Exceptionally Pyramidalized Olefins: A Theoretical Study of the Cyclopropenyl Fused Tricycles Tricyclo[3.2.1.0^{2,4}]oct-2(4)-ene, Tricyclo[3.2.1.0^{2,4}]octa-2(4),6-diene, Tricyclo[3.2.2.0^{2,4}]non-2(4)-ene, and Tricyclo[3.2.2.0^{2,4}]nona-2(4),6-diene

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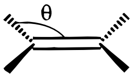
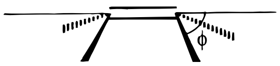
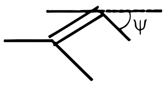
RHF, MP2, and TCSCF ab initio theory and B3LYP, B3PW91, and SVWN density functional theory were used to study the series of cyclopropenyl-fused tricycles **9**−**12**. In each of **9**−**12**, the cyclopropenyl double bond is exceptionally pyramidalized (butterfly angle ψ ~41−50°) with both endo and exo bent isomers. In the norbornyl systems (**9** and **10**), the endo bent isomers are more stable than the exo bent isomers, whereas in the bicyclo[2.2.2]octadiene **12** the reverse is true with the exo bent isomer being the low energy form. The activation barriers for the endo/exo interconversions are calculated to be relatively low ($\Delta H^{\ddagger}$ ~6−13 kcal/mol).

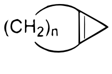
Introduction

It is well-known that strained olefins of low symmetry tend to be nonplanar.[1] Constraining the R−C═C bond angle (θ) to small angles favors pyramidalization ($\phi > 0°$, $\psi > 0°$) in olefins in which the two faces of the double bond are different.[1] Even for symmetrical systems, a pyramidal ground state is favored provided θ is small enough.[1] Theoretical calculations on ethylene ($\theta < 100°$) and the [n.1.0] bicycles **1** predict a pyramidal ground state geometry.[2] X-ray structure determination on **2**, a derivative of **1d**, revealed an essentially planar six-membered ring with a cyclopropenyl butterfly angle of $\psi = 17.6°$.[3]

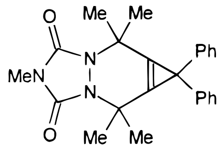








1a, n=1
1b, n=2
1c, n=3
1d, n=4



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The norbornene double bonds are pyramidal with deviations of the olefinic hydrogens, in the endo direction, by about 7° in norbornene (**3**) and about 2−4° in norbornadiene (**4**).[4−6] Fusion of a second norbornyl skeleton onto the norbornene nucleus, as in *syn*-sesquinorbornene (**5**), results in a significant increase in the butterfly bending (once again, in the endo direction).[6] The degree of pyramidalization observed by X-ray crystallography in derivatives of **5** is in the range $\psi = 16−18°$.[7] Introduction of additional unsaturation into **5** leads to even greater deformations[8] culminating in a butterfly bending of $\psi = 22.7°$ for **6**.[9] However, it should be noted that in *anti*-sesquinorbornene (**7**) the double bond is planar with a very low barrier to butterfly bending.[6,10] Due to this flat torsional energy surface, unsymmetrically substituted

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[1] For an excellent review of pyramidal alkenes, see: Borden, W. T. *Chem. Rev.* **1989**, *89*, 1095.

[2] Wagner, H.-U.; Szeimies, G.; Chandrasekhar, J.; Schleyer, P. v. R.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 1210.

[3] Ando, W.; Hanyu, Y.; Takata, T. *J. Am. Chem. Soc.* **1984**, *106*, 2216.

[4] Rondan, N. G.; Paddon-Row, M. N.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 2436, and references therein.

[5] Ermer, O.; Bell, P.; Mason, S. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1239.

[6] Holthausen, M. C.; Koch, W. *J. Phys. Chem.* **1993**, *97*, 10021.

[7] (a) Watson, W. H.; Galloy, J.; Bartlett, P. D.; Roof, A. A. M. *J. Am. Chem. Soc.* **1981**, *103*, 2022. (b) Hagenbuch, J.-P.; Vogel, P.; Pinkerton, A. A.; Schwarzenbach, D. *Helv. Chim. Acta* **1981**, *64*, 1818. (c) Paquette, L. A.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Bass, L. S.; Clardy, J. *J. Am. Chem. Soc.* **1983**, *105*, 3136. (d) Paquette, L. A.; Hayes, P. C.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Blount, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 3148. (e) Paquette, L. A.; Hsu, L.-Y.; Gallucci, J. C.; Korp, J. D.; Bernal, I.; Kravetz, T. M.; Hathaway, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 5743. (f) Paquette, L. A.; Kravetz, T. M.; Hsu, L.-Y. *J. Am. Chem. Soc.* **1985**, *107*, 6598.

[8] (a) Bartlett, P. D.; Combs, G. L., Jr. *J. Org. Chem.* **1984**, *49*, 625. (b) Paquette, L. A.; Green, K. E.; Gleiter, R.; Schäfer, W.; Gallucci, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 8232. (c) Paquette, L. A.; Künzer, H.; Green, K. E.; De Lucchi, O.; Licini, G.; Pasquato, L.; Valle, G. *J. Am. Chem. Soc.* **1986**, *108*, 3453.

[9] (a) Paquette, L. A.; Shen, C. C.; Krause, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2351. (b) Shen, C. C.; Paquette, L. A. *J. Am. Chem. Soc.* **1990**, *112*, 1159.

[10] Williams, R. V.; Edwards, W. D.; Gadgil, V. R.; Colvin, M. E.; Seidl, E. T.; van der Helm, D.; Hossain, M. B. *J. Org. Chem.* **1998**, *63*, 5268.

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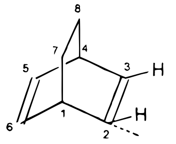
Table 1. Geometric Properties of 8 and 13 Calculated with the 6-31G* Basis Set and Selected Experimental Parameters[10] for 13[a]



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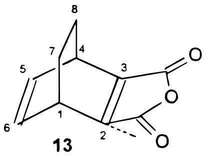

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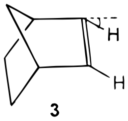
	HF	MP2	B3LYP	B3PW91	SVWN	HF	MP2	B3LYP	B3PW91	SVWN	expt
C_1C_2	1.521	1.511	1.521	1.516	1.502	1.502	1.488	1.499	1.493	1.477	1.496 (2)
C_2C_3	1.318	1.343	1.335	1.335	1.336	1.316	1.347	1.341	1.339	1.343	1.340 (2)
C_4C_5	1.521	1.511	1.521	1.516	1.502	1.527	1.517	1.529	1.523	1.509	1.340 (2)
C_4C_5	1.521	1.511	1.521	1.516	1.502	1.527	1.517	1.529	1.523	1.509	1.526 (2)
C_5C_6	1.318	1.343	1.335	1.335	1.336	1.320	1.345	1.336	1.335	1.337	1.350 (2)
C_1C_7	1.562	1.567	1.577	1.571	1.559	1.567	1.574	1.584	1.577	1.566	1.580 (2)
C_7C_8	1.549	1.543	1.551	1.544	1.530	1.553	1.546	1.554	1.547	1.533	1.519 (2)
$C_1C_7C_8$	108.6	108.8	108.7	108.8	109.0	109.5	109.8	109.6	109.7	110.0	110.0 (1)
$C_1C_2C_3$	113.8	113.6	113.8	113.8	113.8	115.3	115.2	115.3	115.2	115.3	114.8 (1)
ψ	2.3	3.1	2.7	2.7	3.1	2.6	3.4	3.0	3.0	3.4	
$\psi 2$						2.4	3.9	2.7	2.8	3.2	~3

[a] Distances are in angstroms and angles in degrees. ψ = butterfly bending angle (H substituted double bond). $\psi 2$ = butterfly bending angle (anhydride substituted double bond of **13**, $C_2{=}C_3$).

derivatives of **7** are pyramidal.[10,11] Similarly, we recently demonstrated, both by theory and experiment, that the double bonds in bicyclo[2.2.2]octadienes are pyramidal with a butterfly angle (ψ) for the parent hydrocarbon (**8**) of about 3°.[10,12] Similarly by X-ray crystallography, Chou et al. found an ~3.6° pyramidalization in a bicyclo[2.2.2]-octadiene derivative.[13] In contrast with the norbornenes, the olefinic out-of-plane bending in the bicyclo[2.2.2]-octadienes is in the exo direction. There has been much debate as to the origin of olefin pyramidalizations with most proposals falling into one of the two main categories of either torsional or hyperconjugative effects.[1,14] Holthausen and Koch concluded from a detailed analysis of their results on a variety of norbornenes that both hyperconjugation and torsional effects are important in determining the extent of olefin pyramidalization.[6]



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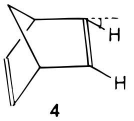

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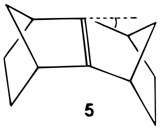

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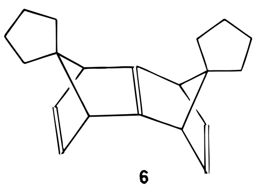

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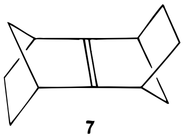

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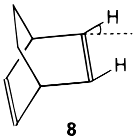

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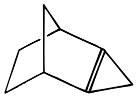
The recent syntheses of the cyclopropenyl tricycles tricyclo[$3.2.1.0^{2,4}$]oct-2(4)-ene (**9**),[15,16] tricyclo[$3.2.1.0^{2,4}$]-octa-2(4),6-diene (**10**),[16,17] and tricyclo[$3.2.2.0^{2,4}$]non-2(4)-ene (**11**)[18] and our continuing interest in pyramidal olefins[10,12,19−21] prompted us to initiate a theoretical investigation of these compounds and the related tricyclo-[$3.2.2.0^{2,4}$]nona-2(4),6-diene (**12**). A particularly interesting feature of this study is the determination of the ground state geometry of the highly symmetrical **11**. The two faces of the double bond in **11**, just as in *anti*-sesquinorbornene (**5**), are identical, and thus, on symmetry grounds, a planar geometry might be predicted. However, **11** is extremely ring strained,[18] perhaps sufficiently to favor a pyramidal geometry. In concurrence with Holthausen and Koch,[6] we found that ab initio methods employing a large basis set with the inclusion of electron correlation reliably predicted the pyramidalization in strained olefins.[10,20,21] We and others have also shown that density functional theory (DFT) may be used to successfully model such systems.[20−22] DFT predicts similar geometries, including pyramidalizations, to those observed by X-ray crystallography and neutron diffraction and calculated using correlated (MP2) ab initio methods.[20,21] In the present study, we reexamined the bicyclo[2.2.2]octadienes **8** and **13** using DFT methods (Tables 1 and 6). Once again, there is excellent agreement between each of the DFT, experimental, and MP2 results.[10]



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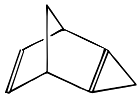

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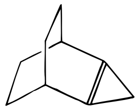

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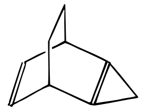

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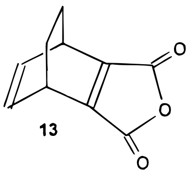

13

Results and Discussion

Initial geometries, which were further optimized using the Gaussian 94 and 98 suite of programs,[23] were

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[11] Ermer, O.; Bödecker, C.-D. *Helv. Chim. Acta* **1983**, *66*, 943.

[12] Williams, R. V.; Gadgil, V. R.; Garner, G. G.; Williams, J. D.; Vij, A. *Tetrahedron Lett.* **1999**, *40*, 2689.

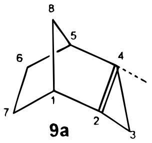
[13] Chou, T.-C.; Jiang, T.-S.; Hwang, J.-T.; Lin, K.-J.; Lin, C.-T. *J. Org. Chem.* **1999**, *64*, 4874.

[14] (a) Spanget-Larsen, J.; Gleiter, R. *Tetrahedron* **1983**, *39*, 3345. (b) Houk, K. N.; Rondan, G.; Brown, F. K.; Jorgensen, W. L.; Madura, J. D.; Spellmeyer, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 5980. (c) Houk, K. N. In *Stereochemistry and Reactivity of Systems Containing π Electrons*; Watson, W. H., Ed.; Verlag Chemie International: Deerfield Beach, 1983; p 1.

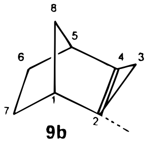
[15] Chenier, P. J.; Bauer, M. J.; Hodge, C. L. *J. Org. Chem.* **1992**, *57*, 5959.

[16] Lee, G.-A.; Huang, A. N.; Chen, C.-S.; Li, Y. C.; Jann, Y.-C. *J. Org. Chem.* **1997**, *62*, 3355.

Table 2. Geometric Properties of 9a and 9b Calculated with the 6-31G* Basis Set[a]



9a



9b

	HF	TCSCF	MP2	B3LYP	B3PW91	SVWN	HF	TCSCF	MP2	B3LYP	B3PW91	SVWN
C_1C_2	1.516	1.520	1.508	1.518	1.512	1.498	1.518	1.518	1.508	1.519	1.513	1.498
C_2C_3	1.495	1.496	1.508	1.509	1.503	1.495	1.492	1.493	1.504	1.505	1.500	1.492
C_2C_4	1.304	1.337	1.351	1.332	1.332	1.337	1.308	1.349	1.358	1.336	1.336	1.341
C_5C_6	1.554	1.551	1.556	1.565	1.559	1.545	1.546	1.546	1.546	1.556	1.550	1.537
C_6C_7	1.554	1.555	1.547	1.557	1.550	1.534	1.559	1.560	1.556	1.565	1.558	1.544
C_1C_8	1.547	1.547	1.546	1.555	1.549	1.536	1.558	1.553	1.557	1.567	1.560	1.548
$C_1C_8C_5$	94.7	94.4	94.7	94.6	94.7	95.0	94.0	94.2	94.1	93.9	94.0	94.3
$C_1C_2C_4$	108.7	107.9	107.8	108.3	108.2	108.0	108.7	107.8	107.8	108.3	108.2	108.1
C_2C_3C4	51.7	53.1	53.2	52.4	52.6	53.1	52.0	53.7	53.6	52.7	52.9	53.4
$C_3C_2C_4$	64.1	63.5	63.4	63.8	63.7	63.5	64.0	63.1	63.2	63.7	63.6	63.3
ψ	42.7	46.91	46.1	44.2	44.2	46.6	43.7	49.4	46.9	44.9	44.7	46.2

[a] Distances are in angstroms and angles in degrees. ψ = butterfly bending angle.

obtained using the SPARTAN programs.[24] Geometries for the exo and endo minima were optimized using a 6-31G* basis set with a series of quantum chemical methods. Hartree−Fock (HF), two-configuration HF (TCSCF), second-order Möller−Plesset perturbation theory with frozen core electrons (MP2), and DFT with a local functional SVWN (Slater exchange[25] with Vosko, Wilk, Nusair correlation[26]) as well as two nonlocal functionals: B3LYP (Becke 3-parameter hybrid exchange[27] with Lee−Yang−Parr correlation[28]) and B3PW91 (Becke three-parameter hybrid exchange[27] with Perdew−Wang 1991 gradient corrected correlation[29]). Analytical energy second derivatives were calculated at the HF- and B3LYP-optimized structures to confirm that these were minima. Additionally, transition state structures were optimized using HF and B3LYP and verified to be true first-order saddle points using analytic energy second derivatives. Even at the HF level of theory, each of **9**, **10**, **11**, and **12** exhibited considerable pyramidalization of the cyclopropenyl double bond (Tables 2−5). As previously observed, inclusion of electron correlation resulted in increased butterfly bending and is essential to obtain results in close agreement with experiment.[6,10,20,21] A fascinating result from our calculations is that, unlike the single minimum torsional energy surfaces found for **3**, **5**, **7**,[6] and **8**,[10] the tricycles **9**−**12** each have double minimum surfaces with both endo (**9**−**12a**) and exo (**9**−**12b**) bent optimized structures. The stepwise torsional potential for **9** was investigated by scanning the cyclopropene butterfly angle between −70 and +70° (positive angle values correspond to endo bending) at the RHF/6-31G* level. All remaining geometrical parameters were optimized at each point of the scan. The resulting potential curve (Figure 1) reveals that there are indeed two minima, **9a** with the cyclopropene bent in the endo direction (ψ =

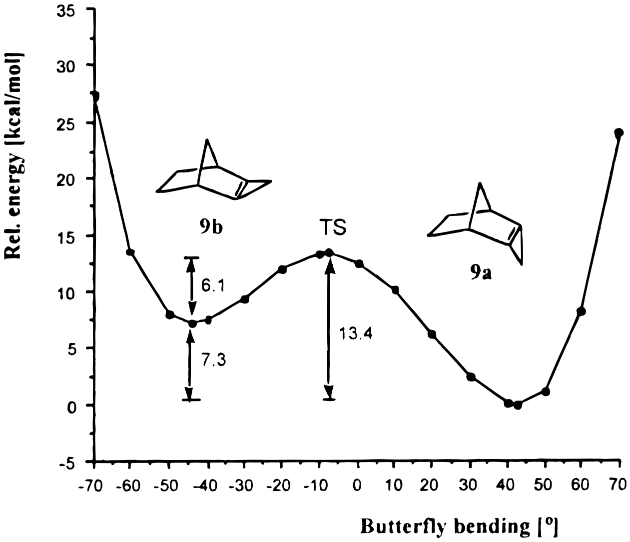


Figure 1. Torsional energy surface (HF/6-31G*) for **9a** and **9b**.

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(17) Mühlebach, M.; Neuenschwander, M. *Chimia* **1991**, *45*, 24.

(18) Chenier, P. J.; Southard, D. A., Jr. *J. Org. Chem.* **1990**, *55*, 4333.

(19) Williams, R. V.; Sung, C.-L. A.; Kurtz, H. A.; Harris, T. M. *Tetrahedron Lett.* **1988**, *29*, 19.

(20) Antol, I.; Eckert-Maksic, M.; Margetic, D.; Maksic, Z. B.; Kowski, K.; Rademacher, P. *Eur. J. Org. Chem.* **1998**, *1403*, 3.

(21) Margetic, D.; Warrener, R. N.; Tiekink, E. R. T. *Electronic Conference on Heterocyclic Chemistry '98*; Rzepa, H. S., Kappe, O., Eds.; Imperial College Press: London, 1998; Article 064, ISBN-981-02-3549-1; see also http://www.ch.ic.ac.uk/ectoc/echet98.

(22) Camps, P.; Font-Bardia, M.; Méndez, N.; Pérez, F.; Pujol, X.; Solans, X.; Vázquez, S.; Vilalta, M. *Tetrahedron* **1998**, *54*, 4679.

(23) Gaussian 94, Revisions B.3 and E.1: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1995. Gaussian 98, Revision A.4: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; W. Gill, P. M.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1998.

(24) Spartan v. 5.0, Wavefunction, Inc. 18401 Von Karman Avenue, Suite 370, Irvine, CA, 92612, 1997.

(25) Slater, J. C. *Quantum Theory of Molecules and Solids. Vol. 4: The Self-Consistent Field for Molecules and Solids*; McGraw-Hill: New York, 1974.

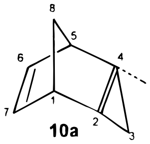
(26) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(27) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

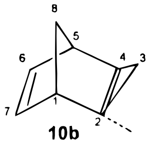
(28) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B 37*, 785. Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.

(29) Perdew, J. P. *Phys. Rev.* **1986**, *B 33*, 8822.

Table 3. Geometric Properties of 10a and 10b Calculated with the 6-31G* Basis Set[a]



10a

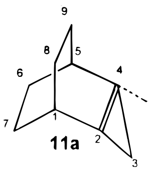


10b

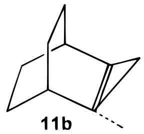
	HF	TCSCF	MP2	B3LYP	B3PW91	SVWN	HF	TCSCF	MP2	B3LYP	B3PW91	SVWN
C_1C_2	1.528	1.532	1.520	1.531	1.524	1.510	1.540	1.540	1.533	1.545	1.538	1.523
C_2C_3	1.492	1.493	1.505	1.507	1.501	1.493	1.494	1.496	1.508	1.509	1.503	1.495
C_2C_4	1.303	1.339	1.350	1.329	1.330	1.333	1.306	1.345	1.353	1.331	1.332	1.335
C_5C_6	1.546	1.540	1.541	1.552	1.546	1.535	1.526	1.527	1.518	1.529	1.524	1.512
C_6C_7	1.319	1.319	1.343	1.334	1.334	1.334	1.322	1.323	1.349	1.340	1.339	1.340
C_1C_8	1.556	1.555	1.557	1.566	1.559	1.547	1.562	1.557	1.563	1.572	1.565	1.552
$C_1C_8C_5$	93.1	93.0	93.3	93.0	93.2	93.5	92.8	92.9	93.1	92.8	93.0	93.3
$C_1C_2C_4$	108.2	107.4	107.5	108.0	107.9	107.7	108.1	107.3	107.4	107.8	107.8	107.6
C_2C_3C4	51.8	53.3	53.3	52.4	52.6	53.0	51.8	53.4	53.3	52.4	52.6	53.0
C_3C_2C4	64.1	63.4	63.4	63.8	63.7	63.5	64.1	63.3	63.3	63.8	63.7	63.5
ψ	43.0	47.3	46.1	44.1	44.1	45.8	45.1	49.7	47.5	46.1	46.0	47.4
$\psi2$	0.7	1.5	1.1	0.9	1.0	1.2	5.0	4.9	6.7	6.0	6.2	6.8

[a] Distances are in angstroms and angles in degrees. ψ = butterfly bending angle (cylopropene double bond, $C_2{=}C_4$). $\psi2$ = butterfly bending angle (norbornene double bond $C_6{=}C_7$).

Table 4. Geometric Properties of 11a/11b Calculated with the 6-31G* Basis Set[a]



11a



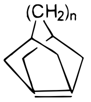
11b

	HF	TCSCF	MP2	B3LYP	B3PW91	SVWN
C_1C_2	1.499	1.502	1.488	1.498	1.492	1.477
C_2C_3	1.493	1.495	1.507	1.507	1.503	1.494
C_2C_4	1.296	1.329	1.341	1.323	1.323	1.329
C_5C_6	1.555	1.551	1.546	1.566	1.560	1.547
C_6C_7	1.554	1.554	1.546	1.555	1.548	1.533
C_1C_8	1.543	1.542	1.541	1.551	1.545	1.530
C_8C_9	1.559	1.558	1.555	1.564	1.557	1.542
$C_1C_8C_9$	110.6	110.5	110.6	110.6	110.7	110.8
$C_1C_2C_4$	116.8	115.8	115.9	116.4	116.3	116.1
$C_2C_3C_4$	51.4	52.8	52.8	52.1	52.2	52.8
C_3C_2C4	64.3	63.6	63.6	64.0	63.9	63.6
ψ	41.2	46.8	45.8	43.1	42.9	46.2

[a] Distances are in angstroms and angles in degrees. ψ = butterfly bending angle.

42.6°) and **9b** correspondingly bent in the exo direction ($\psi = 43.7°$). **9b** is computed to be less stable than the **9a** by 7.3 kcal/mol at RHF/6-31G*, 7.5 kcal/mol at MP2/6-31G*, and 7.0 kcal/mol at B3LYP/6-31G* (Table 6). The energy of the transition state, optimized independently of the stepwise potential (Figure 1), linking the two bent minima, **9a** and **9b**, is 13.4 kcal/mol at RHF/6-31G* (relative to **9a**) and corresponds to a structure possessing a butterfly bending of −10°.

The energy differences between the *endo*/*exo* bent forms **10a**/**10b** and **12a**/**12b** are much smaller than the corresponding differences for **9a**/**9b** and are computed, at all levels of theory, to be in the range 2.2−3.3 kcal/mol (Table 6). In agreement with our previous results,[10,12] the preferred mode of pyramidalization for the bicyclo[2.2.2]octadiene nucleus is in the exo direction with **12b** lower in energy than **12a** at all levels of theory examined (Δ = 2.2−3.3 kcal/mol). As expected from symmetry, **11a** and **11b** are degenerate and have exactly equivalent but complementary geometries. The degree of butterfly bending in **9**−**12** is similar, exceedingly large, and comparable to that calculated for **1a** ($\psi = 41.9°$ at MP2/6-31G*).[30] The butterfly angles (ψ) in **9**−**12** are some of the largest to be found for "untethered" pyramidalized olefins.[1,9b,30] Untethered olefins are considered to be those in which the pyramidalization is *not* assisted/induced by a constraining bridge such as the methylene bridges (tethers) in Borden's tricyclo[3.3.*n*.$0^{3,7}$]alk-3(7)-enes (**14**).[1]



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Despite the symmetry-based expectation that the double bond in **11** should be planar, it is significantly pyramidalized (MP2/6-31G*, $\psi = 45.8°$) in the degenerate ground states (**11a**/**11b**). The substantial ring strain (manifested in the highly constrained olefinic bond angles MP2/6-31G*, θ $C_2C_3C_4$ = 63.59°) in **11** presumably facilitates the observed pyramidalization.[1,2] Interconversion of **11a** and **11b** is predicted to be facile proceeding through a transition state with a planar double bond and an activation barrier (B3LYP/6-31G*) of only 6.41 kcal/mol (Table 7).

Our primary goal was to determine the degree of pyramidalization of the olefinic bonds in **9**−**12** and to compare the geometries obtained using the various quantum mechanical methods. The key structural parameters from each computational method are collected in Tables 1−5. Inspection of these tables reveals that the butterfly bendings (ψ) are the smallest for HF with the MP2 values significantly larger and those using the B3LYP and B3PW91 density functionals falling intermediate between HF and MP2. The SVWN functional yields ψ's similar to those obtained using MP2, and the TCSCF method results in the largest ψ's. There are only small variations between the HF, TCSCF, MP2, and DFT calculated saturated bond lengths and angles.

Hess, Schaad, Schaefer et al.[30] found that the inclusion of electron correlation in their calculations on **1a** using the MP2 method resulted in a gross overestimation of the olefinic bond length (HF/6-31G*, 1.344 Å; MP2/6-

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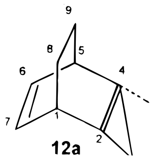
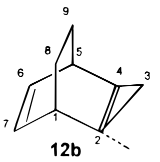
[30] Hess, B. A., Jr.; Allen, W. D.; Michalska, D.; Schaad, L. J.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1987**, *109*, 1615.

Table 5. Geometric Properties of 12a and 12b Calculated with the 6-31G* Basis Set[a]



12a



12b

	HF	TCSCF	MP2	B3LYP	B3PW91	SVWN	HF	TCSCF	MP2	B3LYP	B3PW91	SVWN
C_1C_2	1.502	1.507	1.492	1.502	1.496	1.480	1.508	1.512	1.499	1.509	1.502	1.487
C_2C_3	1.492	1.493	1.505	1.505	1.501	1.493	1.495	1.497	1.509	1.509	1.505	1.497
C_2C_4	1.296	1.330	1.340	1.322	1.322	1.326	1.295	1.327	1.338	1.321	1.321	1.325
C_5C_6	1.536	1.531	1.527	1.538	1.533	1.519	1.519	1.520	1.508	1.520	1.515	1.500
C_6C_7	1.320	1.320	1.344	1.336	1.335	1.336	1.322	1.323	1.349	1.340	1.339	1.340
C_1C_8	1.560	1.558	1.564	1.575	1.568	1.556	1.568	1.562	1.573	1.584	1.576	1.564
C_8C_9	1.557	1.557	1.551	1.559	1.552	1.537	1.551	1.552	1.541	1.550	1.543	1.527
$C_1C_8C_9$	109.9	109.7	110.1	109.9	110.0	110.3	109.9	109.8	110.1	110.0	110.1	110.3
$C_1C_2C_4$	116.1	115.1	115.5	115.9	115.9	115.8	116.0	115.1	115.4	115.7	115.7	115.7
$C_2C_3C_4$	51.5	52.9	52.9	52.1	52.3	52.8	51.3	52.6	52.6	51.9	52.5	52.6
C_3C_2C4	64.2	63.5	63.6	64.0	63.9	63.6	64.3	63.7	63.7	64.0	64.0	63.7
ψ	41.9	47.23	45.8	43.2	43.2	44.8	42.9	47.5	46.4	44.3	44.3	46.9
$\psi 2$	4.7	4.0	6.1	5.8	5.9	6.7	0.6	0.7	0.6	0.8	0.8	1.1

[a] Distances are in angstroms and angles in degrees. ψ = butterfly bending angle (cylopropene double bond, $C_2{=}C_4$). $\psi 2$ = butterfly bending angle (bicyclo[2.2.2]octene double bond, $C_6{=}C_7$).

Table 6. Total Energies (Hartrees) of 8−13

compd[a]	HF/6-31G*	MP2/6-31G*	B3LYP/6-31G*	B3PW91/6-31G*	SVWN/6-31G*
8	−308.715 889	−309.746 793	−310.818 763	−310.709 337	−309.056 448
9b	−308.600 683	−309.650 128	−310.717 458	−310.612 971	−308.966 178
9a	−308.612 341	−309.662 145	−310.728 620	−310.624 607	−308.979 827
Δ (kcal/mol)	7.316	7.541	7.004	7.302	8.565
10b	−307.396 560	−308.440 156	−309.472 207	−309.364 854	−307.711 791
10a	−307.401 711	−308.444 047	−309.476 387	−309.369 231	−307.716 416
Δ (kcal/mol)	3.232	2.442	2.623	2.747	2.902
11a/11b	−347.669 672	−348.847 814	−350.063 10	−349.447 20	−348.096 47
12a	−346.471 060	−347.642 062	−348.822 798	−348.701 702	−346.846 430
12b	−346.474608	−347.646683	−348.826620	−348.705566	−346.851 718
Δ (kcal/mol)	−2.226	−2.900	−2.398	−2.425	−3.319
13	−607.914194	−609.712884	−611.522387	−611.298560	−608.243 517

[a] Note: In the norbornyl systems endo bending is preferred, whereas in the bicyclo[2.2.2]octadienes exo bending is preferred. Δ = difference in energy (kcal/mol) between endo (**9**−**12a**) and exo (**9**−**12b**) bent forms.

Table 7. Activation Barriers for the Butterfly Bending of 9−12a ⇌ 9−12b ($\Delta H^{\ddagger}$, kcal/mol), the Butterfly Bending Angle (ψ, deg) of the Cyclopropene Double Bond ($C_2{=}C_4$) in the Transition State, and the Estimated (TCSCF) Radical Character (%) of 1a and 9−12 All Calculated with the 6-31G* Basis Set

compd	$\Delta H^{\ddagger}$ HF[a]	$\Delta H^{\ddagger}$ B3LYP[a]	ψ HF (in TS)[b]	ψ B3LYP (in TS)[b]	%
1a					8.3
9a	13.43	12.99	−7	−7	7.1
9b	6.11	5.98			9.0
10a	12.68	11.57	−4	−4	7.8
10b	9.45	8.95			8.9
11	6.28	6.41	0	0	6.9
12a	6.86	6.55	+1	+2	7.4
12b	9.08	8.95			6.9

[a] $\Delta H^{\ddagger}$ = difference in energy (kcal/mol) between the transition state and the bent forms. [b] Positive angle values correspond to endo bending.

31G*, 1.412 Å) compared with the other correlated methods they used (TCSCF/6-31G*, 1.375 Å; 2R CISD/6-31G* 1.385 Å). They concluded that the single reference (MP2) method was perhaps not suitable for calculations on bicyclo[1.1.0]but-1,(3)-ene, which they proposed may possess significant diradical character. In the less strained bicyclo[2.2.2]octadiene anhydride **13**, we previously found the C_2C_3 olefinic bond length from MP2 (1.347 Å) to be in excellent agreement with the X-ray structure (C_2C_3 = 1.340(2) Å)[10] and better than the HF result of 1.316 Å; see Table 1. Similarly, Holthausen and Koch's MP2 results were in good agreement with experimental geometries, e.g., for anhydride **15**, C_2C_3: HF/6-31G*, 1.322 Å; MP2/6-31G*, 1.349 Å, experiment, 1.342 Å.[6] While we do observe a large increase in the cyclopropenyl olefinic bond lengths in progressing from HF to MP2 calculations, the increase is not as severe as that observed by Hess, Schaad, Schaefer et al. for **1a**.[30] Our DFT and TCSCF cyclopropenyl bond lengths for **9**−**12** are intermediate between the HF and MP2 distances. A similar trend is observed for the butterfly angles in **9**−**12** (excluding the TCSCF and SVWN results vide supra). As already noted, all other structural parameters (**9**−**12**) are in reasonable agreement for each theoretical method that we used. Camps et al. also found that their DFT (B3LYP/6-31G*) results for the alkene bond lengths and pyramidalizations in the highly strained **14** (n = 0) and some of its derivatives were intermediate between the HF and MP2 values.[22] Allinger et al. concluded from an extensive comparison of calculated vs experimental bond lengths that for molecules with only first-row atoms B3LYP/6-31G* bond lengths are better than the corresponding MP2/6-31G* lengths.[31] However, in that study only essentially strain-free molecules were considered. The weight of evidence suggests that the HF level of theory tends to underestimate the bond length and pyramidal-

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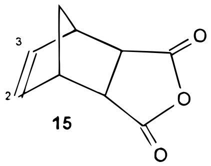
(31) Ma, B.; Lii, J.-H.; Schaefer, H. F., III; Allinger, N. L. *J. Phys. Chem.* **1996**, *100*, 8763.

ization in strained olefins. MP2 methods give excellent results for strained olefins but tend to overestimate both of the above parameters in the most highly strained systems such as **1a**. We suggest that the "compromise" values obtained using DFT methods are probably the most reliable (barring the computationally very expensive MCSCF calculations). In Table 7, we list the estimated radical character of **9**−**12** obtained from the squares of the coefficients of the TCSCF states. It is clear from our TCSCF results that **9**−**12** exhibit diradical character similar to that calculated for **1a**.[30]



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The introduction of the second double bond in **10** and **12** has very little effect on the cyclopropenyl olefin pyramidalization angle. The exo bent dienes **10b** and **12b** show the greatest change in ψ (∼1°) when compared with the corresponding monoenes. Another interesting feature is that exo bending of the cyclopropene ring in **10b** and endo bending in **12a** have a dramatic effect on the pyramidalization of the $C_6{=}C_7$ olefinic bond. The computed values of ψ are about 5° larger for **10b** and **12a** than for the corresponding bending of $C_6{=}C_7$ in **10a** and **12b**.

The cyclopropenyl double bonds of **9**−**12** are significantly pyramidalized (ψ ∼41−50°) and are predicted to be some of the most pyramidalized strained olefins. We have demonstrated that the computationally economical B3LYP method gives results in excellent agreement with experiment, and we suggest that its use is preferred to that of the more expensive, and in some cases less accurate, MP2 method for the study of highly pyramidalized olefins.

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Supporting Information Available: Cartesian coordinates for all calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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