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Pyramidalized Cycloalkenes (Cyclohexene, Cycloheptene, and *cis*-Cyclooctene): An MM4 and ab Initio Study

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The molecular geometries of the most stable conformers of *cis*-cycloalkenes, C_nH_{2n-2}, with $n = 6-8$, were optimized by both the MM4 molecular mechanics force field and by MP2 calculations using the 6-31G** basis set. Both computational methods agree that in each of these molecules the olefinic carbon atoms show small but definite pyramidality, contrary to the usual assumption made in structural studies. This is in agreement with both computational and experimental studies of related systems and can be understood in terms of the molecular mechanics model.

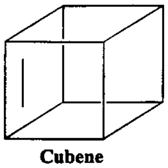
Introduction

It is well known that the sp^3 and sp^2 hybridized carbon atoms are associated with idealized bond angles of 109.47° and 120°, respectively. The latter value also implies a planar arrangement of chemical bonds around the sp^2 carbon. As additional and more accurate structural data became available, they allowed Mislow to conclude in 1965 that “the regular tetrahedral angle is the exception rather than the rule in organic chemistry.”[1]

An essentially similar limiting statement was formulated for olefinic carbons:

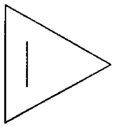
Planarity is not expected if the molecule does not have a plane of symmetry passing through the sp^2 carbons and all four corresponding ligands.[1]

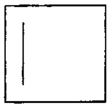
However, a planar trigonal arrangement of the sp^2 carbons remained for decades one of the most obvious assumptions used in many structural studies. On the other hand, structural data on highly strained compounds such as cubene[2], anti-Bredt olefins[3−5] and other olefins[6−8] clearly show that the bond angles in these compounds do not fit the widely accepted generalization (more examples can be found in a recent paper by Mastryukov and Boggs[9]). From these examples, one might think that the pyramidalization of olefinic carbons is a direct consequence of the geometric constraints introduced in the molecules. Can we still expect a pyramidality of olefinic carbons when less geometric constraint is imposed?



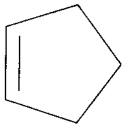
Cubene

Cycloalkenes, C_nH_{2n-2}, seem to be good candidates to examine in an attempt to answer this question. Although some geometric constraint does exist because of the cyclization, at the same time the vinyl hydrogens in these molecules are free to adopt the geometry of minimum energy. Therefore, these hydrogens can serve as an indicator of the sp^2 carbon pyramidalization. Small cycloalkenes, cyclopropene and cyclobutene, have a planar heavy-atom skeleton, and according to Mislow's statement they must have a planar arrangement around the double bonds.





In the higher cycloalkenes (1−4), the carbon skeleton is no longer planar, and one may expect to find the sp^2 carbon atoms pyramidalized.



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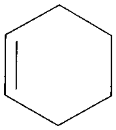

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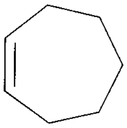

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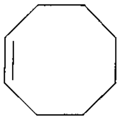
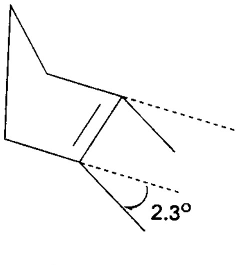


(4)

Cyclopentene (1) was an object of a high level ab initio quantum chemical study by Allen, Csaszar, and Horner in 1992.[10] This molecule provides an excellent illustration of the importance of symmetry stressed by Mislow.[1] When the five-membered ring is forced to be planar, the calculations by Allen et al. showed that the vinyl hydrogens were to be found in the same plane. However, when the molecule was allowed to adopt the equilibrium “envelope” conformation, the sp^2 carbons were pyramidalized.



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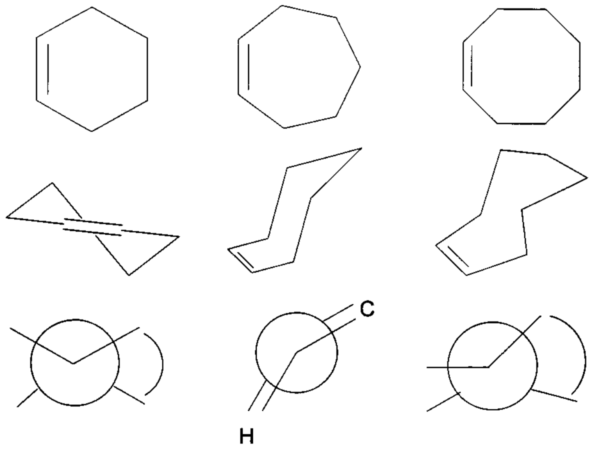
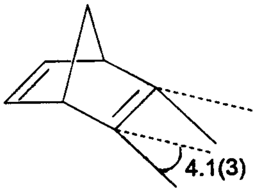


Figure 1. Most stable conformers of cyclohexene, cycloheptene, and *cis*-cyclooctene. The projections along the double bond are shown at the bottom.

The direction of the departure of the vinyl hydrogens from the plane is easy to predict. It will be that direction which reduces the torsional energy between those hydrogens and the substituents on the adjacent saturated carbon. The magnitude of the departure of the vinyl hydrogens from the plane was found to be comparable with the value measured experimentally by Knuchel, Grassi, Vogelsanger, and Bauder[11] in norbornadiene, which may be viewed as composed of two cyclopentene moieties. (Even if the calculations and experiment were both exact, these numbers are expected to be different, because the ab initio calculation gives the equilibrium value, while the experiment (depending on what kind of an experiment it is) gives some type of a vibrationally averaged value.



Cyclohexene (2) exists in a half-chair conformation (discussed later, see Figure 1) in which the double bond is expected to be slightly twisted. As a consequence, the olefinic atoms are expected to be pyramidalized. However, in all experimental studies of this molecule by both microwave spectroscopy[12,13] and gas-phase electron diffraction,[14−16] the planarity of the double bond was assumed. In 1981, Saebo and Boggs[17] carried out ab initio calculations for cyclohexene with a basis set similar to 4-21G. As in the previously discussed case of cyclopentene, what these authors found was also consistent with the symmetry principle: where the carbon ring is planar, the vinyl hydrogens lie in this plane; when the ring is not planar, the vinyl hydrogens are out-of-plane.

Cycloheptene (3) was investigated by electron diffraction assisted by molecular mechanics (MM2) calculations,[18] and later by ab initio calculations.[19] In the electron diffraction study, planarity around the double bond was assumed.

cis-Cyclooctene (4) has been investigated by the MM4 force field by Nevins, Chen, and Allinger,[20] but the structural parameters were not reported. Isomeric *trans*-cyclooctene received attention previously because of its unusual structure. It was studied as early as 1958,[21] and it was concluded, based on the large dipole moment of the molecule and other evidence, that the unsaturated carbons were strongly pyramidal. This was later confirmed by electron diffraction,[22] X-ray diffraction[23] and ab initio calculations.[19]

The purpose of this communication is to report MM4 and ab initio calculations for cyclohexene, cycloheptene, and *cis*-cyclooctene in search of the sp^2 carbon pyramidality, and to try to better understand why it occurs.

Computational Methods. Geometry optimizations were carried out using the MM4 program[20] and the Gaussian92[24] and Gaussian94[25] program packages, at the Hartree−Fock and MP2 levels of theory with the 6-31G** or larger basis sets, to show that the conclusions reached in the present work were not significantly changed as a function of basis set size or electron correlation over those ranges. At higher levels, pyramidalization occurs where it should according to Mislow's rule, in agreement with the best experiments. In cyclohexene, for example, the $H-C{=}C-H$ torsion angle has the value 1.4 ± 0.2° for HF/6-31G**, MP2/6-31G** and MP2/6-311++G(2d,2p) calculations.

Results and Discussion

The most stable conformers of the three cycloalkenes studied are shown in Figure 1, together with their projections along the double bond. Calculated structural parameters for cyclohexene and cycloheptene have been reported several times[17−20] with similar results, and our present results differ from those by very little. We will here concentrate our attention on the geometric parameters characterizing the pyramidality of the olefinic carbon atoms, which are displayed in Table 1.

As summarized in Table 1, each of the molecules considered in this work exhibits definite pyramidality of the olefinic carbon atoms. The effect, however, is small, and it is difficult to measure directly by existing experimental methods. From the computational point of view, it is also somewhat sensitive to the level of theory used. For the most part the higher the level of theory, the stronger the pyramidality. The first illustration is provided by cyclohexene, for which the ab initio results are listed in Table 1. The MP2/6-31G** results show a slightly increased pyramidality (0.3°) compared with the HF calculations. The second example comes from the calculations for cycloheptene. Burkert,[26] who used the MM2 force field, concluded that cycloheptene has a planar double bond, whereas present calculations with the MM4 force field and the MP2 calculations both show a slight pyramidality (Table 1). A similar phenomenon was observed in ab initio calculations, i.e., at the STO-3G level the double bond is planar, whereas at the MP2/6-31G** level the vinyl hydrogens are out of plane by 0.6° (in torsion angle).

Cyclohexene was also chosen as a simple molecule from which to learn how the pyramidality is affected by the substitution. For this reason, both vinyl hydrogens were replaced by fluorine atoms, and HF/6-31G* calculations were carried out for both cyclohexane and the 1,2-difluoro derivative. The three dihedral angles (as in Table 1) were 1.1, 1.2, and 1.1° for the hydrocarbon, and 1.3, 1.7, and 1.5° for the difluoride. These values show that the more electronegative substituents increase the dihedral angles in question by 0.2°−0.5°. The differences are small but systematic, and they suggest that other substituents might be found where the differences are larger.

The four cycloalkenes (1−4) mentioned in the Introduction may now be discussed together because they show two different ways in which the pyramidality can occur in cycloalkenes. These are directly related to the number of carbon atoms in the ring. The odd-membered rings (cyclopentene and cycloheptene) display a simpler pattern; these molecules have C_s symmetry with the four carbon atoms $C-C{=}C-C$ lying in a plane. In

TABLE 1: Dihedral Angles (in degrees) Characterizing the Pyramidality of the Olefinic Carbon Atoms in Cyclohexene, Cycloheptene, and Cyclooctene

	cyclohexene		cycloheptene		*cis*-cyclooctene	
dihedral angle	MM4	MP2/6-31G**	MM4	MP2/6-31G**	MM4	MP2/6-31G**
C−C═C−C	1.2	1.4	0.0	0.0	2.4	3.4
H−C═C−H	3.1	1.6	0.0	0.0	0.5	0.5
Δ(C−C═C−H)[a]	1.0	1.5	0.3	0.6	5.6, 3.7	4.5, 1.6

[a] Deviation of the C−C═C−H dihedral angle from 180°. For *cis*-cyclooctene, because of low symmetry (C_1), the two values given are for the two different directions.

the even-membered rings (cyclohexene and *cis*-cyclooctene), if C_s symmetry were present, it would lead to an eclipsed conformation for the C−C bond which is just opposite to the double bond. The relief from torsional strain is achieved through a twist around this bond, which amounts to 63.1° (63.5°) in cyclohexene, and to 103.1° (102.6°) in *cis*-cyclooctene (the first value refers to the MM4 calculations, and the value in parentheses is the MP2/6-31G** result). This effect might be thought of as transferred to the opposite side of the ring where the double bond is twisted in response. Therefore, in these molecules, the C−C═C−C fragment is no longer planar, and the hydrogen atoms follow this movement, as is clearly seen on the projections along the C═C bond (see Figure 1). This type of behavior is quite similar to what has been observed in the appropriate deformations of the ethylene molecule studied quite recently.[9]

It is important to recognize that the reasons for pyramidalization in different molecules may be different. There is the general statement due to Mislow. Depending on the case, the deformation corresponding to this statement may be large or small. The actual physical reason that underlies the deformation resulting from the lack of symmetry is usually easy to understand in terms of a molecular mechanics model. If we consider the most simple example, propene, one of the hydrogens of the methyl group eclipses the double bond in the ground state, leading to C_s symmetry. The symmetry plane includes the two alkene carbons, plus the four atoms attached to them. One hydrogen on the methyl exactly eclipses the double bond. If the hydrogen eclipsing the double bond is forced out of the plane (in a larger molecule this can happen as a result of various kinds of constraints), then the alkene carbons will pyramidalize. There is a force that tends to keep the alkene carbons and the four attached atoms in a plane (which is formulated as out-of-plane bending, or improper torsion in molecular mechanics). But if any other force is applied unequally to the two different sides of the plane, the molecule will deform in response to this force. Specifically, if the hydrogen that was eclipsing the double bond in propene is forced out-of-plane by say 20°, a restoring force will tend to put it back where it was. But if this cannot be achieved because of other constraints, pyramidalization of the alkene carbons will occur in such a direction as to tend to move the symmetry plane to where the hydrogen is (rather than the other way around). The plane, of course, is lost in the process, so we are talking now about a mean plane defined by the two alkene carbons and the four attached atoms. As a rough rule, the larger the force acting that tends to push the hydrogen (or other substituent) out-of-plane, the greater the deformation from a symmetrical position, and the greater the nonplanarity that will result. This general effect may be conveniently examined as specific effects in particular cases. For example, in *trans*-cyclooctene, the two methylene groups attached to the alkene carbons are simply too far apart to allow the molecule to be bridged with the normal polymethylene chain, so the molecule deforms in an effort to bring them closer together. Imagine that the deformation is a twist, or torsion about the double bond, and it proceeds far enough that the molecule is significantly nonplanar about the double bond. What then happens? The two hydrogens may either stay where they are, in which case we would have two planar trigonal carbon atoms, with a substantial torsional angle between them, or the alkene carbons may pyramidalize, in which case the two hydrogens can have the torsion angle separating them reduced. The latter means that the torsion energy is also reduced, and the out-of-plane bending energy is increased. In general, when there are two competing forces trying to deform the molecule in different ways, there will be some weighted average resultant, depending on the relative strengths of the forces. And so in this case, as expected, one does not have just torsion, and one does not have pyramidalization to the point where the two hydrogens are eclipsed, but one has a system that is somewhere in between.[21]

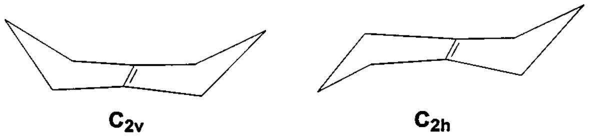


Figure 2. Conformations of Bicyclo[3.3.0]oct-1,5-ene.

Another interesting case is the conformations of bicyclo[3.3.0]-oct-1,5-ene (Figure 2). First, consider the double bond as being planar in the two conformations. One of these has C_{2v} symmetry, the other has C_{2h} symmetry, as shown. In the C_{2v} molecule, the substituents on one side of the double bond are exocyclic to a five-membered ring, and want to bend in the opposite direction from the way the tip of the envelope bends, to minimize the eclipsing. The substituents on the other side, related by symmetry, bend in the same direction. Hence, the double bond in this molecule becomes nonplanar, and the molecule retains C_{2v} symmetry.

On the other hand, if we look at the C_{2h} molecule as shown, bending two of the substituents on the double bond downward, in the direction of the peak of the cyclopentene to which they are exocyclic, causes the double bond to bend from planarity in one direction, but bending the two substituents on the other ring in a similar way causes it to bend in the opposite direction. These forces are equal and opposite, so the molecule remains in a geometry with a planar double bond (the C_{2h} symmetry is retained).

These seem like very different cases because one contains a double bond which is planar, and the other is nonplanar, but these results are easily understood in terms of the earlier discussion.

Strain Energy and Reactivity. The norbornene double bond is highly strained, by the chemical test of adding phenyl azide.[27] It is also highly reactive, undergoing similar additions thousands of times faster than cyclohexene does. According to Fukui,[28] hyperconjugation phenomena are responsible for the large electronic exo lobes in the structure of norbornene, which in turn are expected to lead to enhanced reactivity. These are accompanied by the nonplanarity (bending of the hydrogens attached to the double bond carbons out of the plane in the endo

TABLE 2: Selected C═C and ═C−H Stretching Frequencies[a](cm^{-1}).

compound	C═C	═C−H
cis-4-octene[b]	1650	3010
trans-4-octene[b]	1670	(3027)[d]
cis-cyclooctene[c]	1664	3010
trans-cyclooctene[c]	1658	3000
cyclohexene	1650	3020
norbornene[b]	1575	3070

[a] All spectra are with liquid films. [b] N. Sheppard and D. M. Simpson, *Quant. Rev.*, 1982, *6*, 1. [c] See ref 21. [d] Not reported for this compound, but homologues have this bend at 3025−3029 cm^{-1}.

direction) and place a much larger electron density on the exo side of the double bond. It is a case where the pyramidalization raises the ground state energy (relative to a double bond that is not pyramidalized). The pyramidalization reduces slightly the torsional energy, but the resulting double bond is still highly strained, mostly from the bending energy (the C−C═C angle is about 107°). So the reactivity results, not from a lower energy transition state but from a higher energy ground state. Note, however, that the strain energy in this pyramidalized alkene comes from a quite different source than from that found in *trans*-cyclooctene. In *trans*-cyclooctene, the carbons are similarly but more severely pyramidalized, but the strain is largely from torsion, rather than from bending. In norbornene, the strain is mostly from the in-plane bending of the double bond. This is perhaps most easily understood in terms of an orbital explanation, and can be clearly seen in the vibrational spectra.

When *trans*-cyclooctene pyramidalizes, the electron density on one side (the outside of the ring) of the double bond is much increased, and the pyramidalization is accompanied by torsion, with bending of the substiuents on the double bond toward the inside of the ring. This leads to a highly reactive pi electronic system. It also leads to a large dipole moment (0.82 D) from the unequal electron distribution with respect to the alkene plane.[21] Finally, because what is happening in orbital terms is that *s* character is being transferred into the orbital that would have been pure *p* if the alkene were planar, and the result is that the amount of *s* character in the C−H bond attached to the pyramidalized carbon, and also in the C−C sigma component of the double bond, is reduced, with the result that the C−H bond becomes slightly weaker. The C−C bond sigma component also becomes slightly weaker too in this picture. The C−H stretching frequency is accordingly somewhat reduced in *trans*-cyclooctene, relative to that in the cis isomer, or in *cis*-4-octene, the open-chain analogue. The C═C stretching frequency is intermediate between those observed for the two model compounds (Table 2). The result is that the hybridization changes in this molecule lead to a large change in the dipole moment, but to rather small changes in the infrared stretching frequencies.

This may be contrasted with the situation in norbornene.[32] The norbornene molecule has a slightly nonplanar double bond, and hence the electron density should be higher on one side (the exo side) of the ring. However, the dipole moment of norbornene (0.40 D[32]) is perfectly ordinary, so the electronic asymmetry induced here in the pi system would appear to be small. On the other hand, if one looks at the C−H and C═C stretching frequencies (Table 2), one sees that the C−H frequency is unusually high (some 50 cm^{-1} above that of cyclohexene), whereas the C═C stretching frequency is unusually low (75 cm^{-1} below that of cyclohexene). Why are these numbers so different from those in *trans*-cyclooctene? There seem to be two reasons. First, the distortion of the pi-system out-of-plane is much larger in *trans*-cyclooctene, leading to a sizable increase in the dipole moment. There is an out-of-plane distortion in norbornene, but the major distortion is in-plane and is brought about by the fact that the normal 120° bond angle for the C−C═C angle is very much constrained by the five-membered rings (it is only 107° in norbornene, by MM4 calculation). So in norbornene, most of the distortion is in the sigma-system, not in the pi-system. This small C−C−C bond angle in norbornene leads to a substantially increased *p* character in the C═C−C sigma bonds. This in turn leads to a much reduced C═C stretching frequency (and presumably to a C−C stretching frequency as well, although this frequency would be mixed in with other similar frequencies, and does not appear to have been sorted out in previous spectroscopic work). On the other hand, when one increases *p* character in some bonds at an atom because *s* and *p* characters are conserved, there must be increased *s* character in some other bond. Indeed, the geometry requires that the C−H bond obtains the extra *s* character, hence becoming much stronger, and this frequency increases considerably.

So here, we have a case where there are two distorted double bonds, both pyramidalized from planarity, but in quite different ways with quite different physical results, but a similar chemical result. The reactivities increase greatly in both cases, but the spectroscopic situation is totally different, and the electron distributions, as revealed by their dipole moments, also are quite different. The chemical reactivity of norbornene and *trans*-cyclooctene are both greatly enhanced, but for somewhat different reasons. Norbornene represents a case of what is usually called *I*-strain.[29] *I*-strain (for internal strain) comes about when a reactant contains some kind of strain that is diminished in going to the product, and is hence diminished in the transition state. Raising the ground state energy of the starting material more than that of the transition state leads to increased chemical reactivity. So this is simple angle strain, being released as one goes from the formally alkene geometry to the formally alkane geometry, and the zero of angle strain goes formally from about 120° to about 110°. The *trans*-cyclooctene case is different, because the strain comes from a combination of torsion about the double bond, and out-of-plane bending. Double bond addition leads to a product of having a sp^3 type geometry, so these distortions are greatly relieved in the reaction product (and in the transition state) relative to the ground state. Again, this reactivity can be viewed as release of I-strain. So both of these compounds are highly reactive because of a release of strain in the transition state, but the type of strain is formally different in the two cases.

In our earlier paper discussing the reactivity of the double bond in norbornene,[27] we mentioned that Fukui's nonequivalent orbital extension[28] was not supported by MNDO or MINDO/3 calculations, which were the best quantum mechanics calculations that were usually carried out at the time (before 1980). However, in norbornene the strain is primarily in the sigma system, so the nonequivalent orbital extension is only a minor contributor to reactivity in that molecule (but a much more important contributor to the high reactivity of *trans*-cyclooctene). The reactivity of norbornene comes mainly from simple I-strain in the sigma system.

Conclusions

In most previous experimental studies of the *cis*-cycloalkenes, the planarity of the double C═C bond was assumed and never questioned. However, present results, together with those taken from the literature, clearly show that the olefinic carbon atoms in all these molecules larger than cyclobutene are slightly but definitely pyramidalized in accordance with a idea of a broken symmetry. Further experimental studies would be desirable to confirm these predictions. A combination of different techniques (recently reviewed by Mastryukov[30]) might be useful to measure such a small effect. In particular, liquid crystal (LC) NMR data can be helpful because they are sensitive to the proton positions. Another possibility consists of finding an appropriate substituent for which the effect is more pronounced.

And why does this pyramidalization occur? In the molecular mechanics model, it is simply a matter of torsional strain. In the alkenes discussed here, except *trans*-cyclooctene, the vinyl hydrogens generally have dihedral angles of 20−40° with respect to vicinal alkane hydrogens, in the range where the torsional potentials are steep. Total energy minimization is influenced by these potentials, so the dihedral angles are deformed in the direction of the nearest minimum (60°) until the lowering of the energy due to improved torsion angles is balanced by other forces, largely out-of-plane bending. This is an important point. The pyramidalization does not occur if there is a plane of symmetry containing the double bond and the four attached atoms because the forces perpendicular to the plane are the same from both sides. But if the torsion angles between the vinyl hydrogens and the substituents are at a stationary point on the potential surface, they will not experience any net force, and the double bond will not pyramidalize, no matter what the symmetry. In the quantum mechanical model, a similar thing is true, where the torsional forces are a result of the ethane-type barrier.[31] Such torsional forces are zero when the torsion angles put the molecule at a stationary point. In cases such as cycloheptene,[31] the torsion angle is only 1° or so, and this may be too small to have a detectable effect on planarity.

Finally, we should note that the MM4 results reproduce those from quantum mechanical calculations quite well. The MM4 alkene model was chosen with care to reproduce as well as possible the structural data available on small alkene molecules, and it automatically takes into account the behavior of the molecules described here. (No MM4 parameter adjustment was involved in the present work.) An important advantage of the molecular mechanics model is that it allows us to understand the physical phenomena involved in terms of straightforward (classical) mechanical effects, which can be easily extended conceptually to physically related cases.

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