Over the past 35 years and coincident with the development of orbital symmetry theory (the Woodward-Hoffmann Rules), chemists have been fascinated by the thermal, photochemical, and metal-ion-catalyzed behavior of the class of compounds with formula \((CH)_{10}\). Note that these have six unsaturations, but by also specifying that there is one H per carbon we eliminate a huge number of structures from the larger set of \(C_{10}H_{10}\) (e.g., there can be no substituted benzene rings). A recent article (with many authors from five universities) ties together much of chemistry from the past couple of decades and provides new experimental determinations of the heats of formation and structures of some of these hydrocarbons. If you choose this problem, it will merely be necessary to do either Part A or Part B; use MMX to get the heat of formation and structural parameters for all of the molecules shown; compare these with experimental and calculated data found in Tables 1 and 7 of the cited reference.

A. Here are five \((CH)_{10}\) isomers with rather exotic names and surprisingly complex mechanisms for rearrangement. The thermolysis of basketene, for example, does not proceed by the “obvious” cleavage of two \(C\) bonds of the cubane portion. The evidence? When basketene-\(d_2\) is thermolyzed the isotopes in the product are distributed as shown to the right. For 1/8 of a point on the next Chem 550 exam, propose a mechanism to explain this.

B. Bullvalene and three isomers whose names suggest that they are its close relatives are all converted into \(cis\)-9,10-dihydronaphthalene, the thermodynamic sink for all of the \((CH)_{10}\) isomers.


382. Consider molecules of the type \((X-CH_2)_4C\) for which the simplest example is neopentane (\(X = H\)). The two-dimensional drawing to the right obscures how complicated the conformational analysis is for cases where \(X \neq H\). Using the drawings in Scheme 1 of the article as your guide, do MMX calculations of the relative energies of the important conformations when \(X = CH_3\). Then do the same for \(X = Cl\) and for \(X = Br\). You should compare your results with those in Table 2 and you should come to some conclusions about which steric interactions are the most important in determining energies.

383. Triptycene is a symmetrical hydrocarbon with three benzene rings fused to the two-carbon bridges of bicyclo[2.2.2]octane. The substituted triptycene to the right has three distinct conformations involving the two ethyl groups when \( R = \text{H} \) (see CHART 1 in the cited reference). Compute the relative energies of these conformations and decide why their energies are in the order obtained. Then do exactly the same for the three conformations when \( R = \text{CH}_3 \). Comment on similarities and differences in the conformational energies for the two different compounds.


384. The two preceding problems were concerned with rotations about a C–CH$_2$CH$_3$ bond. This problem and the one that follows require you to focus on rotation about a C–CH(CH$_3$)$_2$ bond. In both the Z and E alkenes to the right, steric repulsion forces the phenyl groups to rotate out of coplanarity with the alkene double bond. For each stereoisomer, there are three important conformations involving the two isopropyl groups. Do MMX calculations on these six structures. Compare your computed heats of formation and dihedral angles involving the Ph-C=C fragment with those in TABLE 1 of the cited reference. Decide which steric interactions are most important in determining the energies of these conformations.


385. The minty-smelling menthol and a diastereomer isomenthol are found in nature. Menthol can have all three of its substituent groups equatorial, but there still exist three conformations corresponding to rotation about the C–CH(CH$_3$)$_2$ bond. Calculate their relative energies and decide which factor(s) are responsible. Then do MMX calculations on isomenthol. Unlike the situation with menthol, you'll now need to consider two equilibrating chair conformations, one with methyl as an axial substituent, another with hydroxyl and isopropyl axial. Each chair, of course, has three conformations corresponding to rotation about the C–CH(CH$_3$)$_2$ bond. Do calculations on these six conformations and decide which are the most populated. Compare your energies, bond distances, and dihedral angles with those in Tables 1 and 2 in the cited reference.


386. Because of the sp$^2$-hybridized carbons and the \( n \)-bond from overlap of p-orbitals, alkenes tend to be planar. Two types of distortion from planarity can be imagined: (a) one of the sp$^2$ carbons can twist with respect to the other, thus decreasing the \( n \)-overlap or (b) both carbons can move toward a pyramidal shape as occurs in some of the strained molecules in this exercise. Bicyclooctene, shown to the right, has an unstrained double bond in which the sp$^2$ carbons and the four attached substituents can be coplanar (do an MMX calculation to convince yourself of this; use the dihedral angle for a trans C-C=C-C unit as evidence - it should be 180°). If, however, the starred carbons
are connected by chains of various length, pyramidalization occurs. You should do MMX calculations of the energies and dihedral angles of compounds with a number of CH$_2$ groups varying from four down to zero. Also do calculations on the unsaturated four-carbon bridge (both $E$ and $Z$ stereoisomers are possible) and of the dienyl chain. You might devise other structures that would enforce even greater pyramidalization.


387. Benzene is a symmetrical molecule with all bond lengths 1.39Å (intermediate between typical single and double bond values). **Problem 274** explored the possibility of creating a benzene ring with alternating short C=C and long C-C bonds. Some more molecules that might cause a benzene ring to distort that way are the subject of this problem. Do MMX calculations on the structures to the right. For the first one, there are two isomers (all three CH$_2$ bridges syn or two syn and one anti); the abbreviated second and third drawings should be read as having the identical fused ring(s) at all three sides of the central ring. If none of these show significant deviations from a regular hexagon, perhaps you can devise other molecules that will.


388. Several earlier problems from R. W. Hoffmann's group (265, 369, 371, and updates in the Addendum distributed to the class) have focused on the possibility of so destabilizing certain conformations that certain acyclic compounds exist exclusively (or nearly so) in just one or two staggered conformations. Here is another example of this with regard to the *meso* compound shown to the right. There are five important conformations for this molecule (see Table 2 in the first-cited article) of which only one avoids a severe *syn*-pentane repulsive interaction; this refers to a staggered conformation in which C$_1$-C$_2$ and C$_4$-C$_5$ are parallel (as also occurs in a 1,3-diaxial interaction on a cyclohexane ring). Determine the energies of the five conformations and compare your results with those in the article; see if the energies correlate with the number of *gauche*-butane and *syn*-pentane interactions that you can find.


389. The structures shown here are *meso* compounds. Consider, first, the two molecules in which all three R = H. The methyl groups (which were phenyls in the literature reference) on the two outer rings serve to keep those rings in a single chair conformation because of their equatorial preference; this is reinforced by having the bond from each of the two outer rings to the central ring also equatorial. Nevertheless, five conformations (corresponding to rotation about the single bond between the rings) are possible for the all-chair structures. Probably the easiest way to attack this problem is to take the first structure and, with all three rings as chairs, choose the conformation that has both of the O-C-C-O units *anti*. After calculating the energy of this conformation, use MMX's ROT-B command to generate other conformations around the connecting C-C bonds. By doing this, you can do calculations on the *gauche(+)/anti*, the
gauche(+)/gauche(+), the gauche(-)/anti, and the gauche(+)/gauche(-) structures. You will probably find that the conformations are so similar in energy that all are approximately equally populated. Do the same for the second structure with R = H. Then, see if introduction of methyl groups (R = CH₃) makes enough of a difference in the relative energies that one (or two) of the conformations are highly populated at the expense of the others.


390. [6]-Radialene is the trivial name for hexamethylenecyclohexane. When one terminal H on each carbon is replaced by a methyl group, a number of stereoisomeric radialenes can be produced. Do MMX calculations on the all-anti isomer, shown to the right, and on the various diastereomers produced by rotating about one or more of the double bonds. Use the structures in the article as your guide. Compare these isomers in terms of energy, planarity, etc.


391. As mentioned in the preamble to Problem 381, the Woodward-Hoffmann rules have helped to bring order and understanding to many thermal and photochemical reactions. Consider, now, the cycloaddition of cyclopentadiene with cycloheptatriene. There are ten reasonable structures that are "allowed" by the orbital symmetry rules and ten that are "forbidden". The article that served as the inspiration for this problem set reported quantum mechanical calculations on the reactants, products, and transition states for these many possibilities, all with an eye to distinguishing between concerted and multi-step mechanisms. Your task, should you decide to do this problem, is considerably easier. Either do MMX calculations on the ten allowed products or the ten forbidden. Compare your results with the heats of formation given in the article.

"Allowed" by orbital symmetry


"Forbidden" by orbital symmetry


392. Many years ago, Donald Cram (UCLA) wrote a review article titled "Bent and Battered Benzene Rings". His topic was the cyclophanes, particularly [2,2]-para-cyclophane and its derivatives. Such compounds were the subjects of earlier MMX projects (3, 57, 234, 241, and 244) but a recent paper adds a new "twist" (so to speak) to these compounds. As strained as these cyclophanes are, how much more strained are they if cyclobutane or cyclobutene rings are fused to the aromatic rings?

Do MMX calculations on the three structures shown here and on their three stereoisomers in which the four-membered rings are syn to each other, rather than anti.