Pyramidalized Olefins: A DFT Study of Bicyclo[2.1.1]-, -[3.2.1]-, and -[3.2.2]alkenes and Their Fused Derivatives. Two Rare Examples of π-Facially Symmetric Pyramidal Olefins[†]

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Density functional theory (B3LYP/6-31G*) was used to study a large series of bridged polycyclic alkenes based on the bicyclo[2.1.1], -[3.2.1], and -[3.2.2] nuclei. In those compounds with π-facial dissymmetry, butterfly bending of the strained olefinic bonds was generally predicted. Surprisingly, large pyramidalizations are calculated for the highly strained *but π-facially symmetric* tetracyclo[5.1.1.1.^{3,5}0^{2,6}]dec-2-ene (**28**, $\psi = 19.8°$) and tetracyclo[5.2.2.1.^{3,5}0^{2,6}]dodec-2,8,10-triene (**33**, $\psi = 14.4°$). The preference for propano-directed bending in the bicyclo[3.2.1]octenes is about as strong as that for endo bending in norbornenes.

Introduction

Pyramidal olefins, olefins in which the four substituents and two carbon atoms of the double bond are noncoplanar, frequently result when the R−C═C bond angle (θ) is small. The force constant for butterfly bending decreases for small values of θ, and when the two faces of the double bond are different, pyramidalization ($\phi > 0°$, $\psi > 0°$) Figure 1, results. In rare cases, π-facially symmetric systems even adopt a pyramidal ground state when θ is small enough, e.g., calculations on ethylene ($\theta < 100°$) predict a pyramidal ground state geometry.[1] Recently, we drew attention to the wide disparity in the mode of reporting the degree of pyramidalization in appropriate olefins and highlighted the need for a consistent measure of pyramidalization.[2] In that paper, we reported pyramidalizations in terms of the butterfly bending angle (ψ) which is defined as $\psi = 180° - |D_1|$. D_1 is the dihedral angle 1−2−3−4, Figure 1. Dihedral angles may vary from −180° to +180° with a clockwise "rotation" representing the positive direction. All of the molecules in this work are of at least C_s symmetry with a mirror plane bisecting and perpendicular to the pyramidal double bond. Consequently, D_1 and the dihedral angle 5−3−2−6 (D_2) are of equal magnitude and opposite sign. We again report all pyramidalizations in terms of ψ.

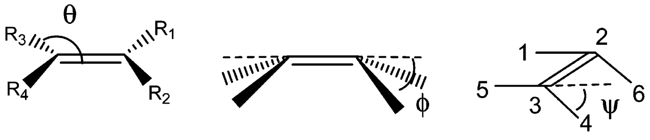

FIGURE 1. Definition of the pyramidalization parameters.

The double bonds of norbornenes and, to a lesser extent, those of bicyclo[2.2.2]octadienes are pyramidal, but in opposite senses with substituents bent in the endo direction for norbornenes and the exo direction for bicyclo[2.2.2]octadienes.[3,5,6] Fusion of these bridged bicycles, through a common double bond, to themselves or to each other produces the sesquinorbornenes (**1** and **2**), the homosesquinorbornenes (**3**−**10**), and the sesquibicyclo[2.2.2]octenes (**11**−**17**), Chart 1. The degree of pyramidalization in each of these systems has been determined by experiment and/or calculation (see Chart 1).[2,3,8] In the homosesquinorbornenes, the more strained norbornenyl nucleus dominates the bicyclo[2.2.2]octadienyl nucleus, always resulting in pyramidalizations in the endo (to the norbornene framework) direction. In the sesquibicyclo[2.2.2]octenes, the pyramidalization of the fused double

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[†] Dedicated to Professor Ronald N. Warrener on the occasion of his 70th birthday.

(1) Reviews, (a) Luef, W.; Keese, R. In *Topics in Stereochemistry*; Eliel, E. L., Wilen, S. H., Eds.; Wiley: New York, 1991; Vol. 20, p 231. (b) Borden, W. T. *Chem. Rev.* **1989**, *89*, 1095.

(2) Margetić, D.; Williams, R. V.; Warrener, R. N. *J. Org. Chem.* **2003**, *68*, 9186.

(3) For a summary of the pyramidalization found in the norbornenyl system, see refs 1 and 4.

(4) Williams, R. V.; Colvin, M. E.; Tran, N.; Warrener, R. N.; Margetić, D. *J. Org. Chem.* **2000**, *65*, 562.

(5) Williams, R. V.; Gadgil, V. R.; Garner, G. G.; Williams, J. D.; Vij, A. *Tetrahedron Lett.* **1999**, *40*, 2690.

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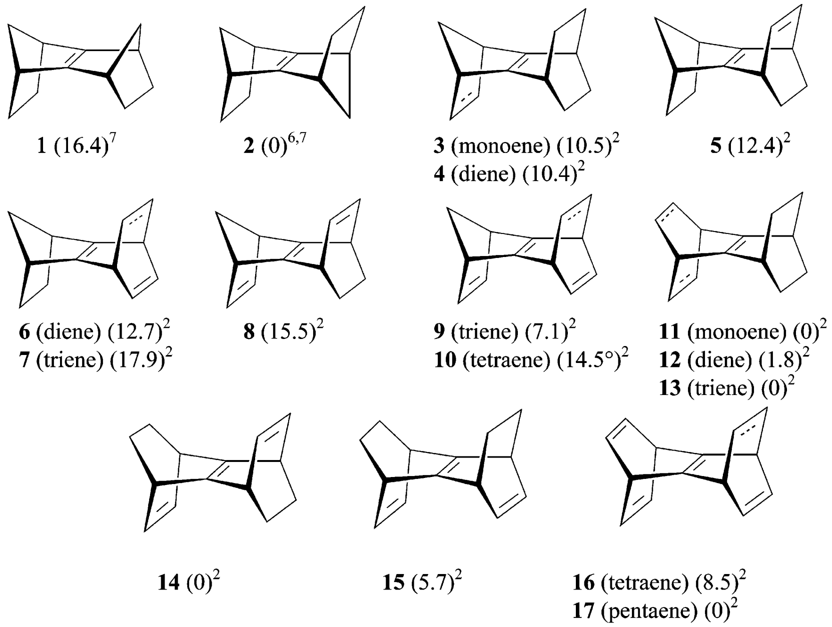
(7) Holthausen, M. C.; Koch, W. *J. Phys. Chem.* **1993**, *97*, 10021.

(8) Saraçoğlu, N.; Menzek, A.; Sayan, S.; Salzner, U.; Balci, M. *J. Org. Chem.* **1999**, *64*, 6670 and references therein.

10.1021/jo0493626 CCC: $27.50

CHART 1. Butterfly Bending (ψ°) for Compounds 1−17

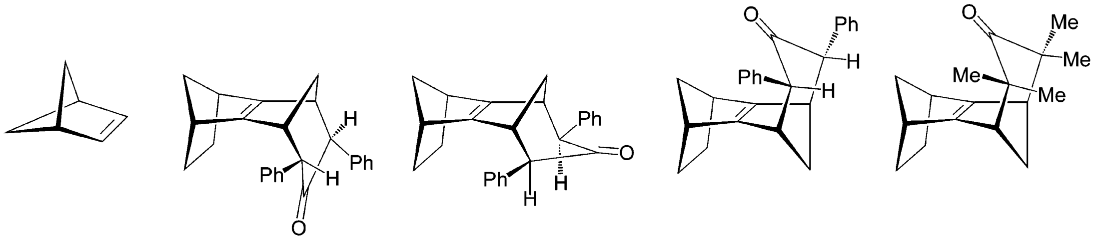


1 (16.4)[7] **2** (0)[6,7] **3** (monoene) (10.5)[2] **4** (diene) (10.4)[2] **5** (12.4)[2]

6 (diene) (12.7)[2] **7** (triene) (17.9)[2] **8** (15.5)[2] **9** (triene) (7.1)[2] **10** (tetraene) (14.5°)[2] **11** (monoene) (0)[2] **12** (diene) (1.8)[2] **13** (triene) (0)[2]

14 (0)[2] **15** (5.7)[2] **16** (tetraene) (8.5)[2] **17** (pentaene) (0)[2]

CHART 2. Butterfly Bending (ψ°) for Compounds 18−22



18 (0) **19** (9.3) **20** (11.8) **21** (11.2) **22** (9.8)

bond is in the exo (to the bicyclo[2.2.2]octadiene moiety) direction.

In this paper, we extend our investigation of pyramidalized olefins to bicyclo-[2.1.1], -[3.2.1], and -[3.2.2] rings and their fused derivatives. There are few experimental structures reported for these systems. As expected from the symmetrical substitution pattern about its double bond, microwave[9] and gas-phase electron diffraction[10,11] determinations on bicyclo[2.1.1]hex-2-ene (**18**) gave structures of C_{2v} symmetry. The only other relevant structure determinations that we are aware of are for the substituted 321−221 compounds **19**−**22** (Chart 2).[12] In each of **19**−**22**, the fused double bond is pyramidal with $\psi \simeq 10°$ (bending in the endo direction with respect to the norbornenyl nucleus).

Results and Discussion

Density functional theory (DFT) using the B3LYP/6-31G* method is very successful in modeling fused polycyclic systems and in predicting the degree of pyramidalization of the fused double bond.[2,4,13−15] We used this method, as instituted in Gaussian 98,[16] to calculate the structures of bicyclo[2.1.1]hex-2-ene (**18**), bicyclo[3.2.1]-oct-2-enes (**23**, **24**), bicyclo[3.2.2]non-2-enes (**25**−**27**), and the fused systems **28**−**87** (Chart 3) derived from these compounds. Analytical energy second derivatives were calculated at all optimized structures to confirm that these are minima or transition states. The calculated butterfly bendings (ψ) and bond angles (θ) to the double

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[9] Wang, C. S.; Harmony, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 1108.

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[11] Zebelman, D. L.; Bauer, S. H.; Chang, J. F. *Tetrahedron* **1972**, *28*, 2727.

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[16] Gaussian 98, Revision A.5: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M.; 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.; Gill, P. M. W.; 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.

CHART 3. Butterfly Bending (ψ°) for Compounds 18 and 23−87

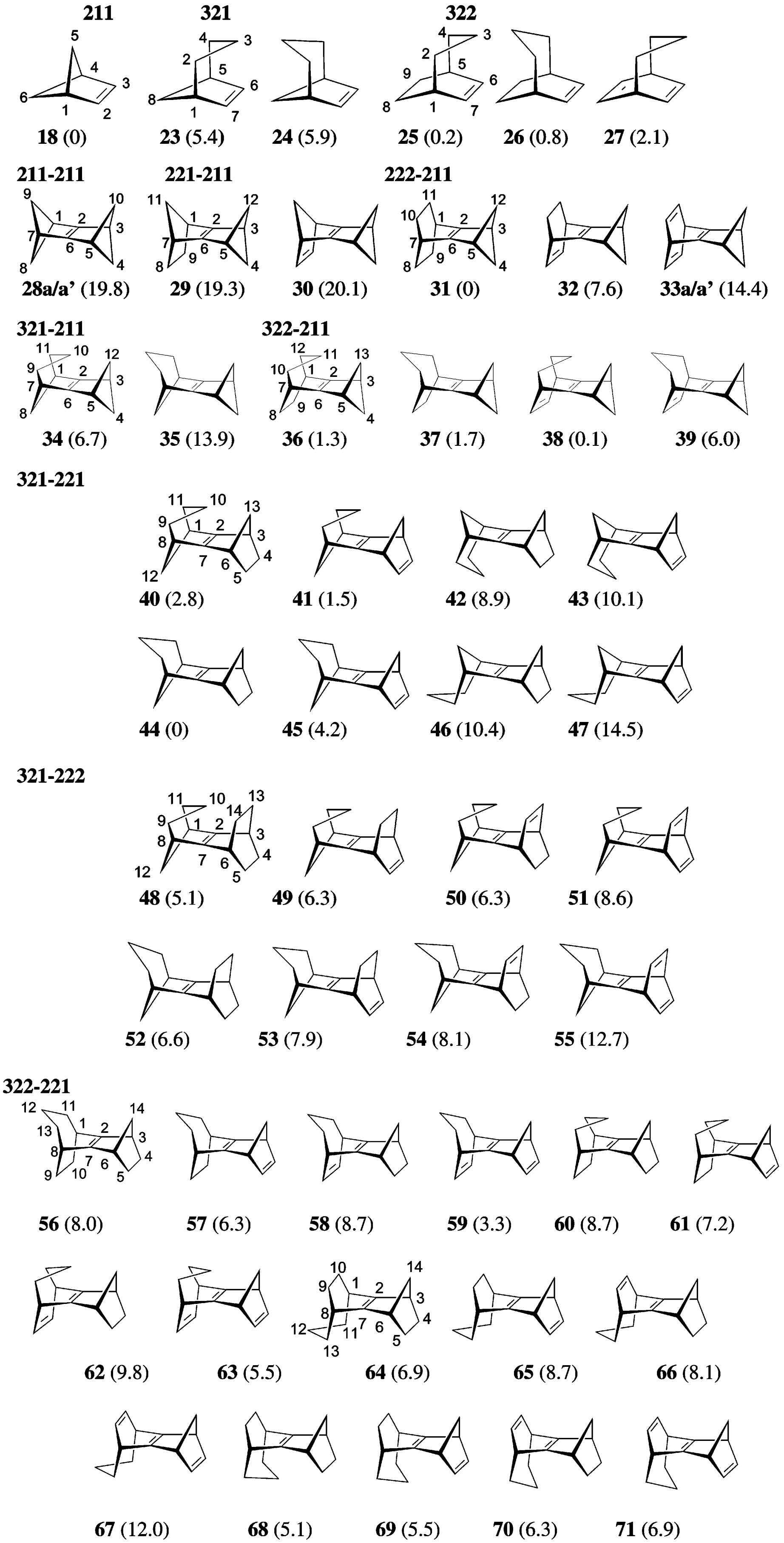


CHART 3 (continued)

322-222

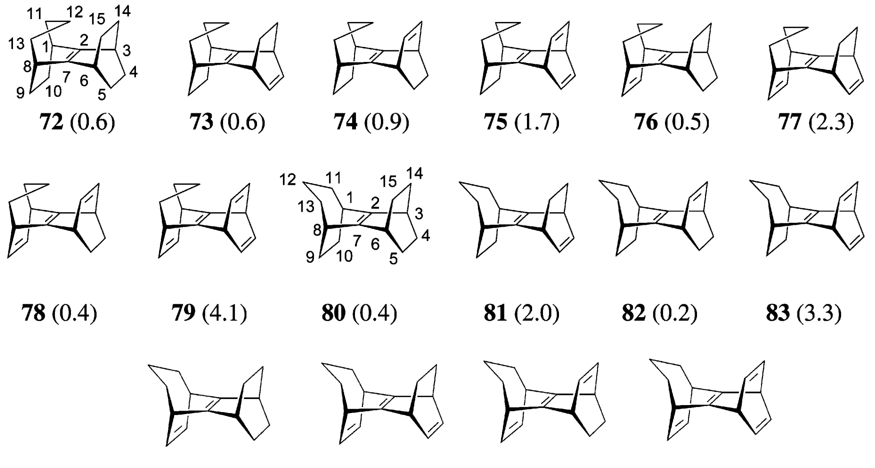
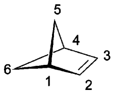
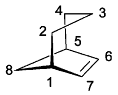
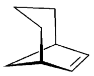
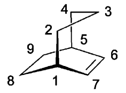
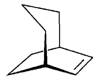
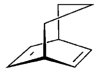


TABLE 1. B3LYP/6-31G* Butterfly Bendings (ψ) and Bond Angles (θ) of 18 and 23-27

	 **18**	 **23**	 **24**	 **25**	 **26**	 **27**
θ /°	C_{2v}	C_s	C_s	C_s	C_s	C_s
$C_1C_2C_3$	103.3	-	-	-	-	-
$C_1C_7C_6$	-	109.8	109.9	118.1	118.4	117.8
$C_1C_8C_9$	-	-	-	113.1	113.1	117.9
ψ /°						
$C_1C_2C_3H_3$	0.0	-	-	-	-	-
$C_1C_7C_6H_6$	-	5.4	5.9	0.2	0.8	2.1
$C_1C_8C_9H_9$	-	-	-	-	-	3.1

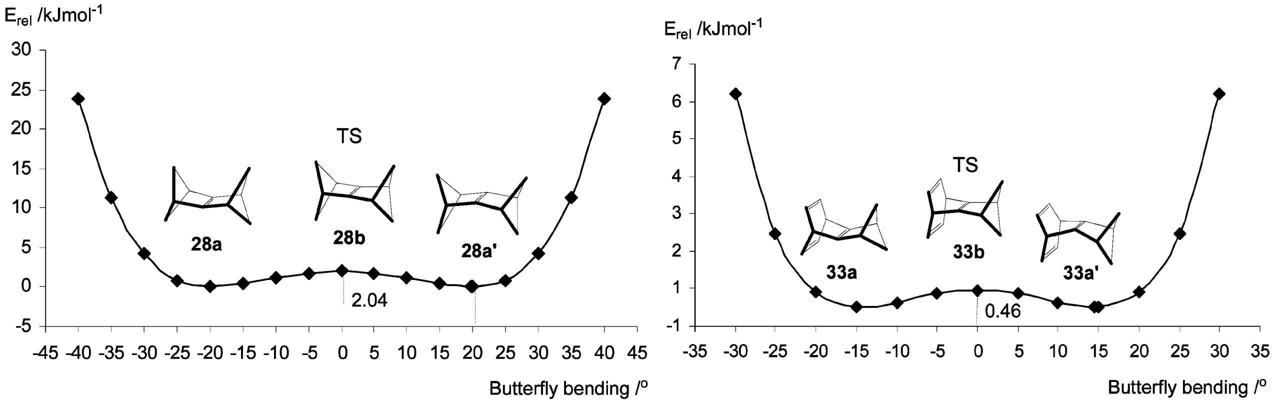


FIGURE 2. Torsional energy surfaces for compounds **28** and **33**.

bonds are shown in Tables 1–9, and selected structural parameters and energies are summarized in the Supporting Information (Tables S1–S13). To confirm that the torsional energy surface for each compound is single- rather than double-minimum, we either carried out a complete scan of dihedral angles (as for **28** and **33**, Figure 2) or reoptimized the structure starting from a geometry with the opposite pyramidalization to that reported in this paper. Except for **28** and **33**, we found all pyramidalized compounds to possess a single-minimum surface.

Parent Compounds 18 and 23–27 (Table 1). Although **18** is the most strained of the parent bicycles with the smallest bond angle to the double bond ($\theta = 103.3°$), its symmetry leads to the anticipated result of a rigorously planar geometry ($\psi = 0°$) for the double bond. Recently, Christl et al. similarly calculated $\psi = 0°$ for **18**.[17] The remaining members of this series (**23**–**27**) each have pyramidalized double bonds in which the vinyl hydrogens are displaced toward the propano-bridge (propano-directed). The minimal strain in the 322 alkenes

TABLE 2. B3LYP/6-31G*-Calculated Butterfly Bendings (ψ) and Bond Angles (θ) of 28−33

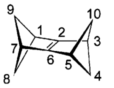
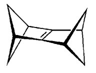
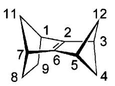
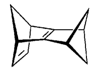
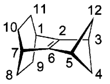
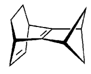
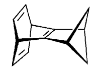
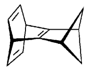
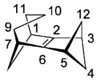
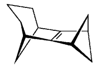
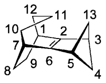
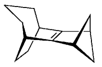
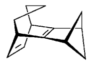
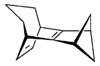
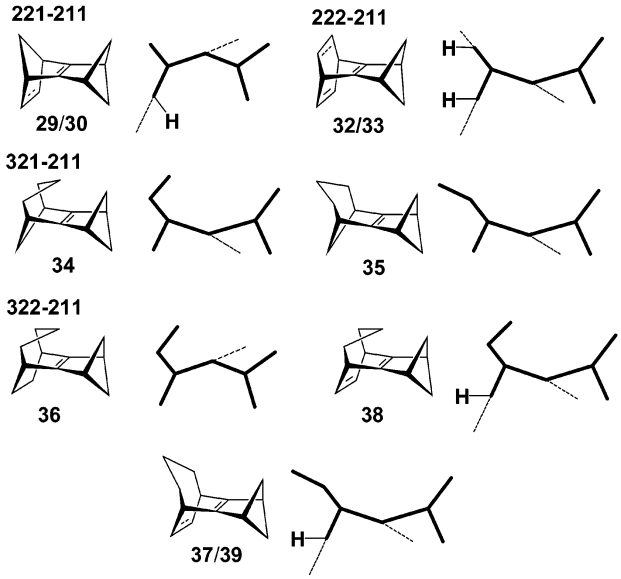
	 **28b**	 **28a/28a'**	 **29**	 **30**	 **31**	 **32**	 **33b**	 **33a/33a'**
θ /°	D_{2h}	C_{2v}	C_s	C_s	C_{2v}	C_s	C_{2v}	C_s
$C_1C_2C_6$	103.9	103.7	108.1	107.8	115.4	114.9	114.2	114.1
$C_1C_2C_3$	152.2	146.2	143.0	142.8	140.9	140.7	141.9	139.8
$C_3C_2C_6$	103.9	103.7	103.6	103.6	103.6	103.6	103.6	103.7
ψ /°								
$C_1C_2C_6C_5$	0.0	19.8	19.3	20.1	0.0	7.6	0.0	14.4
$C_1C_9C_8H_8$	-	-	-	1.4	-	3.2	0.3	2.2
$C_1C_{11}C_{10}H_{10}$	-	-	-	-	-	-	0.3	0.9

TABLE 3. B3LYP/6-31G*-Calculated Butterfly Bendings (ψ) and Bond Angles (θ) of 34−39

	 **34**	 **35**	 **36**	 **37**	 **38**	 **39**
θ /°	C_s	C_s	C_s	C_s	C_s	C_s
$C_1C_2C_6$	110.7	110.8	119.5	119.9	119.1	119.3
$C_3C_2C_6$	103.7	103.7	103.4	103.5	103.5	103.6
$C_1C_2C_3$	144.9	142.8	137.0	136.5	137.3	136.7
ψ /°						
$C_1C_2C_6C_5$	6.7	13.9	1.3	1.7	0.1	6.0
$C_1C_9C_8H_8$	-	-	-	-	4.4	3.0

25−**27** is reflected in the almost normal sp^2 bond angles (θ) and the diminutive pyramidalizations (ψ).

CHART 4. Direction of Pyramidalization in the 221−211, 222−211, 321−211, and 322−211 Systems



211−211, 221−211, 222−211, 321−211, and 322−211 Compounds 28−39 (Tables 2 and 3). Only compound **31**, which exhibits facial symmetry about its double bond, is calculated to have a planar fused double bond. The directions of pyramidalization for **29**−**32**, **34**, and **36**−**39** are illustrated in Chart 4. We calculate for two of the most highly strained members of the series, **28** and **33**, *despite the symmetry based expectation of a planar double bond*, that both are considerably pyramidalized (ψ = 19.8° and 14.4°, respectively). This seeming anomaly is easily explained by consideration of **28b** and **33b**, the planar transition states for the butterfly bending, **28a** $\leftrightarrows$ **28a′** and **33a** $\leftrightarrows$ **33a′**. The internal bond angle (θ) is almost the same in both **28a**/**28a′** and **28b** and **33a**/**33a′** and **33b**; however, the external angle ($C_1C_2C_3$) is considerably expanded in **28b** and **33b** (Table 2). This angle strain is somewhat alleviated in the pyramidal **28a**/**28a′** and **33a**/**33a′**. The double-minimum torsional energy surfaces (Figure 2) for the butterfly bendings **28a** $\leftrightarrows$ **28a′** and **33a** $\leftrightarrows$ **33a′** are flat with an energy difference of only 2.04 and 0.46 kJ/mol respectively between the pyramidal ground states and the planar transition states. At the suggestion of a reviewer, we reoptimized the planar and pyramidal forms of **28** and **33** using the B3LYP/6-311G** and the MP2/6-31G* methods. The results from these methods are entirely consistent with our B3LYP/6-31G* results—pyramidal geometries are predicted for both **28** and **33** with planar transition states between the double-minima. Ψ is calculated to be 21.6° and 24.1° for **28a**/**28a′** and 15.9° and 22.0° for **33a**/**33a′** with the B3LYP and MP2 methods, respectively. Inclusion of zero-point corrections does not alter the preference for a pyramidal ground state (see the Supporting Information for complete details). Radical character has been predicted for examples of the most highly strained pyramidal olefins.[18] To evaluate for the potential of radical contributions for

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(17) The structure of **18** was not discussed in the following paper, but the optimized coordinates (B3LYP/6-31G*) are available in the accompanying Supporting Information. Cohrs, C.; Reuchlein, H.; Musch, P. W.; Selinka, C.; Walfort, B.; Stalke, D.; Christl, M. *Eur. J. Org. Chem.* **2003**, 901.

(18) See ref 4 and: Hess, B. A., Jr.; Allen, W. D.; Mitchalska, D.; Schaad, L. J.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1987**, *109*, 1615 and references therein.

TABLE 4. B3LYP/6-31G*-Calculated Butterfly Bendings (ψ) and Bond Angles (θ) of 40−47

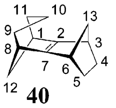
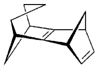
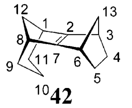
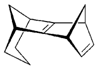
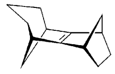
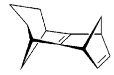
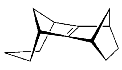
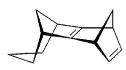
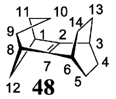
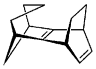
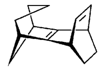
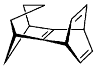
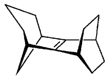
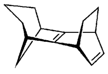
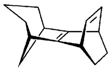
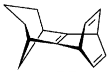
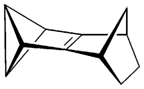
	 40	 41	 42	 43	 44	 45	 46	 47
θ /°	C_s	C_s	C_s	C_s	C_s	C_s	C_s	C_s
$C_1C_2C_7$	110.4	110.6	110.4	110.5	110.6	110.7	110.8	110.6
$C_3C_2C_7$	108.0	107.6	108.0	107.6	108.1	107.6	108.0	107.6
$C_1C_2C_3$	141.3	141.6	140.7	140.5	141.2	141.2	140.1	139.0
ψ /°								
$C_1C_2C_7C_6$	2.8	1.5	8.9	10.1	0.0	4.2	10.4	14.5
$C_3C_4C_5H_5$	-	3.1	-	1.9	-	1.0	-	1.8

TABLE 5. B3LYP/6-31G*-Calculated Butterfly Bendings (ψ) and Bond Angles (θ) of 48−55

	 48	 49	 50	 51	 52	 53	 54	 55
θ /°	C_s	C_s	C_s	C_s	C_s	C_s	C_s	C_s
$C_1C_2C_7$	110.0	110.2	110.3	110.4	110.2	110.3	110.4	110.5
$C_3C_2C_7$	114.9	114.4	114.4	113.6	111.1	114.4	114.5	113.7
$C_1C_2C_3$	134.5	134.7	134.7	134.9	134.3	134.3	134.2	133.9
ψ /°								
$C_1C_2C_7C_6$	5.1	6.3	6.3	8.6	6.6	7.9	8.1	12.7
$C_3C_4C_5H_5$	-	3.3	-	0.2	-	3.2	-	2.0
$C_3C_{13}C_{14}H_{14}$	-	-	4.3	1.7	-	-	4.3	0.4

any of the compounds studied in this paper, we reoptimized the structures of the most strained compound **28a** and **28b** using UB3LYP/6-31G*. In both cases $\langle S^2 \rangle = 0$, clearly indicating an absence of radical character.

The magnitude of the butterfly bendings in the remaining members of the 211 series roughly parallels the degree of strain in these tetracycles. As expected, for the 221−211 species **29** and **30**, the pyramidalizations of the fused double bonds ($C_2{=}C_6$) are some of the largest we report ($\psi = 19.3°$ and 20.1°, respectively) and are in the endo direction with respect to the norbornyl nucleus. The hydrogens on the $C_8{=}C_9$ double bond are also displaced in the endo direction. Similarly, Christl calculated a pyramidalization of 21.2° (at the UB3LYP/cc-pVDZ level) for the more strained tricyclo[3.1.0.0^{2,6}]hexene analogue **88** of **29**.[19] In accord with expectations, **32**, the only



88

π-facially dissymmetric constituent of the 222−211 series, is pyramidal ($\psi = 7.6°$ in the exo direction with respect to the bicyclo[2.2.2]octadiene moiety). Similar to the exceptionally strained and π-facially symmetric **28**, the 211 fused bicyclo[2.2.2]diene **33** is also pyramidal ($\psi = 14.4°$). The syn and anti, **34** and **35**, 321−211 alkenes are both significantly pyramidalized ($\psi = 6.7°$ and 13.9°, respectively) and, paralleling the parent bicyclo[3.2.1]octenes **23** and **24**, the butterfly bending is toward the propano-bridge (propano-directed). The difference in the degree of pyramidalization of syn **34** and anti **35** is accounted for by the noticeable steric compression between H_{10} and H_{12} in **34**. H_{10} and H_{12} are only separated by 2.145 Å in **34** compared with 3.643 Å in **35**. As is apparent in the lightly strained parent 322 alkenes **25**−**27**, the degree of pyramidalization calculated for their fused derivatives **36**−**39** is also very small. Interestingly, the preference exhibited by **25**−**27** for propano-directed butterfly bending is mimicked in **37**−**39**, but in syn **36** the pyramidalization is in the opposite direction (ethano-directed). Clearly, there is a fine balance between the intrinsically preferred direction of bending for the bicyclo[3.2.2]nonenes and the consequential steric interaction between H_{12} and H_{13}. In syn **36** the steric factor dominates while in the more strained syn diene **38** the intrinsic preference for propano-directed bending triumphs (by only 0.1°). Again, as in the parent **27**, the fused derivatives exhibit a greater propano-directed bending of the anti vinylic hydrogens (H_8 and H_9 in **27** and **38**) than for the corresponding syn hydrogens (H_6 and H_7 in **27** and H_8 and H_9 in **39**).

321−221 and 321−222 Compounds 40−55 (Tables 4 and 5). All of the compounds in this series are facially dissymmetric, and as expected, the fused double bond is pyramidal in all but **44**. The direction of pyramidalization is shown in Chart 5. In **40**, **41**, **44**, and **45** the methano- and propano-bridges are oriented on the same face of the fused double bond ($C_2{=}C_7$), and therefore, the intrinsic pyramidalizations of the norbornenyl (endo) and bicyclo[3.2.1]octenyl (propano-directed) nuclei are in opposition. Previously, we reported for the 222−221 compounds **6** and **9**, where the intrinsic pyramidalizations of the norbornenyl and bicyclo[2.2.2]octadienyl nuclei are in opposition, that the norbornenyl moiety dominates and enforces its preferred endo butterfly bending.[2] By anal-

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(19) Fischer, T.; Kunz, U.; Lackie, S. E.; Cohrs, C.; Palmer, D. D.; Christl, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 2969.

TABLE 6. B3LYP/6-31G*-Calculated Butterfly Bendings (ψ) and Bond Angles (θ) of 56−63

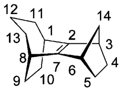
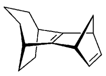
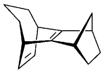
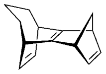
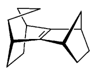
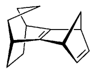
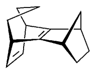
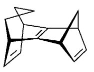
	 **56**	 **57**	 **58**	 **59**	 **60**	 **61**	 **62**	 **63**
θ /°	C_s	C_s	C_s	C_s	C_s	C_s	C_s	C_s
$C_3C_2C_7$	107.7	107.2	107.8	107.4	107.6	107.2	107.7	107.3
$C_1C_2C_7$	119.2	119.5	121.1	118.9	118.9	119.1	118.6	118.8
$C_1C_2C_3$	132.2	132.7	133.7	133.3	132.6	133.0	132.8	133.4
ψ /°								
$C_1C_2C_7C_6$	8.0	6.3	8.7	3.3	8.7	7.2	9.8	5.5
$C_8C_9C_{10}H_{10}$	-	-	3.7	3.1	-	-	4.6	4.8
$C_3C_4C_5H_5$	-	2.9	-	3.7	-	2.9	-	3.0

TABLE 7. B3LYP/6-31G*-Calculated Butterfly Bendings (ψ) and Bond Angles (θ) of 64−71

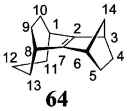
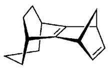
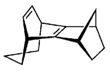
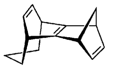
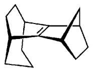
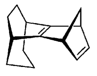
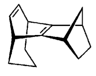
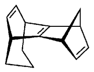
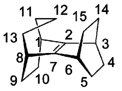
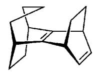
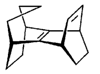
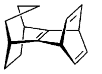
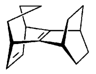
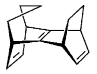
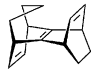
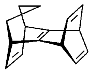
	 **64**	 **65**	 **66**	 **67**	 **68**	 **69**	 **70**	 **71**
θ /°	C_s	C_s	C_s	C_s	C_s	C_s	C_s	C_s
$C_3C_2C_7$	107.6	107.3	107.8	107.4	107.7	107.3	107.8	107.4
$C_1C_2C_7$	119.4	119.6	118.7	118.9	119.0	119.2	118.7	118.9
$C_1C_2C_3$	132.4	132.3	132.8	133.2	133.0	133.2	133.1	133.2
ψ /°								
$C_1C_2C_7C_6$	6.9	8.7	8.1	12.0	5.1	5.5	6.3	6.9
$C_8C_9C_{10}H_{10}$	-	-	2.6	2.5	-	-	3.8	3.9
$C_3C_4C_5H_5$	-	2.5	-	2.1	-	2.6	-	2.3

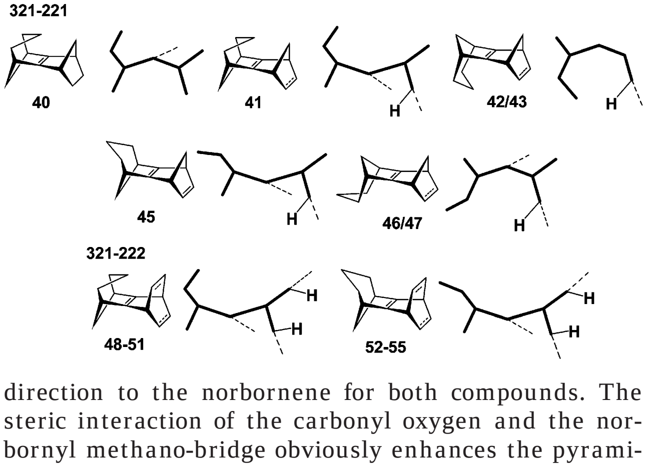
TABLE 8. B3LYP/6-31G*-Calculated Butterfly Bendings (ψ) and Bond Angles (θ) of 72−79

	 **72**	 **73**	 **74**	 **75**	 **76**	 **77**	 **78**	 **79**
θ /°	C_s	C_s	C_s	C_s	C_s	C_s	C_s	C_s
$C_1C_2C_7$	118.4	118.6	118.6	118.9	118.1	118.3	118.3	118.5
$C_3C_2C_7$	114.1	113.7	113.7	113.0	114.3	113.8	113.9	113.1
$C_1C_2C_3$	127.3	110.7	127.5	127.8	127.4	127.6	127.6	127.8
ψ /°								
$C_1C_2C_7C_6$	0.6	0.6	0.9	1.7	0.5	2.3	0.4	4.1
$C_1C_{10}C_9H_9$	-	-	-	-	3.7	3.8	3.8	4.0
$C_3C_4C_5H_5$	-	3.1	-	0.0	-	3.0	-	0.3
$C_3C_{14}C_{15}H_{15}$	-	-	3.4	0.8	-	-	3.7	1.3

ogy, we considered it likely that endo bending, to the norbornenyl framework, would ensue in **40**, **41**, **44**, and **45**. Such is the case for **40**. However, **44** is planar, and **41** and **45** are pyramidalized in the *exo, to the norbornadiene, direction.*

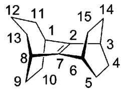
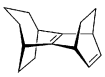
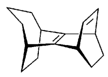
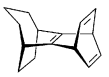
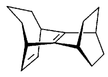
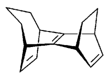
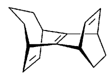
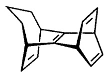
In pyramidal facially dissymmetric olefins, the cause of the pyramidalization was originally attributed to either torsional or hyperconjugative effects.[1] More recently, Holthausen and Koch demonstrated that both of these effects are important in determining the degree of pyramidalization.[7] Clearly, for **40**, **41**, **44**, and **45** in which the opposing intrinsic pyramidalizations of the fused bicycles are closely balanced, a subtle amalgamation of torsional, hyperconjugative, and steric effects must be in operation.

CHART 5. Direction of Pyramidalization in the 321−221 and 321−222 Systems



In agreement with our calculated results, X-ray structure determination on **21** and **22**,[12] substituted analogues of **40**, revealed large butterfly bendings in the endo direction to the norbornene for both compounds. The steric interaction of the carbonyl oxygen and the norbornyl methano-bridge obviously enhances the pyrami-

TABLE 9. B3LYP/6-31G*-Calculated Butterfly Bendings (ψ) and Bond Angles (θ) of 80−87

	 80	 81	 82	 83	 84	 85	 86	 87
θ /°	C_s	C_s	C_s	C_s	C_s	C_s	C_s	C_s
$C_1C_2C_7$	118.7	118.9	118.9	119.2	118.2	118.3	118.4	118.7
$C_3C_2C_7$	114.2	113.8	113.8	113.1	114.1	113.9	113.9	113.2
$C_1C_2C_3$	126.8	126.9	127.1	127.4	127.2	127.4	127.4	127.3
ψ /°								
$C_1C_2C_7C_6$	0.4	2.0	0.2	3.3	2.2	4.0	2.1	7.2
$C_1C_{10}C_9H_9$	-	-	-	-	2.6	2.7	2.8	2.8
$C_3C_4C_5H_5$	-	3.0	-	0.1	-	3.0	-	0.4
$C_3C_{14}C_{15}H_{15}$	-	-	3.3	0.8	-	-	3.6	1.4

dalization in **21** and **22** compared with that in the unsubstituted **40**.

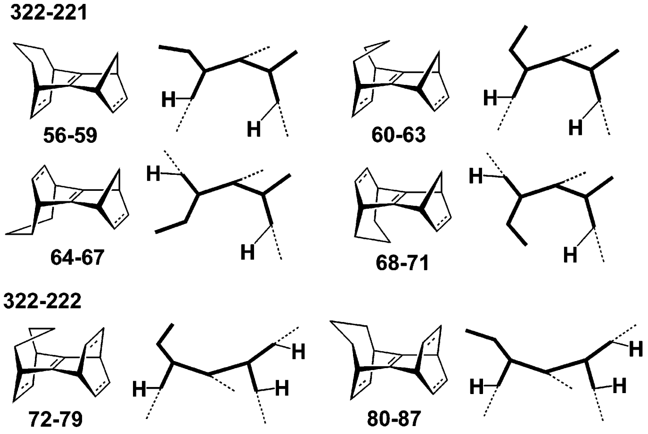
Due to the opposing orientation of the methano- and propano-bridges in **42**, **43**, **46**, and **47**, the intrinsic pyramidalizations of the norbornenyl and bicyclo[3.2.1]-octenyl moieties operate in tandem. Consequently, the pyramidalizations are large for each of these molecules. As a result of steric encumberance between the ethano/etheno and propano subunits, the compounds with syn-oriented propano groups, **42** and **43**, show a reduced pyramidalization compared with the corresponding anti isomers **46** and **47**. Validation of our calculations is provided by the close agreement found between the experimentally determined[12] degree of pyramidalization for **19** ($\psi = 9.3°$) and **20** ($\psi = 11.8°$) with that calculated for the unsubstituted analogues **42** ($\psi = 8.9°$) and **46** ($\psi = 10.4°$).

Very interestingly, the pyramidalization of the whole of the 321−222 series is propano-directed regardless of whether the intrinsic pyramidalizations of the bicyclo-[2.2.2]octadienyl (exo) and bicyclo[3.2.1]octenyl (propano-directed) are in concert or opposition. Not only are all of these pyramidalizations in the same direction, but also the magnitude of the butterfly bending is essentially the same whether the intrinsic pyramidalizations are reinforcing (as in **49** and **53**, $\psi = 6.3°$ and 7.9°, respectively) or opposing (as in **50** and **54**, $\psi = 6.3°$ and 8.1°, respectively).

Our results for **40**, **41**, **44**, and **45** show that the preference for propano-directed bending in bicyclo[3.2.1]-octenes is about as strong as that for endo bending in norbornenes. Reinforcing this conclusion is the complete domination of the bicyclo[2.2.2]octadiene intrinsic exo bending by the propano-directed bending of the bicyclo-[3.2.1]octane nuclei in **50** and **54**.

322−221 and 322−222 Compounds 56−87 (Tables 6−9). Once more, all of the compounds in this series are facially dissymmetric and are pyramidalized in the directions shown in Chart 6. The diminished strain in the bicyclo[3.2.2]nonenes is reflected in the complete control of the direction of butterfly bending by the norbornyl nucleus in **56−63** where the intrinsic bendings of the 322 and 221 moieties are in opposition. Across the series, **64−67**, where the propano and methano groups are "anti oriented" and on opposite faces of the molecules (hence the intrinsic bendings of the 322 and 221 nuclei are in concert), the magnitude of the pyramidalization is greater than that for **56−63**. Steric factors obviously also play a significant role in determining the degree of pyramidalization in the 322−221 series. In **60−63** where the propano group interacts more strongly with the methano group ("syn oriented"), the pyramidalization is greater than for **56−59** where the corresponding interaction ("anti oriented") is diminished. Similarly, for **68−71** where the propano and ethano bridges are "syn oriented" the degree of pyramidalization is ameliorated compared with the "anti oriented" **64−67**.

CHART 6. Direction of Pyramidalization in the 322−221 and 322−222 Systems



Surprisingly, for each member of the 322−222 series control of the direction of butterfly bending is afforded by the 322 nuclei. In all of these compounds the bendings are calculated to be small. Steric factors and strain exert their usual influences.

Conclusions

Overall, we observe the usual trends for compounds **23−87**, the greater the strain of the ring systems the greater the degree of pyramidalization. Steric factors also exert significant influence over pyramidalizations. For the bicyclo[3.2.1] and bicyclo[3.2.2] series, the intrinsic butterfly bendings are propano-directed. Two unexpected findings are perhaps the most important results from our work: (i) the highly strained but π-facially symmetric **28** and **33** have highly pyramidal ground states,[20] and (ii) our results for **40**, **41**, **44**, and **45** show that the preference for propano-directed bending in bicyclo[3.2.1]octenes is about as strong as that for endo bending in norbornenes. Reinforcing this conclusion is the complete domination of the bicyclo[2.2.2]octadiene intrinsic exo bending by the propano-directed bending of the bicyclo[3.2.1]octane nuclei in **50** and **54**. B3LYP/6-311G** and MP2/6-31G* calculations on **28** and **33** are in complete qualitative agreement with our ubiquitous B3LYP/6-31G* results supporting our assertion that the B3LYP/6-31G* method is entirely appropriate for the study of the compounds considered in this paper.

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

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(20) It should be noted that Johnson[21] predicted a highly pyramidal ground state ($\psi = 34.6°$) for **28** using force field calculations. However, this level of theory is, in general, unreliable for the modelling of (potentially) pyramidal olefins as is demonstrated by Johnson's incorrect predictions that **2** and **11** are pyramidal (ψ = 27.3 and 7.5°, respectively).

(21) Johnson, C. A. *J. Chem. Soc., Chem. Commun*. **1983**, 1135.