CHEMISTRY 412/512

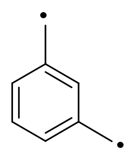
MIDTERM # 2 – answer key

April 02, 2007

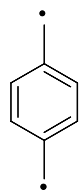
Statistics:

- <u>Average:</u> 32 pts (72%);
- <u>Highest:</u> 42 pts (93%); <u>Lowest:</u> 20 pts (44%)

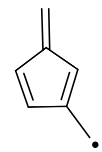
1. (4 pts) Classify each of the following radicals or biradicals as an even alternant, odd alternant or nonalternant hydrocarbon structure.



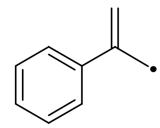
even alternant



even alternant

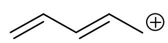


nonalternant

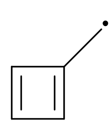


odd alternant

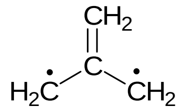
2. (6 pts) Consider the pentadienyl cation. Use the sine methodology to derive qualitatively the shapes of the MOs and order them by increasing energy. Derive the actual coefficients for the nonbonding molecular orbital (NBMO).

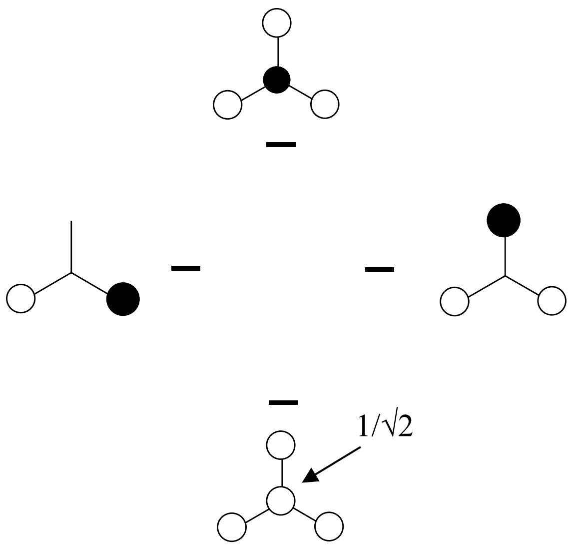


3. (3 pts) The cyclobutadienylmethyl radical (shown below) is an odd alternant species. Derive the coefficients of its nonbonding MO (NBMO) and use the values to determine the odd electron density at particular positions (Taking into account the fact that the odd electron resides in the NBMO, so for 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.

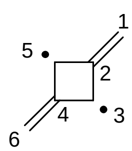


4. (6 pts) The qualitative MOs of trimethylenemetahne are shown below. Derive the actual coefficients at each atomic center, for each MO.

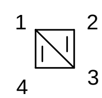




5. (6 pts) Write the secular determinants for the following systems:

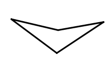


$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 0 \\ 1 & x & 1 & 0 & 1 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 1 \\ 0 & 1 & 0 & 1 & x & 0 \\ 0 & 0 & 0 & 1 & 0 & x \end{vmatrix} = 0$$

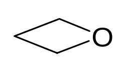


$$\begin{vmatrix} x & 1 & 1 & 1 \\ 1 & x & 1 & 0 \\ 1 & 1 & x & 1 \\ 1 & 0 & 1 & x \end{vmatrix} = 0$$

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



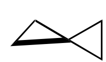
cyclobutane



oxetane

<u>Solution:</u> The reason why cyclobutane exists in a bent conformation is to avoid torsional strain, even though this comes at the cost: Increased angle strain. In oxetane, since there are no H-atoms at the oxygen center, the magnitude of the torsional strain is far lower. Hence the molecule prefers the planar conformation, which has minimum angle strain.

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



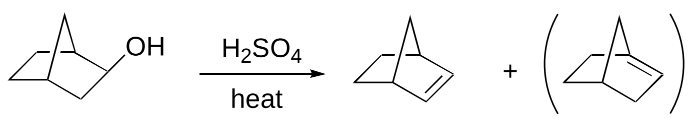
<u>Solution:</u> Strain is considerably greater in the case of spiropentane because one of the C-centers is part of two 3-membered rings, which is worse than two C-atoms, each part of one 3-membered ring.

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.

1 **2**

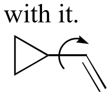
Solution: 1) The case of 1,1,2,2-tetrafluoroethane: C – F bonds are very polar and there are considerable bond dipoles, which would prefer the *anti* arrangement. In addition, F-atoms are not large (almost comparable to H), thus not much geminal repulsion is expected; 2) The case of 1,1,2,2-tetrachloroethane and 1,1,2,2-tetrabromoethane: While bonds are still polar (certainly not as much in the case of C – Br, we are dealing in these two cases with considerably larger groups, which would experience significant geminal repulsion. This would favor the *gauche* arrangement.

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

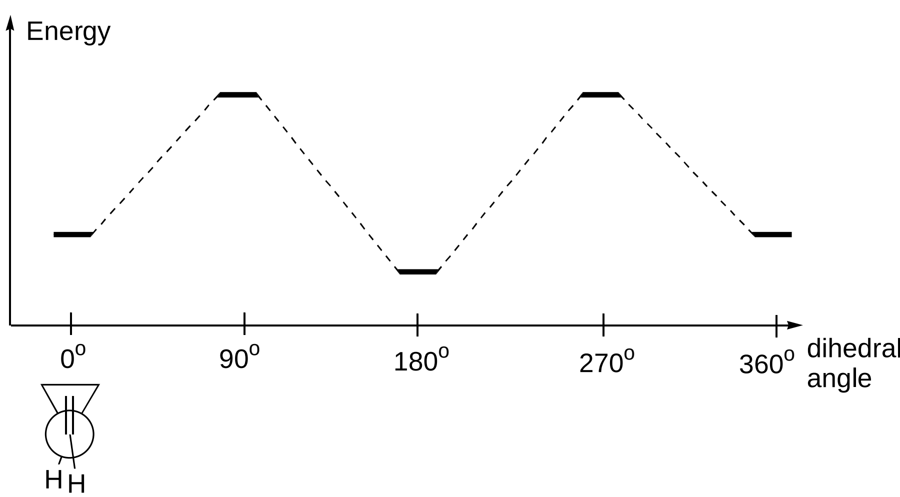


Solution: Second product (in parentheses) contains a double bond at a bridgehead position, and, according to *Bredt's* rule, that is not possible, especially taking into account the fact that the largest ring system present in this bicyclic structure is a 6-membered ring.

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.

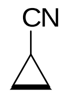


vinylcyclopropane



Solution: Stabilization at 0^o and 180^o comes through favorable interaction of the π* orbital of the C = C bond with one of the occupied *Walsh* orbitals of the cyclopropane ring. That interaction is of the type full – empty orbital and is therefore stabilizing. It is completely suppressed at 90^o and the corresponding conformation is highest in energy (a TS). The difference between the conformations at 0^o and 180^o is due to (unfavorable) *van der Waals* interaction at 0^o, which raises the energy of that conformation. Thus the conformation at 180^o is a global minimum.

11. **(3 pts) Bonus Problem (Complete solution required in order to get credit!!).** Strongly π-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.



Solution: Just as in the previous case, it has to do with interaction of one of the *Walsh* orbitals with a π* of the CN – group. The CN – group is a good electron acceptor, which means that part of the electron density of that *Walsh* orbital is shifted towards the CN – group. However, that Walsh orbital is antibonding between C2 and C3. Depleting it of electrons would mean reduced antibonding interaction along the C2 – C3 bond. It is therefore expected to become shorter and stronger.