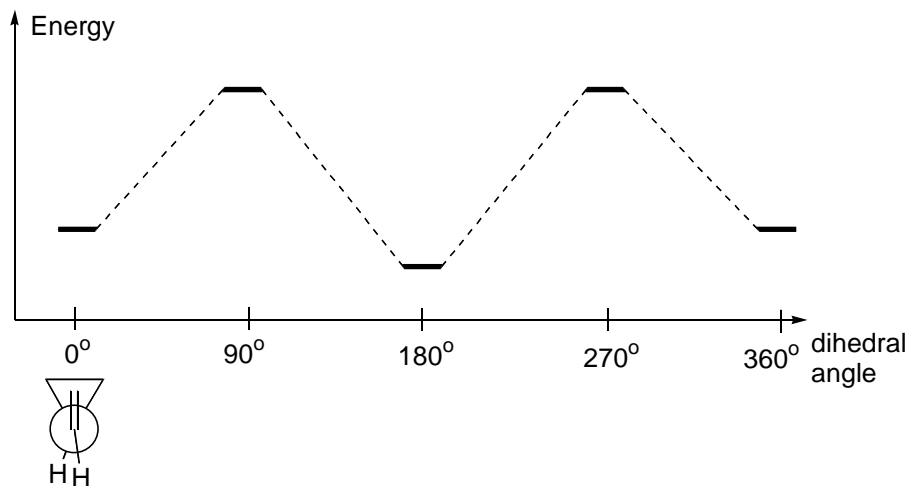
9. (3 pts) Explain the regioselectivity of the following reaction:



10. (5 pts) The rotation around the indicated bond of vinylcyclopropane gives rise to the following qualitative potential energy profile. Provide a structural explanation, consistent with it.



vinylcyclopropane



11. **(3 pts) Bonus Problem (Complete solution required in order to get credit!!).** Strongly  $\pi$ -electron withdrawing groups attached to a cyclopropane ring have the effect to shorten (and strengthen) the C2 – C3 bond of the ring (shown in bold). Provide an explanation.

