Electronic Origins and Consequences of Pyramidalization of Asymmetric Alkenes in Ground and Triplet Excited States

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Abstract: STO-3G and MM2 calculations on *syn*- and *anti*-sesquinorbornene show that the pyramidalization observed in the syn species is caused by torsional effects of the type which cause alkanes to be staggered. The small sp mixing and orbital tilting found in pyramidalized alkenes are analyzed by orbital contour plots. The high thermal addition reactivity of these molecules on the exo face is attributed to torsional interactions which develop in transition states. STO-3G and 3-21G calculations indicate that triplet states of cyclic alkenes are much more significantly bent than ground states, and the stereoselective endo photoreduction of *syn*-sesquinorbornene can be attributed to the fact that only a large exo distortion of the carbon skeleton is feasible in this molecule.

Introduction

Large deviations from planarity have been observed for *syn*-sesquinorbornene and other norbornene derivatives. Such molecules also undergo highly stereoselective thermal and photochemical reactions. These two types of phenomena have engendered a flock of theoretical offspring which purport to explain the origin and electronic consequences of such π-deformations. Only a few of these offspring are legitimate! We have undertaken theoretical studies of the geometries, electronic structures, and reactions of sesquinorbornene and related molecules, and have determined the origin of pyramidalization, the consequences of this pyramidal distortion on electronic structures, and the cause of stereoselectivity in addition reactions of such molecules. In this paper, we report (1) ab initio and force-field calculations on sesquinorbornenes, (2) a detailed analysis of the orbital interactions which are responsible for nonplanar geometrical deformations and lead to small π-orbital distortions, (3) a discussion of the origin of exo-stereoselective thermal reactions, (4) a computational study of triplet states of cyclic and polycyclic alkenes, and (5) a rationalization of the endo-stereoselective photoreduction of *syn*-sesquinorbornene and predictions of the stereoselectivities of photoreductions of other alkene triplets.

Background

In 1980, we reported model calculations on norbornadienes which suggested that the alkene carbons of these molecules should be slightly pyramidalized.[1] Since the two alkene carbons and the four attached atoms do not lie in a plane of molecular symmetry, perfect coplanarity of these atoms is improbable. However, full optimizations of the structures of norbornene, norbornadiene, and related bicyclic hydrocarbons reported by Wipff and Morokuma[2] and our group[3] showed that deviations from planarity could be surprisingly large. At that time, only NMR studies in liquid-crystal solvents gave experimental evidence for pyramidalization of the alkene carbons of norbornadiene, as shown in **1**.[4]
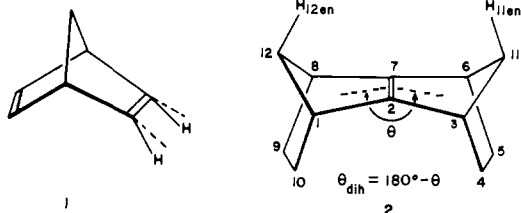
Three experimental determinations indicate that the hydrogens

of norbornadiene are bent downward by 2.3–4.1°, while computational studies give 1.7° (STO-3G),[3] 1.1° (4-31G),[5] 1.8° (MM2),[6] or 3.9–4.1° (EFF)[7] for the out-of-plane (endo) bending of hydrogens.[8] Recently, a number of experimental X-ray crystal structures of highly substituted norbornenes have been reported which show distortions even larger than those predicted for simple systems. Attention has been focused on derivatives of *syn*-sesquinorbornene (**2**) which are 16–18° (θ_{dih}) nonplanar,[9–12] but even simpler norbornenes and 7-oxanorbornenes show substantial deviations from planarity.[10,13]

Many explanations have been proposed for alkene pyramidalization. We have described this as a torsional effect, in which the unsymmetrical arrangement of the three allylic bonds forces the alkene to pyramidalize.[3] Burkert proposed the same explanation.[6] Pyramidalization relieves vicinal torsional interactions between the three allylic bonds and the two σ bonds and π orbital attached to the alkene carbon.[3] This explanation is consistent with

(1) Mazzochi, 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.

(2) Wipff, G.; Morokuma, K. *Chem. Phys. Lett.* **1980**, *74*, 400; *Tetrahedron Lett.* **1980**, *21*, 4446.

(3) Rondan, N. G.; Paddon-Row, M. N.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 2436.

(4) Burnell, E. E.; Diehl, P. *Can. J. Chem.* **1972**, *50*, 3566. Emsley, J. W.; Lindon, J. L. *Mol. Phys.* **1975**, *29*, 531. For a more recent result, see: Cole, K. C.; Gilson, D. F. R. *J. Mol. Struct.* **1982**, *82*, 71.

(5) Wiberg, K. B., unpublished results. We appreciate communication of these results before publication.

(6) Burkert, U. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 572.

(7) Ermer, O. *Tetrahedron* **1974**, *30*, 3103.

(8) Some confusion may have arisen from the fact that both out-of-plane bending of groups attached to alkenes (θ_{oop}) and dihedral angles of folding about the alkene bond (θ_{dih}) have been reported. These are related in the following fashion: $\theta_{\text{oop}} = \sin^{-1}(\sin \theta_{\text{dih}} \times \sin \theta_{\text{angle}})$ where θ_{angle} is the XC=C bond angle for the group of interest.

(9) Watson, W. H.; Galloy, J.; Bartlett, P. D.; Roof, A. A. M. *J. Am. Chem. Soc.* **1981**, *103*, 2022.

(10) (a) Pinkerton, A. A.; Schwarzenbach, D.; Stibbard, J. H.; Carrupt, P.-A.; Vogel, P. *J. Am. Chem. Soc.* **1981**, *103*, 2095. (b) Hagenbuch, J.-P.; Vogel, P.; Pinkerton, A. A.; Schwarzenbach, D. *Helv. Chim. Acta* **1981**, *64*, 1818.

(11) Paquette, L. A.; Carr, R. V. C.; Charumilind, P.; Blount, J. F. *J. Org. Chem.* **1980**, *45*, 4922.

(12) Bartlett, P. D.; Combs, G. L., Jr.; Thi Le, A.-X.; Watson, W. H.; Galloy, J.; Kimura, M. *J. Am. Chem. Soc.* **1982**, *104*, 3131.

(13) (a) Professor W. H. Watson has searched the Cambridge Crystallographic Data Base and has found evidence for alkene pyramidalization in a number of bicyclic alkenes. We thank Professor Watson for this information. (b) **Note Added in Proof:** Additional pyramidal norbornenes have recently been reported: Paquette, L. A.; Schaefer, A. G.; Blount, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 3642.

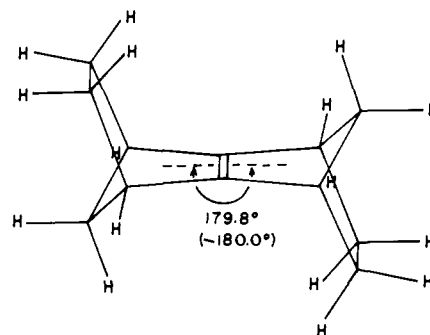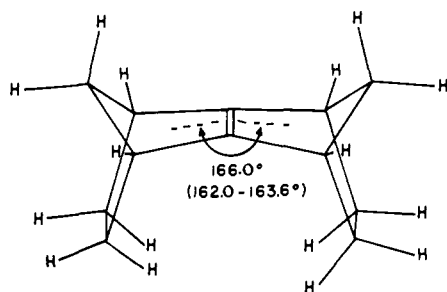[†] University of Pittsburgh.
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Figure 1. MM2 structures of sesquinorbornenes (tricyclo[6.2.1.1^{3,6}.0^{2,1}]dodec-2(7)-enes). The numbers in parentheses are experimental dihedral angles for derivatives, from X-ray crystal structures.

Table I. MM2 Strain Energies and Geometries of Sesquinorbornenes

molecule	θ_{dih} (deg)	steric energy (kcal/mol)
syn-sesquinorbornene	14.0	51.5
syn-sesquinorbornene (tors. = 0)^a	0.8	48.1
syn-sesquinorbornene (C1C2–C1H, tors. = 0)^b	11.3	51.1
planar *syn*-sesquinorbornene^c	0.0	53.6
anti-sesquinorbornene^d	16.0	53.4
anti-sesquinorbornene^e	0.2	53.7

^{a} All torsional parameters about the C1–C2, C2–C3, C6–C7, and C7–C8 bonds were set equal to 0. ^{b} Only the H–C1–C2–C3, H–C3–C2–C1, H–C6–C7–C8, and H–C8–C7–C6 torsional parameters were set to 0. ^{c} C1–C2–C3–C6–C7–C8 were constrained to coplanarity. ^{d} Starting from $\theta_{dih} > 5°$. ^{e} Starting from $\theta_{dih} < 5°$.

the fact that force-field calculations reproduce the ab initio predictions of pyramidalizations of norbornene and related hydrocarbons,[6,7] and force-field techniques are parameterized to reproduce classical torsional effects.

Gleiter and Spanget-Larsen reported extended Hückel calculations which reproduce the direction and magnitude of the pyramidalization of norbornene[14] and *syn*-sesquinorbornene.[15] They concluded that distortion occurs to minimize hyperconjugative interactions between π and "cyclopentane ribbon" orbitals, in particular, the part associated with the monomethylene bridges.[15]

Bartlett, Roof, and Winther concluded that the ground-state distortion occurred to relieve repulsions between the π orbital and H$_{11en}$ and H$_{12en}$ (see **2** above),[16] while Vogel and co-workers concluded that electron correlation effects must account for pyramidalization, since MINDO/3 calculations they performed failed to reproduce this effect.[10b] On the other hand, these authors proposed that π–σ repulsions were in some way responsible for the π-deformation of *syn*-sesquinorbornene analogues.[10b]

We have evaluated these various proposals through a detailed computational study of *syn*- and *anti*-sesquinorbornenes. In the following section, the origin of the pyramidalization of *syn*-sesquinorbornene and related alkenes is discussed.

Ground States of *syn*- and *anti*-Sesquinorbornene

MM2 Calculations. Figure 1 shows computer drawings of *syn*- and planar *anti*-sesquinorbornene obtained by Allinger's MM2 force field.[17,18] The structure of *anti*-sesquinorbornene is sensitive

(14) Spanget-Larsen, J.; Gleiter, R. *Tetrahedron Lett.* **1982**, *23*, 2435.
(15) Gleiter, R.; Spanget-Larsen, J. *Tetrahedron Lett.* **1982**, *23*, 927.
(16) Bartlett, P. D.; Roof, A. A. M.; Winther, W. J. *J. Am. Chem. Soc.* **1981**, *103*, 6520.
(17) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. Quantum Chemistry Program Exchange, No. 395. For an excellent general description of MM2 and force-field calculations, see: Burkert, U.; Allinger, N. L. "Molecular Mechanics"; American Chemical Society: Washington, D.C., 1982; Monograph 177.
(18) Since the CC=C angles are very small in these molecules (109°), we used the small ring parameters for the alkene carbons. With the normal parameters the tendency for alkene pyramidalization upon contraction of C—C=C, while correct,[27] is exaggerated.
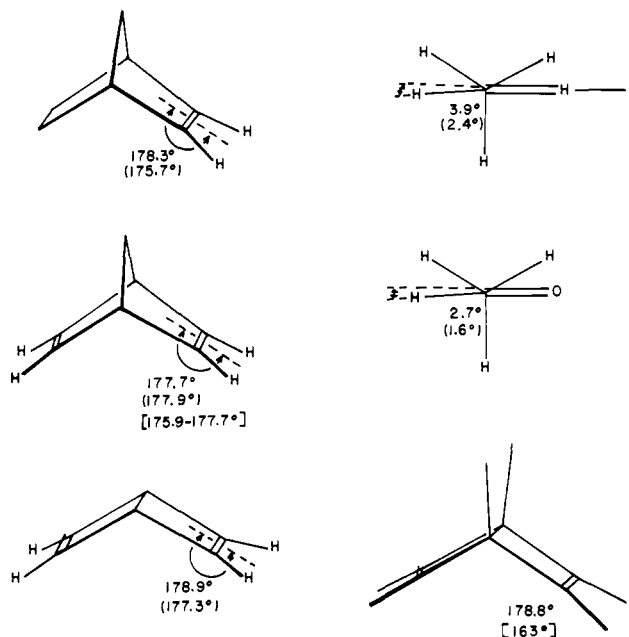

Figure 2. MM2 structures of alkenes and carbonyls. STO-3G data are shown in parentheses, and experimental data in brackets.

to starting geometry. If the optimization begins at an out-of-plane angle of 0–5°, a planar structure results as shown in Figure 1. At a starting angle greater than 5°, a nonplanar structure of slightly lower energy is obtained. We interpret this to mean that the out-of-plane bending force constant is very low, and that the parameterization is not sufficiently accurate to give the planar structure.[51] By contrast, pyramidal *syn*-sesquinorbornene is much more stable than the constrained planar species (Table I). The dihedral angles between the planes of the fused norbornene skeletons are very similar to those shown in parentheses, which are found by X-ray crystallography for derivatives of these species.[9–11] MM2 also predicts small pyramidalizations for a variety of alkenes and carbonyl compounds, some of which have also been studied by ab initio calculations.[3] Some of the structures we have studied are shown in Figure 2. Of particular note are the comparisons of the MM2 and STO-3G structures of propene and acetaldehyde in which one XCCH dihedral angle is fixed at 90°. The structure of hexamethyl(Dewar benzene) is also interesting, since an electron diffraction structure reported an astounding 17° pyramidalization of each olefinic carbon.[19] Our computations suggest that hexamethyl(Dewar benzene) and the unsubstituted compound are pyramidalized to a similar extent.[3]

Since force-field calculations are heavily parameterized to reproduce experimental geometries and heats of formation,[17] it is dangerous to ascribe a calculated structure phenomenon to a particular classical force. Nevertheless, the absence in MM2 of any specific π effects makes it unnecessary to attribute the py-

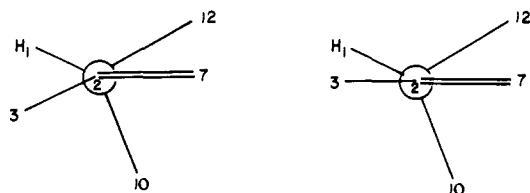(19) Cardillo, M. J.; Bauer, S. H. *J. Am. Chem. Soc.* **1970**, *92*, 2400.

Figure 3. Newman projections looking along bonds from olefinic to bridgehead carbons in (a) optimized and (b) planar *syn*-sesquinorbornene.

ramidalization to nonbonded repulsions between π orbitals and hydrogens[16] or to hyperconjugative effects[14,15] which, by definition, involve $\sigma-\pi$ interactions. On the other hand, the preferred geometries of alkenes, for which MM2 is parameterized, are dictated by both σ and π effects, so that these calculations include vicinal $\sigma-\pi$ effects even without explicit consideration of the alkene π orbital. As we suggested before for norbornene,[3] the pyramidalization of *syn*-sesquinorbornene can be attributed to the relief of torsional repulsions which accompanies endo bending. For *syn*-sesquinorbornene, the relationships between the bonds to alkene carbons and the vicinal allylic bonds are shown in the Newman projection (Figure 3). The dihedral angle between the C2–C3 bond and the C1–H bond is increased upon pyramidalization. We propose that the corresponding relief of torsional interaction is the origin of pyramidalization. If the torsional repulsive interactions cause pyramidalization, then setting the corresponding parameters in the Allinger force field to zero should reduce pyramidalization.

Several different computational tests of this type were performed. The results are summarized in Table I. MM2 calculations on *syn*-sesquinorbornene with the torsional parameters for atoms attached to C-1 and C-2, and the equivalent atoms, set to zero gave a new structure with a nearly planar alkene moiety. The forces which produce most of the pyramidalization of *syn*-sesquinorbornene in MM2 are the torsional repulsions involving the bridgehead CH and CC bonds and the vicinal CC single bond on the other norbornene ring. When these parameters are set equal to zero, the dihedral angle about the alkene is $0.8°$. Setting only the interactions between the four bridgehead CH bonds and the vicinal CC single bonds to zero reduces the bending slightly to $11.3°$. This torsional interaction was noted previously by Schleyer to rationalize predominant exo attack on norbornenes.[20] It is now clear that such torsional interactions alter the structure of the isolated molecules also, but all of the torsional interactions must be considered (at least by MM2) to account for the pyramidalization.

Torsional Interactions in Asymmetric Alkenes. Based on these ideas, the direction of pyramidalization in nonpolar alkenes is readily predictable. That is, the alkene always pyramidalizes to produce a structure which has a partially staggered, rather than eclipsed, arrangement of allylic bonds with respect to bonds to the alkene or carbonyl center.[3] In *syn*-sesquinorbornene, there are four obvious torsional interactions which are relieved upon pyramidalization, those involving C2–C3 and C1–H bonds and the three symmetry equivalent vicinal interactions. In the anti derivative, the same torsional interactions are present, but pyramidalization decreases two of these while increasing the other two, so that bending does not lower the energy of the system.

A qualitative numerical estimate of the difference in torsional interactions also provides support for the postulate of torsional origin of pyramidalization. In the planar species, the dihedral angles are all $23°$. Upon the $14°$ pyramidalization in MM2, the dihedral angles all change to $44°$. Assuming a 1-kcal/mol repulsion between eclipsed bonds, and a cos 3θ relationship (i.e., $E = {}^1/_2 V_3(1 - \cos 3\theta)$, with $V_3 = -1$ kcal/mol), the amount of torsional strain relief is 4×0.52 kcal/mol, or 2.1 kcal/mol. For comparison, the planar and pyramidal *syn*-sesquinorbornenes differ in energy by 2.1 kcal/mol in MM2 and 1.6 kcal/mol by STO-3G
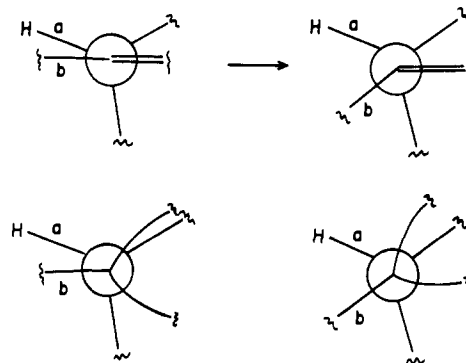
Figure 4. Newman projections of planar and bent alkene carbons attached to an allylic carbon with an unsymmetrical arrangement of allylic substituents. At the top are shown the usual $\sigma-\pi$ representative for planar and bent species, while at the bottom the same situation is represented for localized "banana" alkene bonding orbitals.
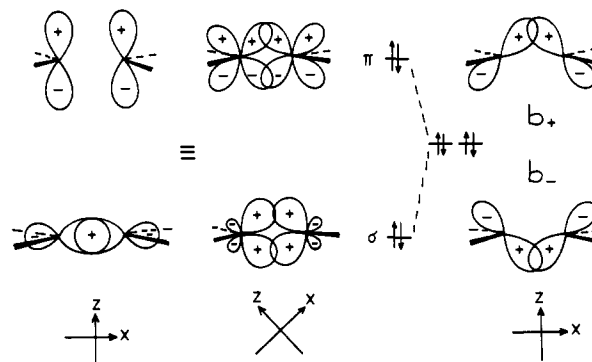
Figure 5. Left: Usual σ,π representation of the double bond of ethylene. Middle: A different, but equivalent representation of the σ and π orbitals of ethylene. Right: Bent-bond representation of the double bond of ethylene. b_+ (the "top banana") is $\sigma + \pi$. b_- (the "bottom banana") is $\sigma-\pi$.

(see below). By contrast, pyramidalization of *anti*-sesquinorbornene decreases two torsional interactions, but increases the other two. A relatively low out-of-plane force constant results.

These various computational tests are all consistent with the idea that *syn*-sesquinorbornene is bent in order to relieve torsional interactions. Indeed, we assert that the factors which cause ethane to be staggered also promote pyramidalization of alkenes in the presence of an unsymmetrical arrangement of allylic substituents.

Are there also $\sigma-\pi$ (hyperconjugative) effects which promote pyramidalization, as proposed by Gleiter and Spanget-Larsen? Although conceptually separable, we will show below that $\sigma-\pi$ hyperconjugation and "torsional repulsions" have the same geometrical dependence and are actually indistinguishable. In Figure 4, we have given Newman projections looking down a bond from an alkene carbon toward a second carbon (e.g., the bridgehead carbon of *syn*-sesquinorbornene) which has the allylic bonds arranged unsymmetrically with respect to the alkene plane. Assuming no drastic distortions of the allylic group, then bending obviously reduces the torsional repulsions between a and b. However, an alternative way of viewing the alkene double bond shows that all three pairs of torsional interactions around the C1–C2 bond are relieved upon pyramidalization.

At the bottom of Figure 4, a localized orbital ("bent-bond" or "banana-bond") description of the bonding in an alkene is shown. Such a model has been found to be of great assistance in interpreting electronic changes accompanying bond deformations.[21] It is correct to represent the double bond of ethylene either as a σ and π orbital, or as linear combinations of these. The resulting hybrid bond orbitals b_+ and b_-, are plus and minus linear com-

(20) Schleyer, P. v. R. *J. Am. Chem. Soc.* **1967**, *89*, 701.

(21) (a) Pople, J. A. *Q. Rev. Chem. Soc.* **1957**, *11*, 273. (b) Honegger, E.; Schmelzer, A.; Heilbronner, E., submitted for publication.

binations of the σ and π orbitals, as shown in Figure 5. This orbital transformation has been discussed by Pople,[21a] Zimmerman,[22] Mislow,[23] and others. The double bond of ethylene is replaced by the overlap of two sp^5 hybrids on each center, assuming perfect 120° bond angles,[22] or $sp^{4.3}$ hybrids,[23] using the ethylene HCH angles of 111°. The total bonding and electron densities, indeed all physcial observables, are identical in the bent-bond representation and in the usual σ,π representation. To facilitate understanding of this, we have also shown an unconventional, but correct, alternate representation of the σ and π orbitals of ethylene in the middle of the diagram. This is the way that the σ and π orbitals would look if the coordinate axes of the basis atomic orbitals were set up in the oblique way shown at the bottom of the figure.

The localized representation makes the relationship between the staggered conformations of alkanes, the preferred conformation of alkenes—one allylic bond eclipsed with the double bond—and the pyramidalization of asymmetric alkenes quite clear. The so-called staggered conformation of propene has three pairs of strong torsional repulsions in the banana representation and is an energy maximum, while the so-called eclipsed conformation has optimum staggering of vicinal bond electron densities, and is 2 kcal/mol more stable. In a σ,π picture, the repulsion between a filled methyl π group orbital and the alkene π orbital is minimized in the "eclipsed" conformation, and the attraction between methyl occupied π group orbitals and alkene π^* orbitals are maximized. Although the language is quite different, the origin of the preferred conformation is the same in both representations.

Returning to Figure 4, it is clear that the torsional repulsions between methyl orbitals and alkene orbitals (σ and π) cause pyramidalization. That is, pyramidalization causes rotation of all three localized ("banana") orbitals of the alkene carbons and reduction of all three pairs of partial eclipsings. We attribute the stabilization to reduction of closed-shell repulsion. We must, however, caution that this interpretation is related to the forever controversial question of the source of the rotational barrier in ethane.[24-26] The explanation of this fundamental effect has been narrowed down to two viewpoints: (1) the eclipsed conformation is destabilized by four-electron repulsions (closed-shell overlap repulsion arising from the Pauli exclusion principle) between vicinal bonds, which have greater overlap in the eclipsed conformation,[24] or (2) the staggered conformation is more stabilized by the anti-periplanar arrangement of six σ_{CH} orbitals with respect to six σ^*_{CH} orbitals. In the eclipsed conformations, these overlaps are of the smaller syn-periplanar variety.[25,26] As a third alternative, both of these effects may contribute to some extent.[26] Whatever the mix of $\sigma-\sigma$ and $\sigma-\sigma^*$ interactions which make the staggered conformation of ethane more stable, a similar blend causes asymmetric alkenes to pyramidalize. That is, closed-shell repulsion between the bond orbitals to the alkene center (two σ's and one π) and the three σ orbitals to the allylic carbon are relieved in the pyramidalized structure, and filled–vacant vicinal orbital interactions may be increased as well.

Electron Donation, Strain, and Pyramidalization. Why are the alkene carbons in *syn*-sesquinorbornene three to four times more pyramidal than those in norbornene? Aside from the relief of eclipsing strain which occurs around four bonds in *syn*-sesquinorbornene as opposed to only two in norbornene, there are two other general effects which promote this pyramidalization.

In our communication on pyramidalization,[3] we showed that electron donors on the trigonal carbons promote this distortion. This can be most easily rationalized as a result of the increase in negative charge in the π system which makes the trigonal carbon
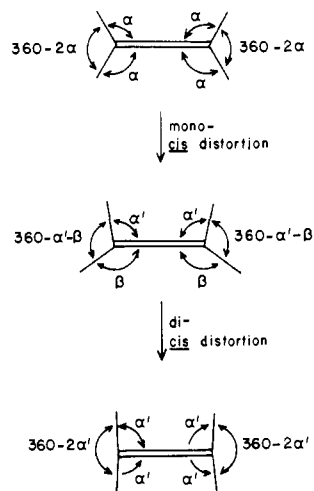

Figure 6. Angle relationships for cis distortions of alkenes in planar geometries.
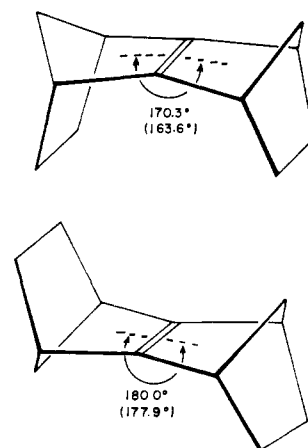

Figure 7. Dihedral angles in STO-3G optimized structures of *syn*- and *anti*-sesquinorbornenes. The CH bond lengths were fixed at 1.09 Å. Experimental values from anhydride derivative[9] are given in parentheses

more carbanion-like, and lowers the out-of-plane bending force constants. On the other hand, electron-withdrawers produce carbocation character and increase out-of-plane bending force constants. Thus, the very electron-rich double bond of sesquinorbornene should have relatively low out-of-plane bending force constants.

Secondly, Wagner et al. have shown that cis angle strain in alkenes decreases out-of-plane bending force constants.[27] That is, by contracting the HCC angle of ethylene, out-of-plane bending becomes easier. Although this can be understood in MO terms as a result of the lowering of the σ^*_{CH} orbital energies upon distortion, with easier mixing of σ^*_{CH} into π as pyramidalization occurs, there is also a classical argument as to why this should be so. As shown in Figure 6, when a mono-cis distortion of an alkene occurs by forcing the normal angle, α, to become the smaller angle, α', as by incorporating an alkene in a relatively small ring, for example, in norbornene, the remaining angles, β and $360 - \alpha' - \beta$ can adjust to accommodate some of the strain. However, both of these angles will be larger than normal. A pyramidalization of the alkene carbons will decrease angles β and $360 - \alpha' - \beta$ for constant α', relieving angle bending strain. In the di-cis-distorted species, as in sesquinorbornene, all α's are small and $360 - 2\alpha'$ must be large. Out-of-plane bending can relieve this angle bending strain. The Wagner et al. calculations indicate that severe distortions of this type can produce spontaneous,

(22) Zimmerman, H. E. "Quantum Mechanics for Organic Chemists"; Academic Press: New York, 1975; pp 138–140.

(23) Mislow, K. "Introduction to Stereochemistry"; W. A. Benjamin: New York, 1966.

(24) Sovers, O. J.; Kern, C. W.; Pitzer, R. M.; Karplus, M. *J. Chem. Phys.* **1968**, *49*, 2592. Stevens, R. M.; Karplus, M. *J. Am. Chem. Soc.* **1972**, *94*, 5140. See also: Mulliken, R. S.; Ermler, W. C. "Polyatomic Molecules"; Academic Press: New York, 1981; pp 182–184.

(25) Brunck, T. K.; Weinhold, F. *J. Am. Chem. Soc.* **1979**, *101*, 1700.

(26) Lowe, J. P. *J. Am. Chem. Soc.* **1970**, *92*, 3799.

(27) Wagner, H.-U.; Szeimies, G.; Chandrasekhar, J.; Schleyer, P. v. R.; Pople, J. A.; Binkley, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 1210.
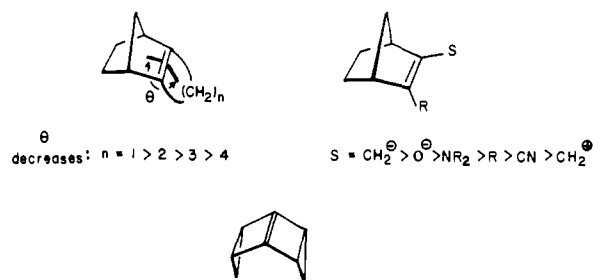
Figure 8. Some alkenes which should have highly pyramidal alkene carbons.

nontorsionally driven, pyramidalization, as in bicyclo[2.1.0]-pent-1(4)-ene.[27]

STO-3G Optimizations of Sesquinorbornenes. Ab initio calculations with the STO-3G basis set[28] were carried out to determine the out-of-plane bending force constants and investigate the electronic structures of the sesquinorbornenes. The GAUSSIAN 80 (Pople et al.) and GAUSSIAN 83 (Hehre et al.) programs were used.[43] The optimizations were performed with the CH bond lengths constrained to 1.09 Å, and the HCC angles for the CH_2 groups were fixed at values obtained from the norbornene optimization.[2,3] All other bond lengths and angles were optimized. The optimized bending angles of *syn*- and *anti*-sesquinorbornenes are given in Figure 7 and are compared with these experimental structural parameters obtained from the X-ray crystal structures of the anhydride derivatives.[9] The alkene pyramidalization is only 9.7° instead of the 16° observed experimentally for the syn isomer. This may arise from the overestimation of force constants by about 20–30% in STO-3G calculations,[28] so that the folding about the alkene is unrealistically difficult in the STO-3G calculations.

The harmonic force constants for the out-of-plane bending in *syn*- and *anti*-sesquinorbornene and in ethylene were estimated from the STO-3G calculations in the following way. For each molecule, the energy required to bend 1° in either direction about the double bond (from the equilibrium value) was calculated with all other parameters held constant.

For *syn*-sesquinorbornene, a change in out-of-plane bending by 1° increases the energy by an averge of 15 cal/mol. A 1% bend away from planarity for *anti*-sesquinorbornene results in a 13-cal/mol energy increase. The corresponding distortion in tetramethylethylene results in a 19-cal/mol increase in energy. Thus, *syn*- and *anti*-sesquinorbornene have similar out-of-plane bending force constants, and both are smaller than that of tetramethylethylene owing to the di-cis distortion of the sesquinorbornenes.

These considerations lead to predictions about where large pyramidalization will be observed. The degree of pyramidalization increases with (a) electron-richness of the double bond, (b) cis-angle contraction, and (c) torsional asymmetry. Norbornene has all three of these effects to some extent, and they are highly exaggerated in *syn*-sesquinorbornene. Other systems shown in Figure 8 should also be strongly pyramidalized. Thus norbornene fused to small rings should be highly pyramidalized, donors on the alkene carbon should increase pyramidalization, and the *syn*-sesquibicyclo[2.1.0]pent-2-ene should be highly bent, since bicyclo[2.1.0]pent-2-ene is already pyramidalized by 4.5°.

The π Bond in *syn*-Sesquinorbornene. The pyramidalization of *syn*-sesquinorbornene, and of norbornene to a lesser extent, has led to the postulate that rehybridization of the alkene carbons causes an increase of HOMO electron density on the exo face.[10,14,15] This "nonequivalent orbital extension" in Fukui's terminology,[29] or "orbital distortion", in Liotta's parlance,[30] arises

from mixing of s orbitals into the π HOMO. However, the extent of this s mixing has been found to be extremely small in calculations performed by us and by Schleyer and Gleiter.[31,32] Nevertheless, the greater electron density on the exo face of norbornene has been suggested as the origin of the preferred exo attack in thermal reactions with norbornene.[32]

On the other hand, we have proposed that the exo face of norbornene is electron-rich owing to the anti-bonding interaction between the π orbital and the σ bonds to the ethano bridge in the HOMO.[33] In order to evaluate these alternatives, we have analyzed the HOMO of *syn*-sesquinorbornene in detail using the STO-3G coefficients obtained in the partially optimized structure, and the orbital plotting program described elsewhere.[34]

The HOMO's of *syn*-sesquinorbornene and norbornene are displayed in Figure 9.[9] In each case, the contour level is ±0.06 au. First, it is apparent that the distortion of the π orbitals is not pronounced. This is analyzed further below with the aid of two-dimensional contour maps. Secondly, mixing between σ orbitals of the bridges and the π orbitals is found. It is most pronounced for the bridgehead to ethano carbon bonds which nearly eclipse the 2p orbitals of the π bonds. The mixing in the HOMO's is antibonding between the π and these σ_{CC} orbitals. Furthermore, the negligible components at the bridgehead carbons reflect some constructive mixings with the σ^*_{CC} orbitals which is characteristic of hyperconjugative interactions;[34] i.e., the HOMO's may be described as $a\pi - b\sigma_{CC} + c\sigma^*_{CC}$ with $a > b > c$. The dominant influence of the C1–C7 and C4–C7 orbital mixing proposed by Fukui is not found here. Furthermore, the dramatic exo extension present in Fukui's plots are absent when a cross section perpendicular to the C1–C2–C3–C4 plan is taken. The contour diagram at the bottom of Figure 9 shows these features.

Figure 10a shows a cross section of the *syn*-sesquinorbornene HOMO with the top lobe corresponding to the exo face of the molecule.[35] Clearly, there is slightly greater extension of the orbital on the exo face, but the largest difference is in the sideways extension. The pyramidalization causes the 2p orbitals to tilt out on the exo face and to tilt in on the endo side. Figure 10b shows the same orbital, but with the coefficients due to atoms other than the alkene carbons (C-2 and C-7) deleted. There is a slight overall growth of the π orbital due to the removal of the antibonding interactions with the bridges. The effect is more significant for the endo lobe (Figure 9) so there is greater growth on the endo side. There is also a reduction in the difference in sideways extension of the exo and endo lobes of the HOMO. Figure 9c shows the effect of omitting s coefficients from Figure 9b. There is a clear increase in the endo lobe at the expense of the exo. This is the Fukui effect, but it can be seen to be quite small and influences mainly the large inner contours, rather than those smaller contours more distant from the nucleus which might be expected to have a more significant influence on bonding with attacking reagents.

Figure 10d shows a more dramatic change in the HOMO when the in-plane p_x orbitals which point along the C-2,C-7 internuclear axis are deleted from Figure 10b. Now, the tilting outwards of the π orbital on the exo face is eliminated, and it is even more obvious how little change is caused by the s orbital distortion effect, which is still present in Figure 10d. Only the innermost contours of the orbital are affected. For comparison of these drawings to calculations, the coefficients on the alkene carbons are: $2p_z =$

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(28) Newton, M. D.; Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1970**, *52*, 4064.

(29) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4057. "Orbital tilting" has recently been proposed as an explanation of norbornene exo reactivity: Ito, S.; Kakehi, A. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1869.

(30) Liotta, C. L. *Tetrahedron Lett.* **1975**, 523. Burgess, E. M.; Liotta, C. L. *J. Org. Chem.* **1981**, *46*, 1703.
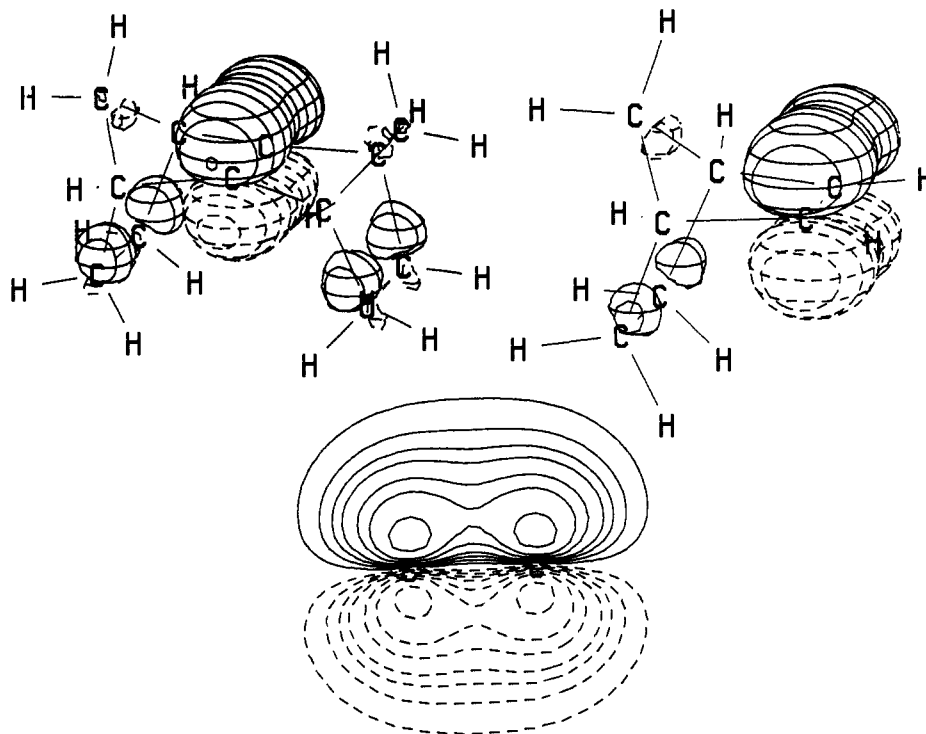
(31) P. v. R. Schleyer (Erlangen) and R. Gleiter (Heidelberg), unpublished results.

(32) Huisgen, R.; Ooms, P. H. J.; Mingin, M.; Allinger, N. L. *J. Am. Chem. Soc.* **1980**, *102*, 3951. Huisgen, R. *Pure Appl. Chem.* **1981**, *53*, 171.

(33) Houk, K. N. In "Stereochemistry and Reactivity of π Systems"; Watson, W. H., Ed.; Texas Christian University: Fort Worth, TX, 1983. Houk, K. N.; Rondan, N. G.; Brown, F. K. *Isr. J. Chem.*, in press.

(34) Jorgensen, W. L.; Salem, L. "The Organic Chemist's Book of Orbitals"; Academic Press: New York, 1973.

(35) Contour levels of ±0.01, ±0.02, ±0.04, ±0.08, ±0.12, ±0.16, and ±0.24 are plotted. This small difference can best be observed by making overhead transparencies of Figure 10 and superimposing the orbitals under discussion.

Figure 9. The STO-3G HOMO's of *syn*-sesquinorbornene and norbornene. The contour level shown is ±0.06 au. (Bottom): Contour plot of the norbornene HOMO in a plane perpendicular to the C1–C4 plane.
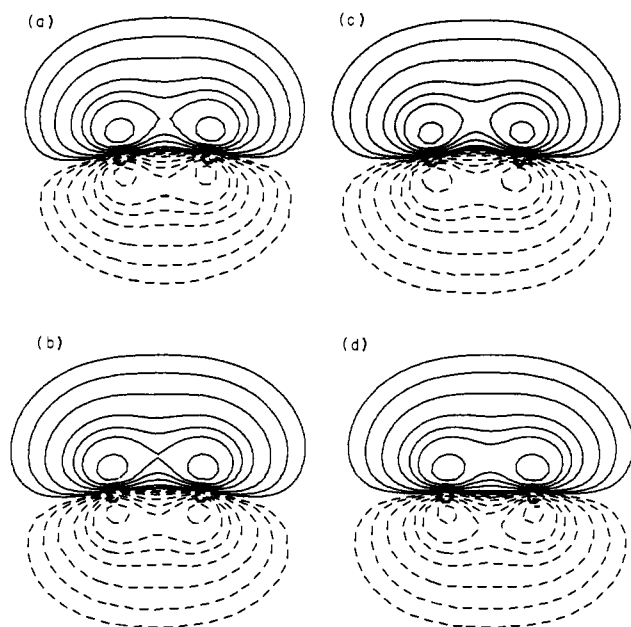

Figure 10. Contour cross sections of the *syn*-sesquinorbornene HOMO:[34] (a) full HOMO; (b) HOMO with only coefficients at C-2 and C-7 included; (c) HOMO as in (b), but with s coefficients deleted; (d) HOMO as in (b), but with p_x (in-plane p) coefficients deleted.

0.59; $2p_x$ = 0.062; 2s = 0.064, which would translate into ≈sp[99]!

We conclude that the orbital distortion due to s–p mixing, or nonequivalent orbital extension, in *syn*-sesquinorbornene is small, and surely chemically insignificant in itself. We cannot conceive that this tiny distortion should have any significant influence on reaction stereoselectivity. The splaying out of the p orbitals of the π bond on the exo face is possibly more significant, though still not pronounced.

Exo Reactivity of Norbornenes. What, then, is the cause of the stereoselective thermal reactions of norbornene and *syn*-sesquinorbornene from the exo face?

We have already proposed a solution to this problem for norbornene.[37] Figure 11 shows norbornene with striped lines added
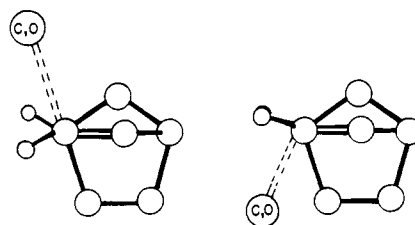

Figure 11. Trajectory of attack on exo and endo faces of norbornene and *syn*-sesquinorbornene.

from a hypothetical reagent, X, attacking from the exo and endo face. The direction of attack of the reagents is chosen from our previously described HCNO plus propene transition structure.[36] The direction of approach is appropriate for attack of 1,3-dipoles, dienes, and radicals, while electrophiles will have a more acute X—C=C angle and nucleophilic a more obtuse angle.[38] The alkene carbons undergoing attack have been pyramidalized to the extent suggested from the transition structure model, while the C=C bond length and the rest of the structure has been maintained at MM2-optimized values for the isolated reagent. Exo attack has a more nearly staggered arrangement of allylic bonds with respect to forming bonds, and the bonds to the alkene are more perfectly staggered with respect to the allylic bonds than for endo attack.

Although we and others have proposed that the bending of the alkene promotes exo attack,[2,3,14] it is actually the staggered arrangement in the transition structure which promotes exo attack.[36-38] The ground-state distortion is caused by relief of torsional strain, and the exo transition state is more stable because of the lower torsional strain present. That is, both ground-state and transition-state effects have the same origin and are always parallel.[36-38] It is correct to say that both phenomena have the same origin, but it is incorrect to say that transition-state effects

(36) Caramella, P. C.; Rondan, N. G.; Paddon-Row, M. N.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 2438.

(37) Rondan, N. G.; Paddon-Row, M. N.; Caramella, P.; Mareda, J.; Mueller, P.; Houk, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 4974.

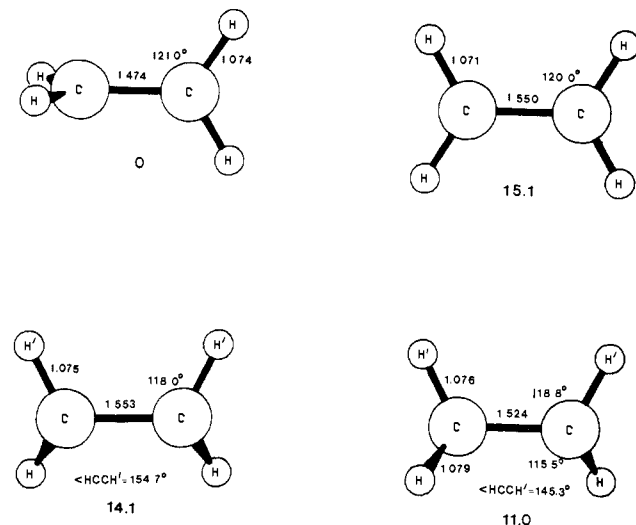(38) Paddon-Row, M. N.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 7162.

Figure 12. Ethylene triplet geometries (3-21G). Relative energies (kcal/mol) are given below each figure.

are caused by ground-state pyramidalization.

Triplet Photoreduction of *syn*-Sesquinorbornene and Geometries of Triplet States of Cyclic Alkenes. By contrast to the preferred exo attack of various reagents on *syn*-sesquinorbornene in thermal reactions to give **3**, Bartlett and co-workers recently reported that the irradiation of sesquinorbornene in acetone solution gives the reduction product **4**, resulting from the abstraction of hydrogen
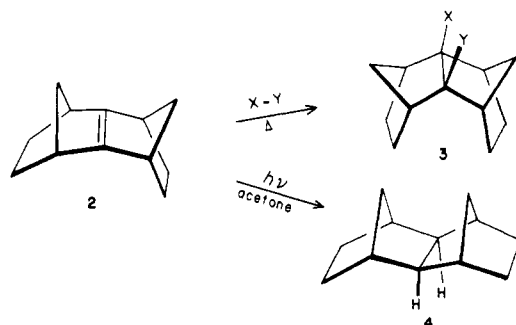
by the triplet excited *syn*-sesquinorbornene on the endo face.[16] Bartlett et al. suggested that the triplet state of **2** pyramidalizes in a direction opposite to that of the ground state, because of the repulsion between the singly occupied π* orbital of the ππ* excited triplet state and the endo hydrogens at C-4, 5, 9, and 10. There is no analogy for such an effect, however, and there is previous experimental evidence that simpler norbornenes abstract hydrogen and attack other alkenes from both the exo and endo faces,[39] even though these same repulsive effects invoked by Bartlett would be present in simpler "mononorbornene" systems. Gleiter proposed that the exo-bent triplet is favored, as predicted by extended Hückel calculations.[15]

In order to determine the distortions present in triplet *syn*-sesquinorbornene as well as other cyclic alkenes, we have performed UHF ab initio STO-3G and 3-21G calculations on the triplet states of models for constrained alkenes such as **2**. These computations provide an explanation of the stereochemistry of the photochemical reactions of **2**, and also provide new insights into the geometries of triplet states of other constrained alkenes.[40]

(39) Kropp, P. J. *J. Am. Chem. Soc.* **1969**, *91*, 5783; **1973**, *95*, 4611, and references therein.

(40) See, for example: Eaton, P. E. *Acc. Chem. Res.* **1968**, *1*, 50. Marshall, J. A. *Ibid.* **1969**, *2*, 33. Scheffer, J. R. *Ibid.* **1980**, *13*, 283. Padwa, A.; Blacklock, T. J.; Cordova, J. M.; Loza, R. *J. Am. Chem. Soc.* **1981**, *103*, 7202. Hixon, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1980**, *45*, 958, and references cited therein. Wexler, A. J.; Hyatt, J. A.; Reynolds, P. W.; Cottrell, C.; Swenton, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 512, describe the photochemistry of α,β-unsaturated ketone triplets which depend upon the rigidity of the triplet state.
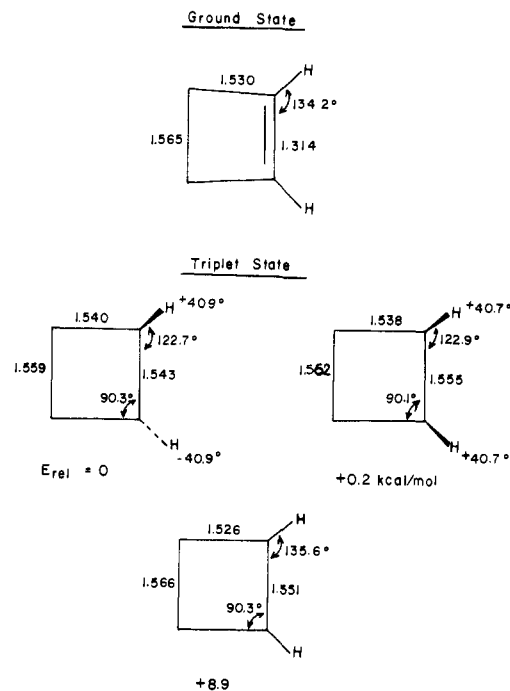
Figure 13. STO-3G ground state and optimized ππ* triplets of cyclobutene. A coplanar carbon skeleton was maintained in each optimization.
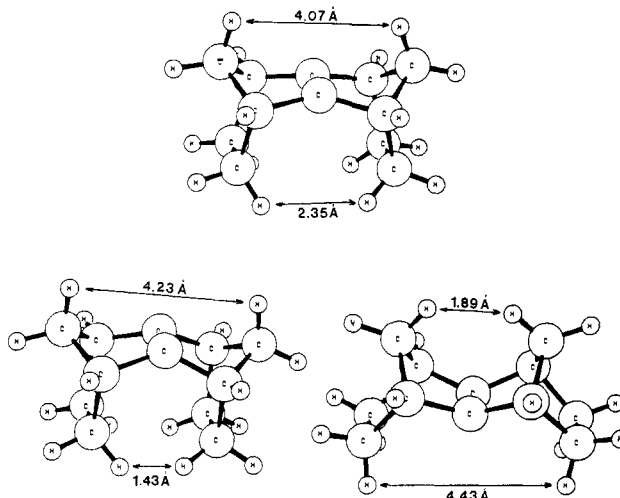

Figure 14. Ground state, endo-bent triplet state, and exo-bent triplet state of *syn*-sesquinorbornene.[18]

The relatively small basis sets chosen have been found to predict the energies and geometries of triplet alkenes quite satisfactorily. For example, the partial geometries and relative energies of planar and perpendicular optimized triplets of ethylene, obtained by Pople and co-workers at various computational levels,[41] are compared in Table II. The differences in CC bond lengths in these two species and the relative energies are quite well predicted at various Hartree–Fock levels. The energies of these species relative to the ground state are poorly predicted at the minimal basis level, but the largest error in the S–T gap is due to electron correlation (primarily of the ground state) rather than to basis set limitations.

Encouraged by these and other[42] comparisons, we performed geometry optimizations on triplet ethylene constrained so that two cis hydrogens were maintained in a plane. The GAUSSIAN 80 program with gradient searches for stationary points was used.[43]

(41) These results were obtained from the Carnegie-Mellon University Quantum Chemistry Archive implemented on the CMU VAX 11/780.

(42) The STO-3G basis set has been found suitable for the description of the triplet states of various conjugated alkenes: Ohmine, I.; Morokuma, K. *J. Chem. Phys.* **1980**, *73*, 1907; **1981**, *74*, 564. Sevin, A.; Bigot, B.; Pfau, M. *Helv. Chim. Acta* **1979**, *62*, 699.

Pyramidalization of Asymmetric Alkenes

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Table II. Comparisons of Optimized Planar and Perpendicular Ethylene Triplet Geometries and Energies (Pople et al.)[41]

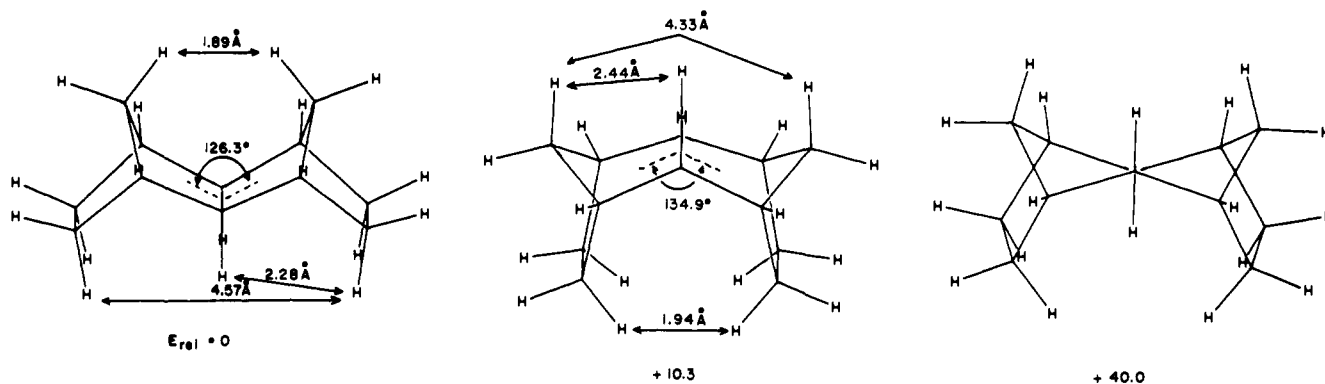| computational level//geometry	planar triplet (D_{2h})		perpendicular triplet (D_{2d})		ground state $(D_{2h}) E_{rel}$ (eV)
	r_{CC} (Å)	E_{rel} (kcal/mol)	r_{CC} (Å)	E_{rel} (kcal/mol)	
STO-3G//STO-3G	1.550	+14.4	1.488	$\equiv 0$	−1.56
3-21G//3-21G	1.550	+15.1	1.474	$\equiv 0$	−1.89
6-31G*//6-31G*	1.534	+14.7	1.469	$\equiv 0$	−1.83
6-31G**//6-31G*		+14.6		$\equiv 0$	−1.83
MP2/6-31G**//6-31G*		+17.6		$\equiv 0$	−2.93
MP4SDQ/6-31G**//6-31G*		+17.1		$\equiv 0$	−2.80

Figure 15. MM2 structures and relative energies of sesquinorbornanes.

The geometries and relative energies of the stationary points obtained with these constraints, with a planarity constraint, or with full optimization, are summarized in Figure 12.[43,44] Triplet ethylene prefers the perpendicular D_{2d} geometry.[45] However, when two hydrogens are constrained to lie in a plane, in order to mimic alkenes which cannot rotate because of incorporation into a relatively small ring, two minima are found. The lowest energy minimum is the trans-bent C_{2h} species, which is 3 kcal/mol lower in energy than the cis-bent C_{2v} species at both the STO-3G or 3-21G levels. The barrier of conversion of the trans-bent to the cis-bent triplet is 3.5 kcal/mol at the STO-3G level.

Thus, triplet alkenes which are incorporated into relatively small rings will pyramidalize, in order to reduce overlap between adjacent p or hybrid orbitals. This reduction of overlap lowers the energy of the singly occupied π^* orbital, which more than compensates for the destabilization of the singly occupied π orbital.[45,46] For molecules like cyclopentene and norbornene, which cannot rotate to a significant degree, the trans-bent triplet is expected to be most stable. This expectation was supported by model STO-3G calculations we carried out on triplet norbornene in which only the olefinic hydrogen angles were optimized. The trans-bent triplet is 6.7 kcal/mol lower in energy than the cis-bent triplet, while the endo-cis-bent triplet is 0.8 kcal/mol higher in energy than the exo-cis-bent triplet.

We have more thoroughly explored the geometries of cyclic *cis*-alkenes by full geometry optimizations of the ground and triplet excited states of cyclobutene. The geometries of the ground state, a triplet state in which the atoms attached to the alkene were forced to lie in a plane, and fully relaxed cis-bent and trans-bent cyclobutene triplets are shown in Figure 13. The lowest triplet

state is a trans-bent species which has the alkene hydrogens bent 40.9° out of the plane! This can be compared with the analogous 54.7° out-of-plane angle (30.3° dihedral angle) for a perfectly tetrahedral system! The cis-bent species also has the hydrogens 40.7° out-of-plane, and is only 0.2 kcal/mol higher in energy. By contrast, when the alkene hydrogens are kept in the plane, the triplet is 8.9 kcal/mol higher in energy. Thus, there is a strong driving force for pyramidalization of alkene carbons in the triplet, and a simple model for these species would consist of a single CC bond joining two tetrahedral carbons.

syn-Sesquinorbornene is even more constrained than norbornene or cyclobutene, and only the cis-bent triplet geometries are feasible. The crystal structures of derivatives of *syn*-sesquinorbornene[9] indicate that **2** has the endo hydrogens separated by only 2.5 Å. Further endo-bending in the triplet state should be difficult. As a rough guide to the amount of bending permitted in the triplet states, we constructed the models shown in Figure 14.[47] As suggested by the H–H distances in these models, the triplet can only be exo-bent.[47] The hydrogens with closest contacts are separated by 2.35, 1.89, and 1.43 Å in **2** and the exo-bent and endo-bent triplets, respectively, when the dihedral angle of the triplets is assumed to be 40° different from that of the ground state (16.2°). The net exo-bend of 23.8° brings the nearest hydrogens to a distance of 2.4 Å, the sum of the van der Waals radii of two hydrogens.[48] The preferred exo-bent triplet can only abstract hydrogen from the endo face, as observed by Bartlett et al.,[16] and we also predict that cycloadditions of the triplet of **2** to alkenes will occur on the endo face.[51]

By contrast, the triplet state of norbornene should abstract hydrogen, or undergo cycloadditions, from both the exo and endo faces, since it will be mainly the trans-bent species. Experimental observations are in qualtitative accord with this view.[39] Since we have shown above that the triplet states of alkenes resemble two tetrahedral carbons joined by a CC single bond, we can also approximate the relative energies of geometrically different triplets from calculations on the corresponding substituted hydrocarbons. Using MM2, we calculated the relative energies of exo-, endo-,

(43) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. GAUSSIAN 80, Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA 15213. Hout, R. F., Jr.; Francl, M. M.; Blurock, N.; Pietro, W. J.; Pollack, S. K.; DeFrees, D. J.; Levi, B. A.; Steckler, F.; Hehre, W. J. GAUSSIAN 83, Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN, to be submitted for publication.

(44) The methylenes of "perpendicular" triplet ethylene actually pyramidalize at the STO-3G level, to give a C_2 species which is 0.4 kcal/mol lower in energy than the D_{2d} triplet, but this pyramidalization disappears at the 3-21G and 6-31G levels.

(45) For a discussion of the various relaxation modes available to the states of ethylene, see: Devaquet, A. *J. Am. Chem. Soc.* **1972**, *94*, 5626.

(46) Merer, A. J.; Mulliken, R. S. *Chem. Rev.* **1969**, *69*, 639.

(47) The drawings of the exo- and endo-bent triplets were prepared starting from the geometry of *syn*-sesquinorbornene constructed from the crystal structure of the phenylsulfonyl derivative of **1**,[9] by substituting H for SO$_2$Ph. The models of the triplets are obtained by bending about the double bond in an exo or endo direction by 40°.

(48) Bondi, A. *J. Chem. Phys.* **1964**, *68*, 441.

and trans-reduced *syn*-sesquinorbornenes (or sesquinorbornanes), shown in Figure 15. As concluded above on the basis of non-bonded interaction, the endo-reduced species is considerably more stable than the exo.[49] Furthermore, the trans-bent species is so high in energy that the trans-bent triplet is clearly impossible for the *syn*-sesquinorbornene triplet.

The identification of pyramidalization without significant rotation of alkene triplets as a relaxation mechanism should bring new insight into the understanding of the transients formed in photochemistry of constrained species.[50]

Conclusions

syn-Sesquinorbornene, like norbornene, is pyramidalized to minimize torsional repulsions between alkene carbon orbitals and allylic bond orbitals. This pyramidalization causes tiny increases in the exo HOMO extension owing to both antibonding interactions with allylic endo σ orbitals and to sp mixing, but the outward tilting on the exo face is a more significant effect. Thermal exo additions occur to minimize torsional strain between the forming bonds and allylic bonds. Triplets of small ring alkenes pyramidalize nearly to sp^3 geometries. Both trans and cis isomers are formed, separated by a small barrier. *syn*-Sesquinorbornene can significantly pyramidalize only in an exo fashion, so only endo photoreduction is observed.

(49) After submission of this manuscript, crystal structures of several derivatives of an exo-bent derivative of sesquinorbornene were reported: Ermer, O.; Mason, S. A. *J. Chem. Soc., Chem. Commun.* **1983**, 53. The nearest hydrogen–hydrogen contacts, corresponding to that between H_{11en} and H_{12en} in **2**, are 1.713 and 1.754 Å in two derivatives. CFF and MM2 force fields predict 0.14–0.13-Å larger separation.

(50) See, for example, Bonneau, R. *J. Am. Chem. Soc.* **1980**, *102*, 3816. Bonneau, R.; Joussot-Dubien, J.; Salem, L.; Yarwood, A. J. *Ibid.* **1976**, *98*, 4329. Dauben, W. G.; van Riel, H. C. H. A.; Hauw, C.; Leroy, F.; Joussot-Dubien, J.; Bonneau, R. *Ibid.* **1979**, *101*, 1901. Dauben, W. G.; van Riel, H. C. H. A.; Robbins, J. D.; Wagner, G. J. *Ibid.* **1979**, *101*, 6383. Bonneau, R.; Jousset-Dubien, J.; Yarwood, J.; Pereyre, J. *Tetrahedron Lett.* **1977**, 235.

(51) **Note Added in Proof:** Optimization of the *syn*-sesquinorbornene triplet at the UHF STO-3G level with CH lengths fixed at 1.09 Å gives two minima, an exo-bent (by 44°) species and an endo-bent (by 32°) species which is 10.3 kcal/mol higher in energy.

(52) **Note Added in Proof:** A pyramidal *anti*-sesquinorbornene structure has been identified by X-ray crystallography: Ermer, O.; Bödecker, C.-D. *Helv. Chim. Acta* **1983**, *66*, 943. This is consistent with the easy deformation of the *anti*-2 sesquinorbornene predicted by MM2.

Intramolecular Excimer Emission of Poly(*N*-vinylcarbazole) and *rac*- and *meso*-2,4-Di-*N*-carbazolylpentane. Model Substances for Its Syndiotactic and Isotactic Dyads

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Abstract: The dimeric model compounds for isotactic and syndiotactic poly(*N*-vinylcarbazole) (PVK), *meso*- and *rac*-2,4-di-*N*-carbazolylpentane, have been prepared and have been found to exhibit the typical carbazole monomer emission together with excimer emission characteristic for each isomer. These meso and racemic excimer emission bands have been correlated with the 420- and 370-nm excimer emission bands found in PVK. New insight in the nature and formation of excimer states was obtained by additional studies of the steric microstructure of PVK. Data of the fluorescence kinetics, of NMR, and of the glass transition temperatures gave evidence that the 420- and 370-nm excimer emission bands derive independently from isotactic and syndiotactic PVK diads.

The photophysical properties of poly(*N*-vinylcarbazole) (PVK) have been the subject of intense study, partly with a view to gaining an insight into its photoconductive properties[1] and partly due to its unique photophysical properties. In contrast to other aromatic-containing polymers, no fluorescence emission from monomer-like moieties has been observed.[2,3] In solution the broad unstructured fluorescence is resolved into two peaks, which have been assigned to two spectrally distinct excimer species.[3–6] One of these, with a λ_{max} of 420 nm, has been attributed to a "sandwich-type" excimer formed between neighboring carbazole groups on the polymer chain in a totally eclipsed conformation[3]

and the other, with a λ_{max} of 380 nm, has been less well characterized, although Johnson[3] has suggested a dimeric structure, with considerable deviation from coplanarity, of the carbazole rings. Itaya et al.[6] on the other hand, have proposed a structure with only one eclipsed aromatic ring from each group.

(1) Penwell, R. C.; Ganguly, B. N.; Smith, T. W. *Macromol. Rev.* **1978**, *13*, 63.
(2) Kloepffer, W. *J. Chem. Phys.* **1969**, *50*, 2337.
(3) Johnson, G. E. *J. Chem. Phys.* **1975**, *62*, 4697.
(4) Ghiggino, K. P.; Wright, R. D.; Phillips, D. *Eur. Polym. J.* **1978**, *14*, 567.
(5) Hoyle, C. E.; Et al. *Macromolecules* **1978**, *11*, 429.
(6) Itaya, A.; Okamoto, K.; Kusabayashi, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2082.

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