JOC Article

Pyramidalized Olefins: A DFT Study of the Homosesquinorbornene and Sesquibicyclo[2.2.2]octene Nuclei†

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Density functional theory (B3LYP/6-31G*) was used to study a series of homosesquinorbornenes and sesquibicyclo[2.2.2]octenes. The compounds in which the two faces of the double bond are different are predicted to have a pyramidal double bond with butterfly bendings (ψ) ranging from 1.8 to 17.9°. The degree of pyramidalization of these central double bonds is greater in the homosesquinorbornenes than in the sesquibicyclo[2.2.2]octenes.

Introduction

In strained olefins of low symmetry, the two carbon atoms of the double bond and their four attached substituents tend to adopt a nonplanar conformation and are termed pyramidal olefins. Constraining the R−C═C bond angle (θ) to small values decreases the force constant for butterfly bending and for olefins in which the two faces of the double bond are different pyramidalization ($\phi > 0°$, $\psi > 0°$) results. Even for symmetrical systems a pyramidal ground state is favored provided θ is small enough, e.g., calculations on ethylene ($\theta < 100°$) predict a pyramidal ground-state geometry.[1] Due to the large disparity in the way in which the degree of pyramidalization is reported in the literature,[1] throughout this paper we use the dihedral angles 1−2−3−4 (D_1) and 5−3−2−6 (D_2), Figure 1, as a measure of the olefin pyramidalization. Dihedral angles may vary from −180° to +180° with a clockwise "rotation" representing the positive direction. All of the molecules studied in this work are of at least C_s symmetry with a mirror plane bisecting and perpendicular to the pyramidal double bond. Consequently, dihedral angles D_1 and D_2 are of equal magnitude and opposite sign and are related to the butterfly bending angle (ψ) by $\psi = 180° - |D_1|$.

Norbornene and its derivatives, especially those resulting from syn fusion of another norbornyl nucleus, e.g., *syn*-sesquinorbornene (**1**), have double bonds that are considerably pyramidalized in the *endo* direction.[1,2] The double bonds in bicyclo[2.2.2]octadienes are similarly pyramidal, but, in contrast with the norbornenes, the butterfly bending is in the *exo* direction and the degree of pyramidalization is somewhat less.[3−5] In comparison with the sesquinorbornenes,[2] there are few structural studies of compounds with a bicyclo[2.2.2]octyl unit fused to the bicyclo[2.2.2]octene nucleus, sesquibicyclo[2.2.2]-octenes, or the norbornene nucleus, homosesquinorbornenes. X-ray crystallography revealed that the double bond of sesquibicyclo[2.2.2]octene (**2**) and a symmetrically cage-substituted derivative, not surprisingly in light of their symmetry, are planar.[6] Balci et al. carried out detailed investigations on both *syn*- and *anti*-cyclopropannelated derivatives of **2** along with some peroxy analogues and reported experimental and calculated structural parameters for compounds **3**−**10**.[7−10] Experimental pyramidalizations ranged from $\psi = 0°$ for the symmetrical **3** to $D_1 = -160.42°$ and $D_2 = 164.61°$ for **5**, determined from the coordinates deposited with the Cambridge Crystallographic Data Centre (CCDC) for the asymmetric crystalline compound.

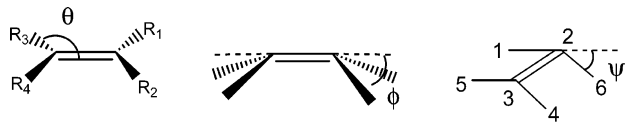

FIGURE 1. Definition of the pyramidalization parameters.

† Dedicated to Professor Reginald H. Mitchell on the occasion of his 60th birthday.

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|| University of Idaho.

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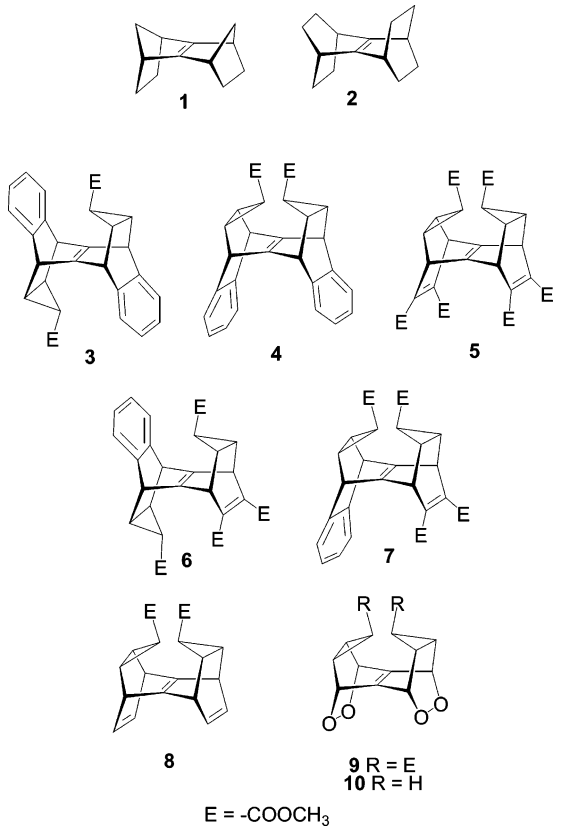
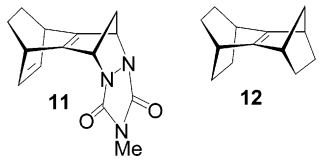


We are only aware of two structural studies on homosesquinorbornenes. Paquette et al. obtained an X-ray structure on the heteroatom-substituted homosesquinorbornene derivative **11**.[11] From the coordinates deposited with the CCDC, we found bendings in the *endo* direction (to both bicycles) for the slightly asymmetric crystalline compound with $D_1 = -167.96°$ and $D_2 = 168.58°$. Calculations at the B3LYP/6-31G+* level on the parent homosesquinorbornene (**12**) by Nelsen and Reinhardt revealed a butterfly bending in the *endo* direction (to the norbornyl nucleus) of $\psi = 11.2°$.[12]



Most studies exploring the degree of pyramidalization of double bonds serving as the point of fusion of two (poly)cyclic ring systems have focused on increasing ring strain (usually associated with increased pyramidalization) by increasing unsaturation and/or decreasing the ring size of the (poly)cycles.[1] Frequently, the norbornenyl nucleus has been the starting point for these endeavors. Considering the dearth of structural studies on *expanded* simple sesquinorbornenes, e.g., sesquibicyclo[2.2.2]octenes, homosesquinorbornenes, and their heterocyclic congeners, and our continuing long-standing interests in bridged polycyclic systems and pyramidal olefins,[13] we decided to undertake a systematic theoretical investigation of these bicyclo[2.2.2]octene derivatives. Our goals were to determine the effect of the ring enlargement (from the bicyclo[2.2.1]heptenyl system) on the degree of pyramidalization in such systems and the result of pitting the *exo*-pyramidalization of the bicyclo[2.2.2]octadiene nucleus against the opposing *endo*-pyramidalization of the norbornenyl moiety in appropriate homosesquinorbornenes.

Results and Discussion

We and others have previously shown that density functional theory (DFT) using the B3LYP/6-31G* method gives results in excellent agreement with experimentally determined geometries for polycyclic systems with pyramidal double bonds.[3,18−20] To further confirm the appropriateness of this method for our present study, we optimized (B3LYP/6-31G*) the geometries of sesquibicyclo[2.2.2]octene (**2**) and the homosesquinorbornene derivative **11**. Comparison of our calculated results with those obtained by X-ray crystallography on **11**[11] (Table 1) immediately reveals the excellent agreement between the B3LYP/6-31G* and the experimental geometry. The maximum variation in C−C bond lengths between the calculated and X-ray structures is only ± 0.016 Å, and most importantly, the calculated and experimental pyramidalization of the central double bond, as measured by the $C_1C_2C_7C_6$ ($C_3C_2C_7C_8$) dihedral angles, agrees within ±0.4°. Similarly, the experimental and calculated N−N (±0.01 Å) and C−N (± 0.02 Å) bond lengths in **11** are in close accord with the experimental values. The experimental[6] and calculated structures for **2** are in reasonable agreement (Table 1). However, the calculated and crystallographic symmetry are quite different (D_{2h}, $P2(1)/n$). Currently, this discrepancy cannot be explained.

Now entirely confident in the reliability of the B3LYP/6-31G* method for our systems of interest, we used this method, as instituted in the Gaussian 98 suite of programs,[21] to calculate the structures of the homosesquinorbornenes **12**−**27** and the sesquibicyclo[2.2.2]-

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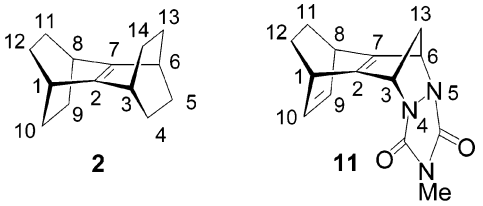
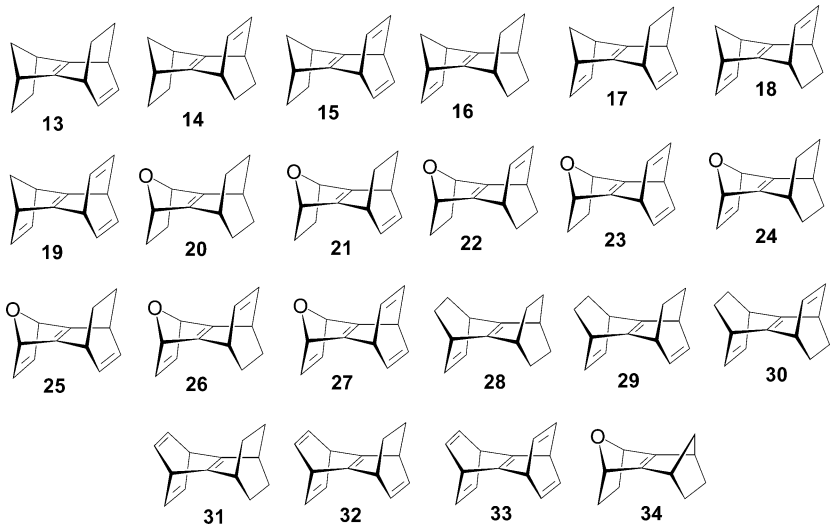
TABLE 1. Selected Experimental and Calculated Geometric Parameters for 2 and 11



	D_{2h}		C_s	
	2 (expt)[a]	**2** (calcd)[b]	**11** (expt)[c]	**11** (calcd)[b]
bond/Å				
1−2 (7−8)	1.502 (1.525)	1.508	1.510 (1.508)	1.509
2−3 (6−7)	1.524 (1.502)	1.508	1.509 (1.510)	1.517
3−4 (5−6)	1.526 (1.531)	1.557	1.517 (1.531)	1.511
4−5	1.536	1.558	1.458	1.448
2−7	1.328	1.345	1.331	1.347
8−9 (1−10)	1.524 (1.503)	1.557	1.535 (1.512)	1.531
9−10	1.545	1.558	1.321	1.337
1−12 (8−11)	1.531 (1.526)	1.557	1.570 (1.562)	1.579
11−12	1.536	1.558	1.555	1.555
6−13 (3−14)[d]	1.503 (1.523)	1.557		
6−13 (3−13)[e]			1.559 (1.524)	1.550
13−14[d]	1.547	1.558		
angle (deg)				
1−2−3 (6−7−8)	131.5 (131.4)	130.8	135.5 (136.3)	136.5
1−2−7 (8−7−2)	114.8 (113.7)	114.6	115.4 (114.2)	114.7
3−2−7 (6−7−2)	113.7 (114.8)	114.6	107.3 (108.2)	107.2
dihedral angle (deg)				
1−2−7−6 (3−2−7−8)	180.0 (180.0)	180.0	−168.0 (168.6)	−168.4
1−10−9−H9 (8−9−10−H10)[e]			−179.5 (−178.7)	−176.3
3−4−5−C=O (6−5−4−C=O)			125.97 (128.63)	131.9

[a] Reference 6 (from the coordinates deposited with the CCDC). [b] This study. [c] Reference 11 (from the coordinates deposited with the CCDC). [d] Compound **2** only. [e] Compound **11** only.

CHART 1



octenes **28**−**33** (Chart 1). The results of these calculations are summarized in Table 2. The excellent agreement between our calculated butterfly bending for **12** (Ψ = 10.5) and that of Nelsen and Reinhardt[12] using B3LYP/6-31G+* (ψ = 11.2) further supports our use of the B3LYP/6-31G* method in this study. Analytical energy second derivatives were calculated at all optimized structures to confirm that these are minima.

We recently reported the B3LYP/6-31G* butterfly bendings for *syn*-sesquinorbornene (**1**, ψ = 15.1°) and the corresponding oxa-bridged derivative **34** (ψ = 15.5°).[22] Replacing a methylene bridge in **1** and **34** with an ethano bridge to produce the corresponding homosesquinorbornenes **12** and **20** resulted in a decrease in butterfly bending by 4.8° and 5.2°, respectively. This decrease in pyramidalization is entirely consistent with the reduction in strain in going from the [2.2.1] to the [2.2.2] systems.[1] Similar to our previous findings[22] and those of Balci and Brickmann,[23] the pyramidalizations of the methano- (**12**−**19**) and corresponding oxa-bridged homosesquinor-

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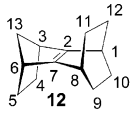
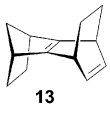
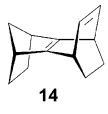
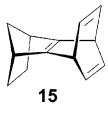
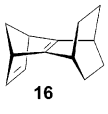
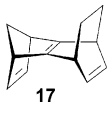
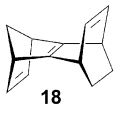
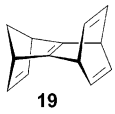
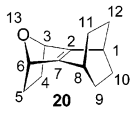
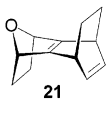
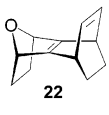
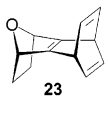
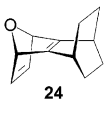
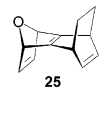
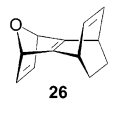
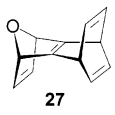
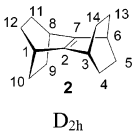
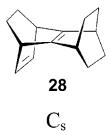
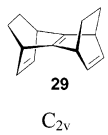
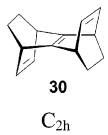
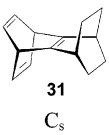
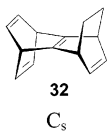
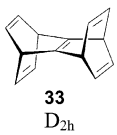
TABLE 2. Selected B3LYP/6-31G* Geometrical Parameters of Molecules 2, 12−19, and 20−33

	 **12**	 **13**	 **14**	 **15**	 **16**	 **17**	 **18**	 **19**
Angle /°	C_s	C_s	C_s	C_s	C_s	C_s	C_s	C_s
$C_3C_2C_7$	107.8	107.9	107.9	107.9	107.4	107.5	107.5	107.6
$C_1C_2C_7$	115.0	114.5	114.5	113.7	115.1	114.6	114.5	113.9
$C_1C_2C_3$	135.9	135.7	135.8	134.8	136.1	137.1	135.2	136.1
Ψ /°								
$C_1C_2C_7C_6$	10.5	12.7	12.4	17.9	10.4	7.1	15.5	14.5
$C_3C_4C_5H_4$	-	-	-	-	2.5	2.8	-	2.2
$C_1C_{10}C_9H_{10}$	-	4.5	-	2.3	-	4.4	1.9	2.0
$C_1C_{12}C_{11}H_{12}$	-	-	2.8	1.0	-	-	2.6	0.7
	 **20**	 **21**	 **22**	 **23**	 **24**	 **25**	 **26**	 **27**
Angle /°	C_s	C_s	C_s	C_s	C_s	C_s	C_s	C_s
$C_3C_2C_7$	105.5	105.6	105.6	105.6	105.1	105.2	105.1	105.2
$C_1C_2C_7$	115.2	114.7	114.7	113.8	115.3	114.8	114.7	113.9
$C_1C_2C_3$	138.0	137.6	137.8	136.4	137.7	138.8	136.6	137.3
Ψ /°								
$C_1C_2C_7C_6$	10.3	12.8	12.6	18.6	12.5	9.2	17.3	17.2
$C_3C_4C_5H_4$	-	-	-	-	3.0	3.5	2.3	2.6
$C_1C_{10}C_9H_{10}$	-	4.7	-	2.5	-	4.7	-	2.3
$C_1C_{12}C_{11}H_{12}$	-	-	2.9	0.9	-	-	2.6	0.9
	 **2**	 **28**	 **29**	 **30**	 **31**	 **32**	 **33**
Angle /°	D_{2h}	C_s	C_{2v}	C_{2h}	C_s	C_s	D_{2h}
$C_3C_2C_7$	114.6	114.2	114.3	114.3	113.4	113.5	113.7
$C_1C_2C_7$	114.6	114.6	114.3	114.3	114.9	114.4	113.7
$C_1C_2C_3$	130.8	131.0	131.1	131.4	131.4	131.3	132.6
Ψ /°							
$C_1C_2C_7C_6$	0.0	1.8	5.7	0.0	0.0	8.5	0.0
$C_3C_4C_5H_4$	-	-	3.1	-	-	3.1	0.6
$C_1C_{12}C_{11}H_{12}$	-	-	-	-	0.3	1.3	0.6
$C_1C_{10}C_9H_{10}$	-	3.1	3.1	3.5	0.3	0.4	0.6
$C_3C_{14}C_{13}H_{14}$	-	-	-	3.5	-	-	0.6

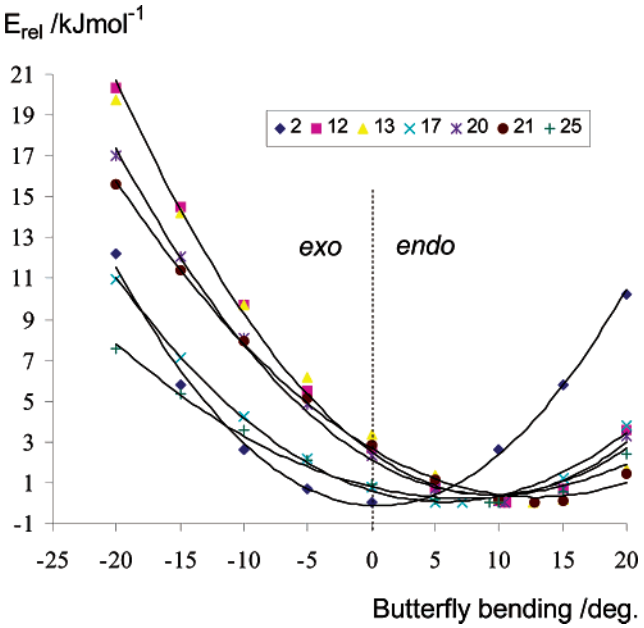


FIGURE 2. Torsional energy surfaces for molecules **2**, **12**, **13**, **17**, **20**, **21**, and **25**. Here, *exo*/*endo* = the direction of butterfly bending with respect to the bicyclo[2.2.1] nucleus. E_{rel} = total E (ψ°) − total E (optimized geometry).

bornenes (**20**−**27**) (Table 2) are little affected by substituting an oxygen bridge for the methylene bridge.

Of particular interest is the situation found in **13**, **17**, **21**, and **25** in which the *endo* bending of the norbornenyl nucleus is in opposition to the *exo* bending of the bicyclo[2.2.2] moiety. In these compounds, it is conceivable that a double minimum potential energy surface could result with minima corresponding to *endo* and *exo* (to the norbornenyl nucleus) bent structures. We were careful to investigate for this possibility and found in each case a single minimum surface (Figure 2) where the preferred *endo* bending of the norbornene completely dominated any tendency for *exo* bending by the [2.2.2] fragment. It is reasonable to anticipate greater pyramidalization in the homosesquinorbornenes where the butterfly bendings of the [2.2.1] and [2.2.2] components reinforce each other (as in **14**, **18**, **22**, and **26**) rather than oppose each other (as in **13**, **17**, **21**, and **25**). This expectation is realized for the homosesquinorbornatrienes where the butterfly bendings in **17** and **25** are approximately half of those in **18** and **26**. However, for the homosesquinorbornadienes, the degree of pyramidalization in **13** and **21** is very similar to that in **14** and **22**. The pyramidalizations in **14** and **22** are doubtless diminished by the steric interactions of the hydrogen atoms on their proximate [2.2.1]/[2.2.2] ethano bridges (H- - - H distances, 2.518 and 2.506 Å, respectively). This notion is supported by the fact that for the diene pairs **13**/**14** and **21**/**22**, **13** and **21** are slightly more stable (∼0.2 kJ/mol) than **14** and **22**, respectively.

Not surprisingly, the degree of pyramidalization predicted for the sesquibicyclo[2.2.2]octenes **28**, **29**, and **32** is significantly less than that calculated for the more strained homosesquinorbornenes **12**−**27**. As expected, on symmetry grounds, the sesquibicyclo[2.2.2]octenes **2**, **30**, **31**, and **33** are calculated to have a rigorously planar (ψ = 0°) central double bond. The diene **28** displays a modest pyramidalization (ψ = 1.8°) while both **29** and **32** are pyramidalized to a greater extent (ψ= 5.7 and 8.5°, respectively). In each of **28**, **29**, and **32** the butterfly bending is, as expected,[3−5] in the *exo* (to the bicyclo[2.2.2]-octadiene moiety) direction. The diminished pyramidalization in **28** is again attributed to the unfavorable steric interaction between the proximate ethano bridges (H- - - H distance, 3.139 Å). Although, **29** similarly suffers from this adverse interaction (H- - - H distance, 2.863 Å), the preferred *exo* butterfly bendings of each bicyclo[2.2.2]-octadiene unit in **29** are in concert resulting in a more pronounced pyramidalization. The maximum pyramidalization is found in tetraene **32** (ψ = 6.9°) where there is no destabilizing interaction between ethano bridges.

The stepwise torsional potentials for **2**, **12**, **13**, **17**, **20**, **21**, and **25** were investigated by scanning the butterfly bending angles between −20 and +20° (positive angle values correspond to *endo* bending with respect to the bicyclo[2.2.1]heptenyl nucleus) at the B3LYP/6-31G* level. All remaining geometrical parameters were optimized at each point of the scan. In each case, a single minimum surface results with the equilibrium geometry pyramidalized in the *endo* direction (to the [2.2.1] nucleus). Clearly, the more pronounced pyramidalizations of the [2.2.1] system overwhelm the lesser butterfly bendings found for bicyclo[2.2.2]octadienes.

Conclusions

The trend in the pyramidalizations found in the related series of fused polycycles is sesquinorbornenes > homosesquinorbornenes > sesquibicyclo[2.2.2]octenes and corresponds with the decreasing strain across the series. A factor influencing the degree of strain and the ease of pyramidalization is the C_B−C=C bond angle (C_B = bridgehead carbon). This angle uniformly increases from ∼105−108° in the sesquinorbornenes[22] to ∼108° for the [2.2.1] and ∼115° for the [2.2.2] nuclei in the homosesquinorbornenes and culminates at ∼115° for the sesquibicyclo[2.2.2]octenes. In the homosesquinorbornenes, including those in which the inherent pyramidalizations of the [2.2.1] and [2.2.2] rings are in opposition, the butterfly bendings are in the *endo* direction to the norbornenyl framework. All of the nonplanar sesquibicyclo-[2.2.2]octenes are bent in the *exo* direction to the bicyclo-[2.2.2]octadiene moiety. The unfavorable interaction between syn ethano bridges is found to significantly decrease the degree of pyramidalization.

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Supporting Information Available: Cartesian coordinates, selected geometric parameters, and total energies for all calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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