CH 637

Key for Exam 1

1. A. These two low-energy conformers appear to agree with the data in suggesting a close H-H distance between the two sets of urea N-H protons, and a longer (but still relatively proximate) interaction among aromatic hydrogens i, j and k. The other N-H-to-$CH_2$ signals are benchmarks for what kind of signal one would expect in the 5-6 Ångstrom range; these distances will be relatively invariant. The two structures are similar to each other with respect to the conformational predictions that will be picked up in the ROESY spectra; since only these two are within 5 kcal/mol of the global minimum, they are effectively the only structures present in enough concentration to be chemically relevant. In general, the minimized structures are in agreement with the ROESY data.

B. In general, no, because the percentage of any of them is so vanishingly small that they should not contribute significantly to the bulk behavior in the NMR spectrum.

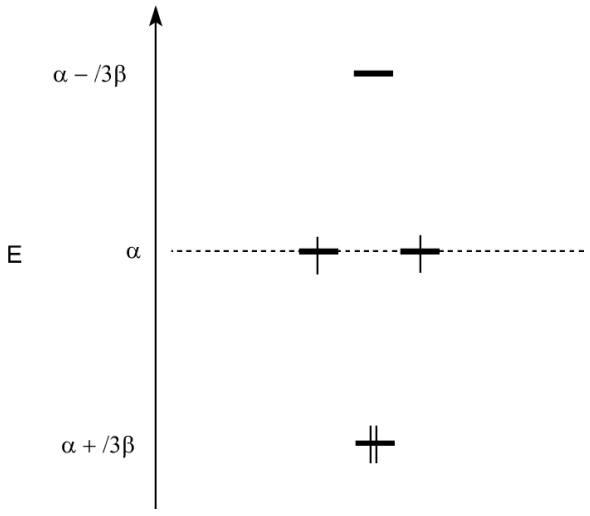
In addition, it is useful to note that between these two, the primary difference lies in the (conformationally flexible) $C_8$ ester chains, suggesting that the bulk of the 852 structures will exhibit variation in the side chains and not in the core structure (which is the issue of interest). There are likely to be isomers that vary in their rotation about the amide-like links, but their high energy renders them inconsequential.

C. The key atoms and bonds that define the conformation of the core of this molecule are the amide bonds in the ureas, and the aromatic C-N bonds. Since protein conformation is determined by similar atoms and bonds, a force field that is appropriate for proteins should be applicable to this problem. In particular, bond stretch, bond angle and torsion angle parameters will model this system quite well. If hydrogen bonding (e.g., from the urea N-H to the ester carbonyl O) is important, this should be effectively modeled as well, given the role such H-bonding plays in establishing protein secondary structure.

2. A. The secular determinant is:

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

B.



C. Because of the symmetry of the system, all C-C bonds are identical. For C1-C2,

$p_{12} = 2(0.707)(0.408) + 1(0)(-0.408) + 1(0)(0.707) = 0.577$

D, E. For C1, the electron density $e = 2(0.707)^2 + 1\ (0)^2 + 1\ (0)^2 = 1$; charge $q = 1 - e = 0$.

For C2, C3 and C4, one can argue from this and by symmetry that q = 0; mathematically,
C2: $e = 2(0.408)^2 + 1(-0.408)^2 + 1(0.707)^2 = 1$ (q = 0)

C3: $e = 2(0.408)^2 + 1(-.408)^2 + 1(-.707)^2 = 1$ (q = 0)

C4: $e = 2(0.408)^2 + 1(0)^2 + 1(0.816)^2 = 1$ (q = 0)

F. Stability: The molecule gains stability versus either (ethylene + 2 p ) or (allyl + p) because of extensive pi delocalization. However, it is a diradical and as such will be fairly reactive and is unlikely to be isolable.

3. A. Consider the frontier orbitals available for the organic fragments:

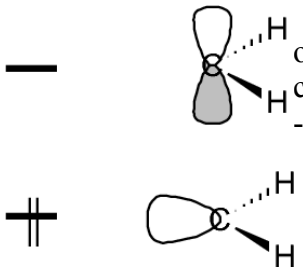
$CH_3-$: a single MO of sigma symmetry (oriented along the bonding axis).

$CH_2=$: A single MO of sigma symmetry, and a single MO of pi symmetry (having a node on the bonding axis)

HC≡: A single MO of sigma symmetry, and two (perpendicular) MOs of pi symmetry.

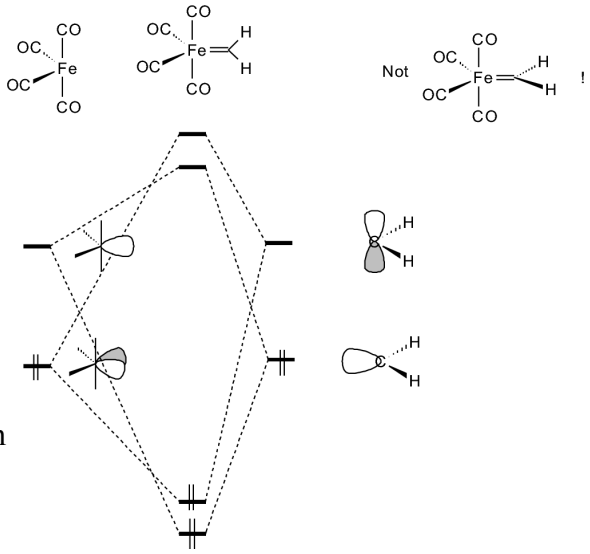
Therefore, $(CO)_5Mn$ is isolobal with $CH_3-$, $(CO)_4Fe$ with $CH_2=$, and Ni(C)(NO) with HC≡.

B.




The sp3-type MO will be lower in energy than the unhybridized p orbital, but a precise measure is not needed to answer the question. For the curious, the same level of computation as for the metal fragments yields values of -0.11 and -0.21 eV.

C. We will form one sigma and one pi bond. The final MO energies will depend on the chosen energies for the carbene fragment MOs, but the overlap for forming the sigma bond will be greater than for forming the pi bond. Note that this predicts the plane of the carbene will lie parallel to the "axial" COs (OC-Fe-CO angle = 180º) and not with the "equatorial) COs (OC-Fe-CO angle = 120º).




It will, of course, be possible to make a complex with Ni(CO)(NO), but there will be one unpaired electron left in a nonbonding MO. This is analogous to (and isoelectronic with) the vinyl radical H2C=CH•.