α- and β-Eremophilane are plant metabolites that possess a cis-decalin core and differ only in the stereochemistry of the isopropyl substituent. Begin with β-eremophilane: do MMX calculations on all three of the staggered conformations that the equatorial isopropyl group can assume; then do the same for the axial isopropyl group in the α epimer. Compare the energies of the three β conformations with one another and with those for the α isomer. Discuss the factors responsible for the energy differences that you find.


In an extension of ideas introduced in Problem 375, consider trispirane (the hydrocarbon shown to the right). As you've seen for many cyclohexane-containing molecules in Chem. 550, a structure drawn with planar rings gives the "correct" answer (but often for the "wrong" reason) to the question of whether a molecule can support optical activity at "ordinary" temperatures. Use Scheme 2 in the cited reference, along with your molecular models, to do MMX calculations on the chiral conformation called III in the article. Then, using your models as a guide, do a chair inversion of Ring A to produce achiral IV; from there, it is alleged that inversion of Ring B produces IV again (check this yourself!); subsequent inversion of Ring C gives III again (check this) which, by inversion of Ring B, produces a new chiral conformation called V. The purpose of this exercise is two-fold: (1) it gives practice in manipulating chair cyclohexanes and determining the factors that lead to different conformational energies; (2) because it will be very difficult for you to convince yourself that the two drawings labeled III are identical, and even harder for the two labeled IV, it becomes easy to be convinced when the MMX calculations come out identically for every component that is included in the overall MMX energy.


Highly congested cyclohexane rings may adopt a twist conformation to relieve the severe steric repulsion. Consider the molecule to the right: do MMX calculations on its twist and its chair conformations to decide which is more stable and why; compare your results with those in the cited reference. Do a similar pair of calculations on the constitutional isomer that has the spiro cyclopropanes at C1, C2, and C4 with the six methyl groups arrayed on the other centers. And then do this for the isomer with cyclopropanes at C1, C2, and C3.

[Shen, Q.; Traetteberg, M. J. Mol. Struct.. 2003, 657, 185.]

In 1,3-diisopropyladamantane (to the right), it would appear that the two substituents are separated enough that they would not interact. Maybe yes, maybe no. Consult Scheme 4 in the cited reference and do MMX calculations on the conformations shown. Compare your results with those for MMX and MM3 calculations in Table 1. Discuss and similarities and differences that you find.


Students in Chem. 550 know, of course, everything there is to know about the conformations of cyclohexane. But what do they know about cycloheptane? Alas, very little. Do MMX calculations on the five conformations of cycloheptane, shown in Figure 3 of the cited reference. Compare your results with those from MM4 and from ab initio calculations in Table 2. Comment on similarities and differences.

**Problem 391** asked for calculations on the various adducts from the reaction of cyclopentadiene with cycloheptatriene. This new problem focuses on the [2+2] dimerization of cyclopentadiene that could produce either symmetrical or unsymmetrical adducts. Adapting the nomenclature used for the perhydroanthracenes and perhydrophenanthrenes (in Chem. 550 lecture), each of the gross structures shown could be cis-syn-cis, cis-anti-cis, etc. Do MMX calculations on all of these and compare your results with those in the cited reference.


399 A summary of MMX problems on cyclophanes appeared in **Problem 392**. This new problem starts with an MMX calculation on [2,2]-paracyclophane (shown to the right); note the high strain energy and bending of the aromatic rings. Now do calculations on unsaturated derivatives that have a C=C at C1-C2; two C=Cs at C1-C2 and C9-C10; one C=C and one C=C; and two C=C. Compare your results (for some of these) with the values in the cited reference.


400 Alkenes are planar ... except when they're not. Put enough stress on a carbon-carbon double bond and it will respond by twisting or pyramidalizing or both (see **Problem 386**). Consider the hydrocarbon framework shown to the right. Do MMX calculations of energy and structure (including the dihedral angle 1-2-7-6) for this molecule and for its several derivatives in which anywhere from one to four C=Cs are introduced at 4-5, 13-14, 11-12, and 9-10. Compare your results with those in **TABLE 2** in the cited reference.


401 Homocubane is shown to the right. Five different bishomocubanes (obtained by insertion of a CH2 into each of the lettered bond s) are possible. **Problem 188** asked for calculations on these molecules, but now new results (experimental and computational) are available. Do MMX calculations on these molecules and compare your results with those in the cited reference.


402 Another set of caged molecules is the subject of this exercise. **Problem 79** asked about the series of strained molecules from [3]prismane through [6]prismane, the two extremes of which are shown to the right; note that 12 C-H bonds have been omitted from the second structure. With their three- and four-membered rings, some of these molecules were severely strained. Consider, now, the extension of these to columnar structures [illustrated, to the far right, for [3]prismane] in which a different kind of strain is now introduced: the central carbons are not tetrahedral - rather each has four bonds on the same side of a plane. Do MMX calculations on the C9H6 compound shown and on the columnar extensions of [4], [5], and [6]prismane. Compare your results with those from more sophisticated calculations in the cited reference.

Each of the hydrocarbons to the right has one sp\(^3\)-hybridized carbon. Upon heating, a [1,5]-
sigmatropic shift occurs; the name
derives from the fact that the H
moves from C\(_1\) to C\(_5\) and the π-
electrons redistribute themselves
accordingly. This new hexaene can
undergo another [1,5] shift in which
the H migrates to C\(^*\); and that
hexaene can undergo one more
shift in which the H is now at C#.
Do MMX calculations on the two
isomers that are shown and on the
two that were just described. Compare their energies and justify why the stability order is as
you've found. [Be sure to specify that the sp\(^2\) atoms are π-atoms for the calculation.] Compare
your computed results with those in the reference.