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Nonplanar Alkenes and Carbonyls: A Molecular Distortion Which Parallels Addition Stereoselectivity

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Alkenes and carbonyls are normally planar. We have found, however, that substituents which are asymmetrical with respect to the local symmetry plane of such unsaturated linkages produce small, but significant pyramidalizations of these moieties. These distortions are of the same order of magnitude as the "methyl tilt".[1] The direction of this pyramidalization follows a predictable pattern and is the same as the direction in which the alkene or carbonyl carbon pyramidalizes preferentially upon attack by nucleophiles or electrophiles, suggesting that there is a relationship between this molecular distortion and the stereoselectivities of addition reactions. While "orbital distortion"[2] due to σ–π mixing has been proposed as the origin of addition stereoselectivity,[3-5] orbital distortion is insignificant in calculations on molecules with planar alkene or carbonyl groups.[6]

The olefinic pyramidalization in seven relevant molecules, optimized by ab initio SCF–MO calculations with the STO-3G basis set,[7] are shown in Figure 1. All geometrical parameters were optimized fully, except that norbornene, norbornadiene, and bicyclo[2.1.0]pentene were constrained to C_s, C_{2v}, and C_s symmetries, respectively, while the propene, fluoropropene, and ethanal calculations were performed on molecules with one HCCC, FCCC, or HCCO dihedral angle constrained to 90°, in order to induce asymmetry into these molecules. The geometry of Dewar benzene was partially optimized by Newton et al.[8] Our full optimization gives the same degree of bending. Electron diffraction structures of hexamethyl[9] and hexafluoro[10] derivatives of Dewar benzene show evidence for the same type of alkene pyramidalization found in our calculations.[11]

Previous model calculations suggested that the olefinic carbons of norbornadiene derivatives would pyramidalize.[12] Upon full optimization of norbornene and norbornadiene, the olefinic CH bonds are bent in the endo direction (away from C-7 and below the $C_1C_2C_3C_4$ plane) by 3.4° and 1.7°, respectively.[13] These distortions are small, corresponding to only 6% and 3%, respectively, of pyramidalization to a tetrahedral geometry. However, these distortions are not energetically insignificant: a 3.4° exo bending of the norbornene olefinic CH bonds produces a structure which is 0.8 kcal/mol higher in energy than the equilibrium structure. The endo bending of the olefinic CH bonds in norbornene is particularly notable, since electrophiles, radicals, and nucleophiles attack this molecule from the exo direction.[12,14-16]

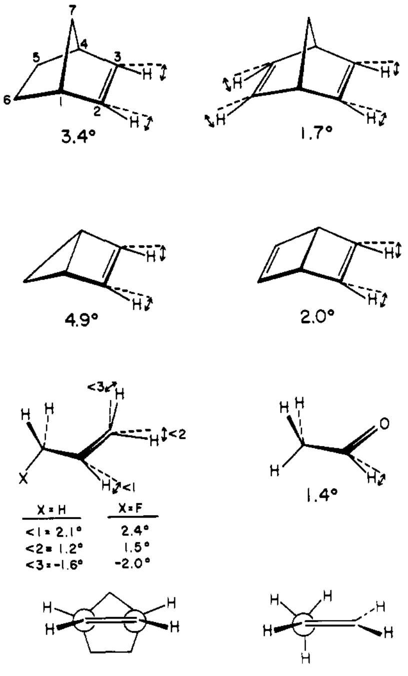

Figure 1. Out-of-plane bending angles for STO-3G optimized geometries of norbornene (C_s), norbornadiene (C_{2v}), bicyclo[2.1.0]pentene (C_s), Dewar benzene, propene (HCCC dihedral angle fixed at 90°), 3-fluoropropene (FCCC dihedral angle fixed at 90°), and ethanal (HCCO dihedral angle fixed at 90°). The dashed lines represent the positions of the bonds, if there were no pyramidalization. The two drawings at the bottom are Newman projections to show the pyramidalization of norbornene (left) and propene (right).

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(6) For example, the 2s orbital mixing contributes 1% to the π-orbital density of cyclohexene.[4] Even in the optimized geometry of bicyclopentene, the olefinic "π" orbital has only 1.6% s character.

(7) (a) The Pople series of programs was used: Hehre, W. J.; Lathan, W. A.; Ditchfield, R.; Newton, M. D.; Pople, J. A. *QCPE* **1973**, *11*, 236 (GAUSSIAN 70). (b) STO-3G basis set: Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

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(10) Ahlquist, B.; Andersen, B.; Seip, H. M. *J. Mol. Struct.* **1974**, *22*, 141.

(11) However, the electron diffraction structure of Dewar benzene does not indicate alkene pyramidalization: McNeill, E. A.; Scholer, F. R.; *J. Mol. Struct.* **1976**, *31*, 65.

(12) Mazzocchi, P. H.; Stahly, B.; Dodd, J.; Rondan, N. G.; Domelsmith, L. N.; Rozeboom, M. D.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1980**, *102*, 6482. Optimized geometries of several norbornene derivatives were reported after completion of this work: Wipff, G.; Morokuma, K. *Chem. Phys. Lett.* **1980**, *74*, 400; *Tetrahedron Lett.*, **1980**, 4445. Radom et al. (Radom, L.; Pople, J. A.; Mock, W. L. *Tetrahedron Lett.* **1972**, 479) showed that twisting about a π bond leads to pyramidalization. N. T. Anh and O. Eisenstein (*Nouv. J. Chim.* **1977**, *1*, 61) found that the energy to distort the carbonyl group of 2-chloropropanal is different for the two possible directions of pyramidalization. After we submitted this manuscript, Professor S. W. Staley of the University of Nebraska pointed out two experimental NMR studies of norbornadiene partially oriented in nematic phases: Burnell, E. E.; Diehl, P. *Can. J. Chem.* **1972**, *50*, 3566. Emsley, J. W.; Lindon, J. C. *Mol. Phys.* **1975**, *29*, 531. These authors find greater endo pyramidalization (4° and °, respectively) than found in our STO-3G calculations. However, the STO-3G calculations are known to overestimate bending force constants by 10–35% (Newton, M. D.; Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1970**, *52*, 4064. Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, 102, 939.), so that experimental pyramidalization may well be larger than calculated by STO-3G.

(13) Force-field calculations also predict the pyramidalization of norbornene (4.2–5.1°) and norbornadiene (3.9–4.3°): Ermer, O. *Tetrahedron* **1974**, *30*, 3103.

(14) (a) Brown, H. C. *Tetrahedron* **1976**, *32*, 197 and references therein. (b) Schleyer, P. v. R. *J. Am. Chem. Soc.* **1967**, *89*, 701.

(15) Nucleophiles: Lehmkule, H.; Reinehr, D. *J. Organomet. Chem.* **1973**, *57*, 29. Corey, E. J.; Shikbasaki, M.; Nicolau, K. C.; Malmsten, C. L., Samuelson, B. *Tetrahedron Lett.* **1976**, 737. Richey, H. G., Jr.; Wilkins, C. W., Jr. *J. Org. Chem.* **1980**, *45*, 5027. Richey, H. G., Jr.; Wilkins, C. W., Jr.; Bension, R. M. *J. Org. Chem.* **1980**, *45*, 5042. Radicals: Davies, D. I.; Parrott, M. J. *Tetrahedron Lett.* **1972**, 2719. Brown, H. C.; Kawakami, J. H.; Liu, K.-T. *J. Am. Chem. Soc.* **1973**, *95*, 2209.

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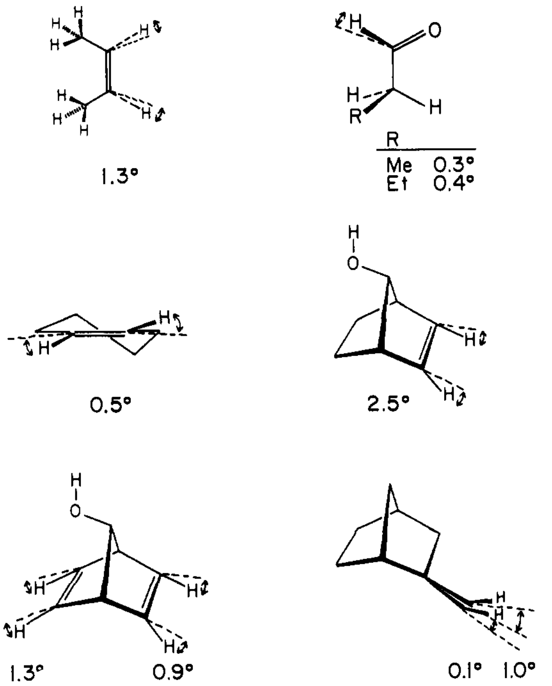


Figure 2. π Pyramidalizations in model alkenes and carbonyls (STO-3G).

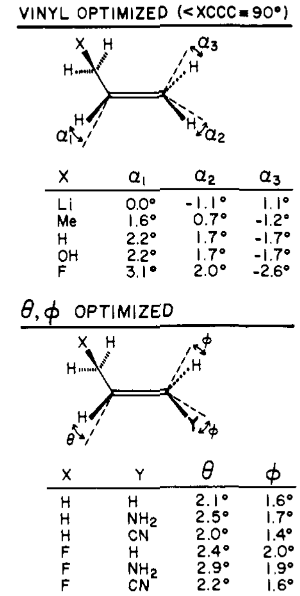
Furthermore, norbornadiene, which shows less endo pyramidalization, also exhibits lower exo stereoselectivity in cycloaddition reactions.[17] Bicyclo[2.1.0]pentene exhibits an even more marked endo pyramidalization of 4.9°. This structure is 1.9 kcal/mol more stable than the corresponding exo bent species.

In propene, 3-fluoropropene, and ethanal (Figure 1), the hydrogen on the central carbon moves toward that allylic bond which is eclipsed with the π orbital in these molecules; that is, pyramidalizations toward staggered geometries occur. At the same time, the terminal methylene of propene and fluoropropene rotates slightly and pyramidalizes in a trans fashion, presumably to preserve p-p π overlap. In the bicyclic molecules, the olefinic hydrogens have also moved toward the bonds most nearly eclipsed with the π orbitals, namely, the C1–C6 and C4–C5 bonds, as represented at the bottom of Figure 1.

The origin and generality of this phenomenon has been explored by model calculation summarized in Figure 2. When two of the allylic hydrogens of *cis*-2-butene are fixed on the same side of the CCC plane with HCCC dihedral angles equal to 90°, the olefinic CH bonds bend toward these allylic hydrogens by 1.3°. Although the strained ring skeletons of the bicyclic molecules are not prerequisites for pyramidalization, the strained molecules are considerably more pyramidal.

Optimizations of propanal or butanal in the conformations shown give slight pyramidalizations of the carbonyl carbon such that the carbonyl hydrogen moves toward the Me or Et group, rather than toward H. In these cases, the hydrogen moves toward the CC, rather than the CH, bond most nearly eclipsed with the adjacent π orbital. Although only an optimization of the olefinic hydrogens was carried out, cyclohexene shows pyramidalization of the olefinic carbons as well, but now in an anti fashion. This direction of pyramidalization corresponds to the usual axial attack observed by electrophiles, radicals, or nucleophiles on cyclohexenes.

Relatively remote substituents may have an effect on pyramidalization, as shown by the structures of the 7-hydroxy derivatives of norbornene and norbornadiene (Figure 2). These smaller endo bendings than in the parent structures are in accord with the lesser preference for exo attack of electrophiles on 7-alkoxy derivatives.[12,18] In 2-methylenenorbornene, for which only the C═CH$_2$ moiety was optimized, the terminal hydrogens are bent in an exo direction, which may be related to the preferential endo attack of electrophilic alkenes on 2,3-dimethylenenorbornenes and related systems.[19]



VINYL OPTIMIZED (<XCCC=90°)

X	α_1	α_2	α_3
Li	0.0°	-1.1°	1.1°
Me	1.6°	0.7°	-1.2°
H	2.2°	1.7°	-1.7°
OH	2.2°	1.7°	-1.7°
F	3.1°	2.0°	-2.6°

θ,ϕ OPTIMIZED

X	Y	θ	ϕ
H	H	2.1°	1.6°
H	NH_2	2.5°	1.7°
H	CN	2.0°	1.4°
F	H	2.4°	2.0°
F	NH_2	2.9°	1.9°
F	CN	2.2°	1.6°

Figure 3. π pyramidalizations in model substituted propenes (STO-3G). "Vinyl optimized" means that only the geometrical parameters of the vinyl groups were optimized. "θ,ϕ optimized" indicates that only θ and ϕ were optimized.

Pyramidalization is favored when the molecule possesses an electron-rich π system and an electron-deficient eclipsing allyl σ bond, since the effect is largest for those molecules containing relatively high-lying π orbitals (alkene vs. carbonyl) and low-lying σ* orbitals (CF rather than CH). In order to test this surmise further, partial geometry optimizations were carried out on two series of substituted propenes shown in Figure 3. In the vinyl-optimized propenes, the degree of bending follows the order of electronegativity of X. In the second series of compounds, standard planar amino or cyano groups were attached to the optimized structures of propene and 3-fluoropropene (Figure 1). The out-of-plane bending of the hydrogen at C-2 (θ) and the dihedral angle (ϕ) of the HCY plane with respect to C$_1$–C$_2$–C$_3$ plane were optimized. For Y = donor, pyramidalization increases; for Y = acceptor, this distortion diminishes.

The pattern observed here is reminiscent of the distortions found in reactive intermediates. For example, the STO-3G optimized structures of the ethyl cation, radical, and anion have each methylene hydrogen bent out of plane by 1.5°, 11.8°, and 36.6°, respectively, toward a staggered geometry.[20] As is well-known, the tendency for pyramidalization increases as the occupancy of the lone-pair orbital increases along the series.[21] For AX$_3$ species,[22] pyramidalization increases as the lone pair orbital on A is raised in energy and the σ^*_{AX} orbitals are lowered in energy. Similarly, in alkenes and carbonyls, pyramidalization increases as the π orbital is raised in energy or allylic inductive electron-

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(16) The preference for endo bending persists at large angles. In norbornene, a 10° exo bend is 2.5 kcal/mol more difficult than a 10° endo bend. This difference is 3.9 kcal/mol for 20° bends.

(17) For example, diphenylnitrilimine, benzonitrile oxide, diazomethane, and phenyl azide react with norbornene to give only the exo adducts (Fliege, W.; Huisgen, R. *Liebigs Ann. Chem.* **1973**, 2038), whereas the first two give 6–20% of the endo adduct with norbornadiene (DeMicheli, C.; Gandolfi, R.; Oberti, R. *J. Org. Chem.*, **1980**, 45, 1209).

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withdrawers lower the σ^* orbital energies.

Secondly, the direction of pyramidalization always occurs toward the bond which is most nearly eclipsed with the π orbital. In other words, the partially staggered geometry is favored over the partially eclipsed in pyramidalized species.[23] While more exotic explanations will no doubt be forthcoming, the same types of orbital arguments which have been used to explain the barrier to rotation in ethane[24] are applicable to the π pyramidalization. That is, the partially staggered pyramidalized species simultaneously maximizes the stabilizing two-electron interaction between the orbitals of the allylic CXYZ group and those of the alkene and minimizes four-electron closed-shell repulsion involving filled orbitals on these fragments. In this sense, the same effect which produces the methyl tilt,[1] causes ethane to be staggered[24] and dictates other conformational preferences,[25] also operates in pyramidal alkenes and carbonyls.[23]

Orbital distortion and alkene pyramidalization arguments generally agree as to the side of alkenes or carbonyls which is most vulnerable to attack. However, whereas orbital distortion is a purely theoretical concept, alkene pyramidalization is an observable physical property which qualitatively varies in the same direction as stereoselectivity for a series of molecules. We do not claim that the pyramidalization, in itself, dictates stereoselectivity. Pyramidalization does, however, reflect interactions in the ground states of molecules which are related to much larger energetic effects occuring in transition states. We shall report on these in due course.[26]

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[23] Computational tests indicate that this is not due merely to CH–CH bond repulsions: bending the C_1–H and C_4–H bonds upward causes an increased endo bending of the olefinic hydrogens and vice versa. Thus, the C_1–H, C_2–H eclipsing, discussed by Schleyer[14b] to account for norbornene addition stereoselectivity, is in itself insufficient to account for the endo pyramidalization.

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Origin of π-Facial Stereoselectivity in Additions to π-Bonds: Generality of the Anti-Periplanar Effect

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The understanding and control of stereoselective additions to asymmetrically substituted unsaturated molecules are subjects of intense current interest.[1] For nucleophilic attack on asymmetric carbonyl compounds, empirical generalizations (Cram's rule and its descendants)[2,3] enable qualitative predictions. Felkin,[3] and later Anh, showed that the success of these predictions arises from the strong preference for attack of nucleophiles to occur anti-periplanar with respect to the vicinal bond to the largest group.[4] "Orbital distortions", or asymmetric orbital extensions, have been proposed as the origin of stereoselective attack of various reagents on alkenes,[5] but this conclusion has been disputed.[6,7] We wish to report that the anti-periplanar, or staggering, effect proposed by Felkin et al.[3] and confirmed theoretically by Anh et al.[4] for nucleophilic additions to carbonyl groups is applicable to π systems in general and electrophilic and radical attacks as well. The effect is large and influences both stereoselectivities and reactivities of unsaturated molecules.

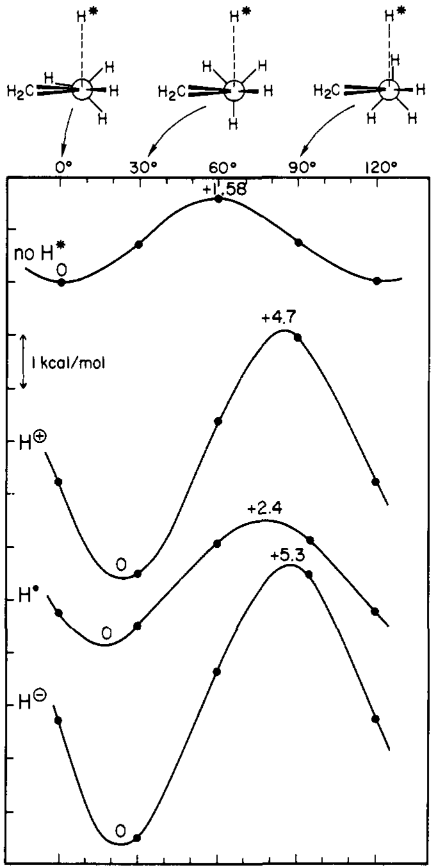

Figure 1. Energies as a function of methyl rotation.[8] Top curve: isolated propene. Second curve: propene plus H^+ placed 2 Å above C-2. Third curve: propene plus H• placed 2 Å above C-2. Bottom curve: propene plus H^- placed 2 Å above C-2.

The top curve in Figure 1 displays the STO-3G energies obtained by rotation of the methyl of optimized propene, which has the HCCC dihedral angle equal to 0°.[8] At the STO-3G level,

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[7] Footnotes 24 and 25 in ref 17.

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