The Influence of Heteroatoms on the Extent of Double Bond Pyramidalization

Hatice Can,[a] Dirk Zahn,[a] Metin Balci,*[c] and Jürgen Brickmann*[a]

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The origin of double bond pyramidalization in the series of norbornene and norbornadiene derivatives and the effect of heteroatoms on the magnitude of the double bond bending are reported. For this purpose, equilibrium geometries, vibrational frequencies, and NBO second-order perturbation energies were calculated by use of B3LYP/6-31G** level wave functions. The optimized geometric parameters calculated for norbornadiene are in good agreement with the available experimental results. NBO second-order perturbation analysis has been used to evaluate the effect of hyperconjugative interactions on double bond pyramidalization. In the second part of this study, the interaction of singlet oxygen with 4,5-dioxatetracyclo[6.6.1.$0^{2,7}$.$0^{9,14}$]pentadeca-2(7),9,11,13-tetraene (**15**) and 4,5,15-trioxatetracyclo[6.6.1.$0^{2,7}$.$0^{9,14}$]pentadeca-2(7),9,11,13-tetraene (**16**) has been studied at the B3LYP/6-31G** level. In the case of addition of singlet oxygen to **15**, 4,5,16-trioxapentacyclo[6.6.1.$1^{2,7}$.$0^{2,7}$.$0^{9,14}$]-hexadeca-9,11,13-triene (**17**) is produced. It was found that the reaction of singlet oxygen addition to the double bond in **16** does not occur. The degree of pyramidalization in this molecule is similar to the analog **12** {4,5,11-trioxatricyclo[6.2.1.$0^{2,7}$]undeca-2(7),9-diene}, in which singlet oxygen addition takes place. The reasons of the lack of chemical reactivity with singlet oxygen in **16** are discussed.
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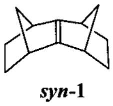
1. Introduction

A number of strained olefins that prefer non-planar structures have received extensive theoretical and experimental attention due to the fact that double bond pyramidalization plays an important role on the π-facial stereoselectivity in addition reactions. Remarkable exceptions are observed if double bonds are included in strained cyclic systems, in which cases considerable deviation from planarity of the double bond can occur.[1] As a consequence of the double bond pyramidalization, the two faces of double bond are no longer equivalent. This extraordinary geometrical feature causes the very noticeable π-facial stereoselectivity in addition reactions to carbon double bonds.[2–4] The degree of pyramidalization is influenced by the electron density of the alkenyl π-bond.[5]

Force-field and ab initio calculations on norbornene and norbornadiene show that the double bond in norbornene is slightly pyramidalized in the *endo* direction (out-of-plane angle of 7°).[5–9] Norbornadiene is bent to a smaller extent in the *endo* direction, the pyramidalization angle being approximately 2–4°.

The origin of the non-planarity of the double bond in norbornene and related systems has been the subject of intense investigations, and several explanations for alkene pyramidalization have been proposed. Houk[5] reported that the pyramidalization is caused by allylic torsional effects, in which the unsymmetrical arrangement of the three allylic bonds forces the alkene to pyramidalize. Gleiter et al.[10,11] interpreted the double bond pyramidalization in terms of hyperconjugative effects that gave rise to an exceptionally low *endo* out-of-plane deformation potential. Furthermore, Schleyer and Pople[12] performed computations on distorted ethylenes in which the H–C=C angle was constrained and suggested that the pyramidalization should be significantly influenced by *cis* angle strain.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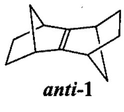
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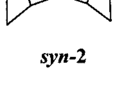
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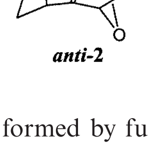
***anti*-2**

Sesquinorbornenes, which are formed by fusion of a second norbonyl skeleton onto the norbornene nucleus, have been investigated both experimentally and theoretically. While *syn*-sesquinorbornene ***syn*-1** has a significant double

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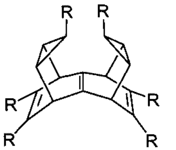
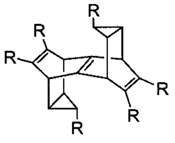
[a] Chemistry Department of Darmstadt University of Technology,
Petersenstr. 20, 64287 Darmstadt, Germany
Fax: (internat.) + 49-(0)6151/16-4298
E-mail: brick@pc.chemie.tu-darmstadt.de
[b] Mersin University,
Ciftlikkoy Kampusu, 33342 Mersin, Turkey
[c] Middle East Technical University,
06531 Ankara, Turkey

bond bending angle (a dihedral angle in the 162−164° range), a very low energy barrier to distortion of planarity is observed in *anti*-sesquinorbornene ***anti*-1**.[13] The 7,7′-dioxa analogues of *syn*- and *anti*-sesquinorbornenes ***syn*-2** and ***anti*-2** have been generated by pyrolytic decomposition of the corresponding β-lactones,[14] and their structures have been studied by variable-temperature photoelectron (PE) spectroscopy. Comparison of the calculated structures of ***syn*-2** and ***anti*-2** shows that their geometries do not differ significantly from those in ***syn*-1** and ***anti*-1**. Balci and his co-workers have intensively investigated the synthesis, structure analysis, and chemical properties of pyramidalized alkenes,[15] studying a series of compounds of structures ***syn*-3** and ***anti*-3**.

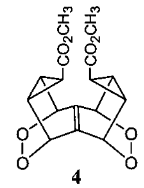


***syn*-3**



***anti*-3**

X-ray analysis results showed that the relevant pyramidalization angle varies between 16.4 and 19.9°, while *anti* isomers have a planar structure. Furthermore, they also showed that the double bond in ***syn*-3** does not undergo any chemical reaction in spite of the central double bond being highly pyramidalized. This lack of reactivity has been interpreted in terms of steric shielding of the double bond by the adjacent cyclopropane rings and substituents at the double bonds. More recently, the tetraoxa analogue **4** has been synthesized.[16]



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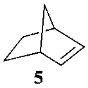
Here we report the pyramidalization properties of a series of compounds **5−12** with pyramidalized double bonds and the influence of heteroatoms on the extent of double bond pyramidalization. We also discuss the formation mechanism of the products formed by photooxygenation reaction of **13** and **14**.



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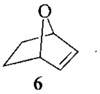

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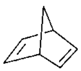

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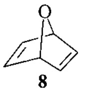

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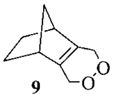

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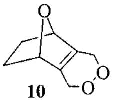

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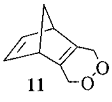

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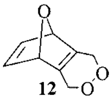

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2. Method

The use of ab initio methods employing a large basis set with the inclusion of electron correlation for reliable determination of the pyramidalization of strained alkenes has been demonstrated.[17] As an alternative to Hartree−Fock approaches, density functional theory (DFT) has been used to investigate pyramidalization features of strained olefins.[14b,17] Excellent agreement with experimentally determined values has been reported for DFT, especially with B3LYP hybrid functional calculations.[14b,16,17] Initial structures of all investigated compounds were created by the use of empirical force fields in the Sybyl 6 software package.[18] DFT calculations were performed by use of Gaussian 94[19−20] at the B3LYP/6-31G** level, full geometry optimizations being carried out for each compound studied. The accuracy of each minimization was checked by vibrational analysis, and the electronic structure was then analyzed by use of the natural bond orbital (NBO)[21−23] features in Gaussian 94. The partial charges were computed on the basis of the electrostatic-potential-derived charges model.

3. Results and Discussion

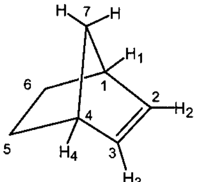
The geometries of **5** and **6** were calculated in order to determine the effect of the bridge oxygen atom on the degree of pyramidalization. The bond lengths, angles, and hyperconjugative stabilization energies estimated by NBO analysis discussed for **5** and **6** are listed in Tables 1 and 2.

Table 1. Geometric properties of **5** and **6**, calculated with B3LYP/6-31G** (bond lengths [Å], angles [°])

	5	**6**
Selected bond angles:		
C5−C4−C7	100.3644	−
C5−C4−O7	−	101.0665
C4−C3−C2	107.5074	105.2480
C1−C7−C4	93.6434	−
C1−O7−C4	−	96.0182
C4−C3−H3	124.7805	125.6761
$H7_{endo}$−C7−$H7_{exo}$	109.7034	−
C3−C4−C7	100.1924	−
C3−C4−O7	−	102.0653
C4−C3−C2−H2	−172.89	173.1783
C1−C2−C3−H3	172.8891	−173.1819
Selected bond lengths:		
C4−C3	1.5228	1.5250
C2−C3	1.3402	1.3360
C4−C5	1.5686	1.5656
C5−C6	1.5614	1.5575
C1−C7	1.5470	−
C1−O7	−	1.4390
C1−C2	1.5230	1.5250
C1−C6	1.5686	1.5656
Out-of-plane angle:		
between plane C1C2C3C4 and plane H2C2C3H3	7.14	6.82

Table 2. Predominant hyperconjugative interactions and their energies [kcal·mol^{-1}] estimated by NBO second-order perturbation theory for **5** and **6**

	5	**6**
σ(C4−C3) → σ*(C2−H2)	5.39	5.96
σ(C1−C2) → σ*(C3−H3)	5.39	5.96
σ(C1−C7) → σ*(C4−H4)	3.63	–
σ(C4−C7) → σ*(C1−H1)	3.63	–
lpO7 → σ*(C1−C2)	–	4.19
lpO7 → σ*(C4−C3)	–	4.19
lpO7 → σ*(C4−C5)	–	4.86
lpO7 → σ*(C1−C6)	–	4.86
π → σ*[C−C(H)]	22.69	24.57



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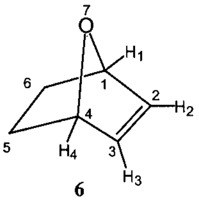

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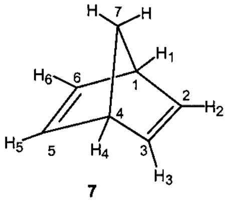
Predominant hyperconjugative interactions for norbornene molecule **5** involve electron transfer from the C1−C2/C4−C3 bonding orbitals through the double bond into the C3−H3/C2−H2 antibonding orbitals. Furthermore, interactions of the methylene bridge (C1−C7 and C4−C7) bonding orbitals and the antibonding orbitals of C4−H4 and C1−H1 are also taken into account. In norbornene, if the methylene bridge is replaced by an oxygen bridge to form **6**, the donor-acceptor stabilization energies for these interactions are slightly increased (Table 2). Donor-acceptor orbital interactions are also found between the oxygen atom lone pair electrons and the C−C bonds (C4−C3 and C1−C2) adjacent to the double bond.

Furthermore, the interactions between the σ(C7−C4) and σ(C7−C1) bonding orbitals and the low-lying σ*(C1−H1) and σ*(C4−H4) antibonding orbitals in **5** stabilize the molecule by 3.63 kcal·mol^{-1}. In molecule **6**, the lone pair donation from the oxygen atom to the formally unfilled σ*(C1−C2)/σ*(C4−C3) and the symmetrically equivalent σ*(C4−C5) and σ*(C1−C6) antibonding orbitals stabilizes the compound by 4.19 kcal·mol^{-1} and 4.86 kcal·mol^{-1}, respectively. Donation of lone pair electrons from the oxygen atom to the antibonding orbitals of the bonds (C4−C3 and C1−C2) adjacent to the double bond makes the double bond much stronger. The stabilization energies of these interactions confirm the strength of hyperconjugation (5.96 kcal·mol^{-1}). Qualitatively, it is understood that the hyperconjugation effect in compound **6**, resulting from the interaction between the lone pair electrons of the oxygen atom and the antibonding orbitals of C1−C2, C4−C3, C4−C5, and C1−C6 bonds, causes a shortening and strengthening of the C1−O7 and C4−O7 bonds (1.439 and 1.438 Å), which stabilizes the system. Furthermore, the double bond in **6** is shorter than in **5**. The out-of-plane bending of the double bond (the angle between the C1C2C3C4 and H2C2C3H3 planes) in **5** was found to be 7.14°. However, the degree of out-of-plane bending in **6** (6.82°) does not differ significantly from that in **5**. This small deviation can be attributed to the shortening of the double bond in **6**, it being well known that the stronger double bond is less susceptible to bending. The increased bending in **5** can also be related to torsional interactions between the hydrogen atom attached to C7 and the π-system. The distances between C7(O7) and the double bond carbon atoms are 2.355 and 2.304 Å in **5** and **6**, respectively. The larger distance between C7 and the double bond carbon atoms in **5** may be explained by torsional repulsion, which may assist slightly more bending of the double bond. Less pronounced hyperconjugative interactions in **5** and **6** are found between the π-system and the σ*(C4−C5) and σ*(C1−C6) orbitals (2.97 kcal·mol^{-1}). Although the interactions between the π-system and σ*(O7−C4) and σ*(O7−C1) occur in **6**, they are not observed in **5**. This may be one of the key interactions responsible for the mechanism of lesser degree of pyramidalization in **6**. The angle [C3−C4−C7(O7)] is larger in **6** than **5**. The π-system bonding orbitals favor coplanarity with the antibonding orbitals of σ*(O7−C4) and σ*(O7−C1), having strong interactions with them and yielding stabilization energies of 2.19 and 2.19 kcal·mol^{-1}, respectively.

In norbornadiene **7**, the presence of an additional double bond reduces the pyramidalization effect. The trend in the degree of pyramidalization (on going from the norbornene to the norbornadiene system) in **5** and **7** (7.14 and 3.85°, Table 3) is in good agreement with earlier calculations.[6,7][15a] This arises from new strong hyperconjugative interactions. In addition to σ(C1−C2) → σ*(C3−H3) and σ(C3−C4) → σ*(C2−H2) interactions, symmetrically and energetically equivalent extra interactions are found in **7** (Table 4). The corresponding stabilization energies are 5.61 kcal·mol^{-1} in **7** and 5.39 kcal·mol^{-1} in **5**. Since the relatively stronger hyperconjugative interactions involve the double bonds, the tendency towards double bond bending is diminished. In compound **8**, orbital interactions qualitatively similar to those in **7** are observed. However, lone pair electron donation from the oxygen atom to the antibonding orbitals of C4−C5, C4−C3, C1−C6, and C2−C1 is found. The main orbital interactions, namely σ(C1−C2) → σ*(C3−H3), σ(C1−C6) → σ*(C5−H5), σ(C3−C4) → σ*(C2−H2), and σ(C4−C5) → σ*(C6−H6), are stronger in **8** (6.13 kcal·mol^{-1}) than in **7** (5.61 kcal·mol^{-1}). Since the main interactions take place through the double bonds, this makes the double bond in **8** shorter and less susceptible to bending. Anyway, a slightly higher pyramidalization angle in **8** is observed, this may be related to the interactions between the double bond orbitals and the antibonding orbitals of (C1−O7) and (C4−O7), which are not found in **7**.



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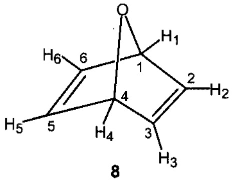

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Table 3. Geometric properties of **7** and **8**; calculated with B3LYP/6-31G** (bond lengths [Å], angles [°])

	7	**8**	**7** (Exp.[a])
Selected bond angles:			
C2–C1–C7	98.2920	–	98
C2–C1–O7	–	99.9921	
C1–C2–C3	107.1273	104.7716	108
C4–C7–C1	92.0620	–	92.2
C4–O7–C1	–	94.8325	
C1–C2–H2	124.6300	125.5693	123
H7–C7–H7′	110.6222	–	110
C3–C4–C7	98.2918	–	
C3–C4–O7	–	100.0072	
C4–C3–C2–H2	176.6614	176.1897	
C1–C2–C3–H3	176.6587	176.1435	
Selected bond lengths:			
C3–C4	1.5445	1.5513	1.533
C2–C3	1.3358	1.3318	1.339
C1–C2	1.5445	1.5518	1.533
C5–C6	1.3358	1.3317	
C1–C7	1.5600	–	1.571
C1–O7	–	1.4416	
C4–C5	1.5445	1.5509	
C1–C6	1.5445	1.5518	
Out-of-plane angle:			
between plane C1C2C3C4 and plane H2C2C3H4	3.29	3.85	

[a] E. E. Burnell, P. Diehl, *Canadian J. Chem.* **1972**, *50*, 3566–3568.

Table 4. Predominant hyperconjugative interactions and their energies [kcal·mol^{-1}] estimated by NBO second-order perturbation theory for **7** and **8**

	7	**8**
σ(C4–C3) → σ*(C2–H2)	5.61	6.13
σ(C1–C2) → σ*(C3–H3)	5.61	6.13
σ(C4–C5) → σ*(C6–H6)	5.61	6.13
σ(C6–C1) → σ*(C5–H5)	5.61	6.13
σ(C7–C4) → σ*(C1–H1)	3.63	–
σ(C7–C1) → σ*(C4–H4)	3.63	–
lpO7 → σ*(C1–C2)	–	4.37
lpO7 → σ*(C4–C3)	–	4.37
lpO7 → σ*(C1–C6)	–	4.37
lpO7 → σ*(C4–C5)	–	4.37
π → σ*[C–C(H)]	19.74	20.88

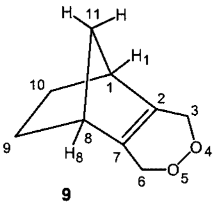
The double bond in compound **9** has a larger bending angle (with respect to **5**) of 9.46°. The extra ring formed by a peroxide bridge and two carbon atoms makes the compound sterically more bulky than the molecules described before. Predominant hyperconjugative orbital interactions through the double bond – σ(C8–C7) → σ*(C2–C3) and σ(C1–C2) → σ*(C7–C6) – and donation from the lone pair of O4 to σ*(C3–H3$_{exo}$) and from the lone pair of O5 to σ*(C6–H6$_{exo}$) stabilize the system by 5.62, 5.51, 5.67, and 5.51 kcal·mol^{-1}, respectively. One of the consequences of these interactions is the shortening of the double bond. These interactions occur in **10**, but their energy values (in the same order) are 6.12, 6.02, 5.61, and 5.31 kcal·mol^{-1}. From this, the shorter double bond in **10** than in **9** can be explained (Table 5). The total stabilization energy of interactions of the double bond as a donor with the rest of the molecule is 39.33 kcal·mol^{-1} in **9** and 43.18 kcal·mol^{-1} in **10** (Table 6). The analogous energies in **5** and **6** are 22.69 and 24.57 kcal·mol^{-1}, respectively. The stronger donor-acceptor interactions between the π-system and the rest of the molecule in **9** and **10** stem from the fusion of the peroxide bridge (O4–O5 bond), which may cause more pyramidalization of the double bond by withdrawing electrons from the double bond.

Table 5. Geometric properties of **9** and **10**, calculated with B3LYP/6-31G** (bond lengths [Å], angles [°])

	9	**10**
Selected bond angles:		
C9–C8–C11	100.3494	–
C9–C8–O11	–	101.0794
C8–C7–C2	107.6456	105.3778
C1–C11–C8	93.9552	–
C1–O11–C8	–	96.4478
C8–C7–C6	130.4108	132.4108
H11$_{endo}$–C11–H11$_{exo}$	109.7171	–
C7–C8–C11	99.8836	–
C7–C8–O11	–	101.6196
C8–C7–C2–C3	172.8782	187.3080
C1–C2–C7–C6	168.1625	191.8090
Selected bond lengths:		
C8–C7	1.5212	1.5240
C2–C7	1.3406	1.3368
C8–C9	1.5695	1.5655
C9–C10	1.5581	1.5581
C1–C11	1.5495	–
C1–O11	–	1.4404
C1–C2	1.5200	1.5230
C1–C10	1.5696	1.5651
Out-of-plane angle:		
between plane C1C2C7C8 and plane C2C3C6C7	9.46	9.70

Table 6. Predominant hyperconjugative interactions and their energies [kcal·mol^{-1}] estimated by NBO second-order perturbation theory for **9** and **10**

	9	**10**
σ(C8–C7) → σ*(C2–C3)	5.62	6.12
σ(C1–C2) → σ*(C7–C6)	5.51	6.02
lpO5 → σ*(C7–C6)	5.25	5.39
lpO5 → σ*(C6–H$_{exo}$)	5.51	5.31
lpO4 → σ*(C2–C3)	5.22	5.26
lpO4 → σ*(C3–H$_{exo}$)	5.67	5.61
σ(C6–H$_{exo}$) → σ*(O5–O4)	5.09	5.04
σ(C3–H$_{exo}$) → σ*(O5–O4)	5.28	5.29
π → σ*[C–C(H)]	39.33	43.18



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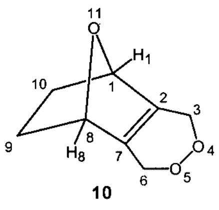

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A slightly increased degree of pyramidalization was observed for **10**, which has the largest bending angle in the series. On replacement of the methylene bridge in **9** with an oxygen atom, additional hyperconjugative interactions take place between the lone pair electrons of oxygen (O11) and the antibonding orbitals of the (C8−C9) and (C1−C10) bonds.

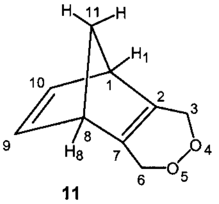
As observed in **7** and **8**, incorporation of an additional double bond causes the decrease of pyramidalization of the double bond in **11** and **12**. However, the bending of double bonds in **11** and **12** is larger than in **7** and **8**. It may be inferred that peroxide bridge withdraws the electrons from the double bond (Tables 7 and 8).

Table 7. Geometric properties of **11** and **12**, calculated with B3LYP/6-31G** (bond lengths [Å], angles [°])

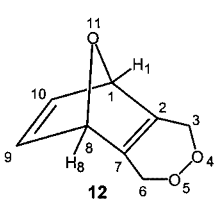
	11	**12**
Selected bond angles:		
C8−C7−C2	107.3031	105.0356
C9−C8−C11	98.2496	−
C9−C8−O11	−	99.9556
C8−C11−C1	92.3692	−
C8−O11−C1	−	95.3023
C8−C7−C6	131.0822	133.2638
$H11_{endo}$−C11−$H11_{exo}$	110.5760	−
C7−C8−C11	98.1162	−
C7−C8−O11	−	99.3390
C8−C7−C2−C3	183.8435	169.9183
C1−C2−C7−C6	171.4383	185.4450
Selected bond lengths:		
C8−C7	1.5411	1.5477
C2−C7	1.3358	1.3324
C8−C9	1.5470	1.5525
C9−C10	1.3362	1.3322
C1−C11	1.5627	−
C1−O11	−	1.4422
C1−C2	1.5404	1.5480
C1−C10	1.5463	1.5533
Out-of-plane angle:		
between the plane C1C2C7C8 and plane C2C3C6C7	6.48	7.03

Table 8. Predominant hyperconjugative interactions and their energies [kcal·mol^{-1}] estimated by NBO second-order perturbation theory for **11** and **12**

	11	**12**
σ(C8−C7) → σ*(C2−C3)	5.80	6.18
σ(C1−C2) → σ*(C7−C6)	5.71	6.27
σ(C1−C10) → σ*(C9−H9)	5.50	6.02
σ(C8−C9) → σ*(C10−H10)	5.51	6.04
lpO5 → σ*(C7−C6)	5.20	5.28
lpO5 → σ*(C6−H_{exo})	5.48	5.50
lpO4 → σ*(C2−C3)	5.27	5.33
lpO4 → σ*(C3−H_{exo})	5.51	5.26
σ(C6−H_{exo}') → σ*(O5−O4)	5.16	5.26
σ(C3−H_{exo}') → σ*(O5−O4)	5.22	5.09
π → σ*[C−C(H)]	38.39	39.75

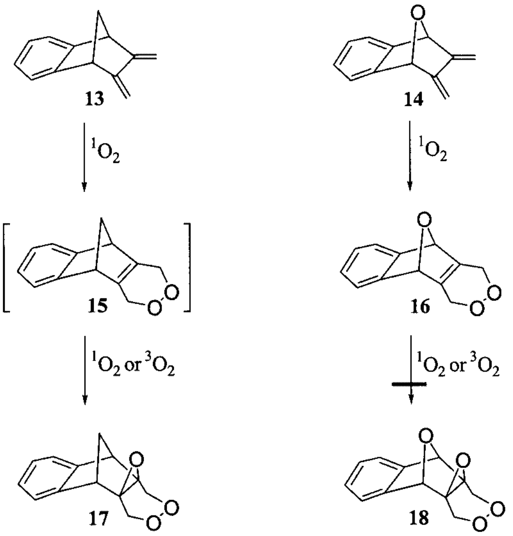


11



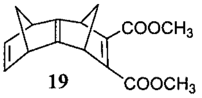
12

The second part of the work is a comparison of the addition reactions of singlet oxygen to the double bonds in pyramidalized olefins such as **15** and **16**. Recently, Atasoy et al. reported that treatment of 2,3-dimethylene-1,4-methano-1,2,3,4-tetrahydronaphthalene **13** with singlet oxygen results in the formation of epoxy endoperoxide **17** (Scheme 1).



Scheme 1

The expected intermediate, endoperoxide **15**, could not be isolated.[24] We assume that the reactivity of the double bond in **15** is very high, resulting in spontaneous formation of the epoxide **17** through reaction with singlet or triplet oxygen present in the reaction medium. A similar observation has been reported by Paquette and Carr,[25] who found that the central double bond in **19** reacts exothermally in air to give the corresponding *exo*-epoxide.



19

On the other hand, photooxygenation of **14** yields the isolable endoperoxide **16**.[26] Compound **12**, analogously to **16**, was also found to be more inert to oxygenation than **11**. On the basis of our calculations we have shown that the endoperoxides **11** and **12** have similar degrees of pyramidalization. We can now address the question of why the endoperoxide **16** does not undergo epoxidation, although the two compounds **15** and **16** also have similar degrees of pyramidalization.

We first calculated the energy differences in deoxygenation of **17** and **18**. The basis set superposition error was taken into account by use of the Counterpoise correction method. From our calculations, the oxygen bridge in **17** was found to be more stable than that in **18** by 0.2 kcal·mol^{-1}. This rather small difference surely cannot be responsible for the drastic contrast in the reactivities of **15** and **16**. Consequently, the activation energy to form the oxygen bridge might then be expected to be much larger for **16** than for **15**. We studied the inductive effect of replacement of the methyl bridge in **15** by an oxygen bridge as found in **16**. The change in partial charges on the carbon atoms forming the double bond was found to be only −0.05 e. Again, this effect should be too small to explain the stability of **16** against oxygenation. However, the two bridge fragments have significantly different partial charges, the charge on the bridge oxygen atom being about −0.4 while the total charge of the methyl bridge is roughly zero. Accordingly, we believe that the electrostatic repulsion between the lone pair electrons of the oxygen bridge in **16** and the nonbonding electrons of incoming molecular oxygen prevents the approach of singlet or triplet oxygen to form the epoxide ring.

4. Conclusion

The structural properties of norbonene and norbornadiene derivatives have been considered, in order to understand the influence of heteroatoms on the extent of the double bond pyramidalization. It is reported that the B3LYP/6-31G** DFT method excellently reflects the geometrical features of large strained olefins, as is evident from comparisons with experimental results. The magnitudes of double bond pyrimidalization in **5−12** are interpreted in terms of hyperconjugative interactions and geometrical parameters. The results reported offer a very consistent picture of the effects induced by the oxygen bridge or epoxide bridge on the double bond pyramidalization. Total hyperconjugative interaction energies between the double bond as a donor and the rest of the molecule as an acceptor excellently reflect the effect of the oxygen and peroxide bridge on the double bond bending tendency.

A large electrostatic repulsion between the lone pair electrons of singlet oxygen and the lone pair electrons of the oxygen bridge seems to prevent the production of **18** from **16**. Fusion of an epoxide bridge and two carbon atoms to the norbornene and norbornadiene increased the double bond pyramidalization.

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