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Ab Initio/GIAO−CCSD(T) Study of Bicyclic and Related Strained Olefins. Structures and ^{13}C NMR Chemical Shifts

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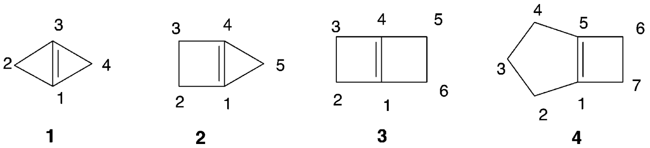
Bicyclic and related strained olefins were studied by the ab initio/GIAO−CCSD(T) method. Structures and ^{13}C NMR chemical shifts of the olefins were calculated using ab initio/GIAO−CCSD(T) method. The δ^{13}C of the olefinic carbons of the yet unknown bicyclo[1.1.0]but-1,3-ene **1** and bicyclo[2.1.0]pent-1(4)-ene **2** were computed to be 69.4 and 212.4, respectively, at the GIAO−CCSD(T)/qzp/tzp//MP2/cc-pVTZ level. The δ^{13}C of the olefinic carbons of the intriguing (larger and also yet unknown) tricyclo[3.3.1.0^{3,7}]non-3(7)-ene **6** and cubene **7** were calculated to be 172.5 and 187.4, respectively, at the GIAO−CCSD(T)/tzp/dz//MP2/cc-pVTZ level. In a related study, the relative energies of the various conformers of ethylene were computed and were found to correlate extremely well with the ^{13}C NMR chemical shifts, reflecting the linear dependence of the ^{13}C NMR chemical shifts on the internal strain of the molecules.

Introduction

The simplest and most strained[1] symmetrical bicyclic olefins (among olefins with collinear π orbital angle vectors[1]) are bicyclo[1.1.0]but-1,3-ene **1**, bicyclo[2.1.0]pent-1(4)-ene **2**, bicyclo[2.2.0]hex-1(4)-ene **3,** and bicyclo[3.2.0]hept-1(5)-ene **4** (Scheme 1). The olefins **1** and **2** themselves have not yet been prepared, and only their substituted derivatives were characterized by trapping experiments.[2] Casanova and Rogers[3] and Wiberg et al.[4] prepared the olefin **3** and studied its reactivity. Casanova and co-workers[3] also succeeded in isolating the pure olefin and obtained its ^{1}H and ^{13}C NMR, IR, and Raman spectra. Theoretical ab initio calculations of Wagner, Schleyer, et al.[4a] and Wiberg and co-workers[4b] predict that **3** should exist in the planar D_{2h} conformation.

In fact, the ^{13}C NMR chemical shifts of strained hydrocarbons are indicative of the relative hybridization state of carbons. As the internal strain of the molecules increase, the strained olefinic carbons become increasingly deshielded. This effect was explained as due to the torsionally induced rehybridization.[4c] The olefinic δ^{13}C absorptions for dimethylcyclobutene,[5] bicyclo[4.2.0]oct-1(6)-ene,[5] **4**,[5] and **3**[3] are 136.6, 141.7, 150.2, and 163.5, respectively, reflecting a gradual increase in ring strain in this series. The corresponding chemical shifts for the strained pyramidalized[6] olefins **2** and **1** would be expected to be even more deshielded. However, because of extreme reactivity, the synthesis and NMR characterization of these olefins remain elusive.

SCHEME 1



Vazquez has reported[7] DFT/GIAO-DFT calculated ^{13}C NMR chemical shifts of several highly pyramidalized olefins including **3**. Very good agreement between calculated and experimental values was found. We have previously reported[8] the calculated ^{13}C NMR chemical shifts of the bicyclic olefins **1**−**4** using the ab initio/IGLO method. The computed values compare with the experimental data reasonably, but show a systematic drift with increasing strain. The δ^{13}C values of the olefinic carbons of **1** and **2** were computed to be extremely deshielded at 455.5 and 284.5.[8] However, recent studies indicate that electron correlation contributions are necessary to calculate the accurate chemical shifts. IGLO is not a correlated method. GIAO-MP2 is a widely used correlated method included in several widely used quantum chemistry programs including *Gaussian 03*.[9] Correlated ^{13}C NMR chemical shift calculations can also be carried out by the GIAO−CCSD(T) and other coupled cluster methods. The GIAO−CCSD(T) method is currently available through the ACES II program.[10] The GIAO−CCSD(T) method of calculating the accurate ^{13}C NMR chemical shifts of carbocations and other organic molecules have been demonstrated in several recent studies.[11−15] Since strained olefins resemble the carbocations in their ground-state geometry, the GIAO−CCSD(T) calculations for these olefins would be expected to closely compare with the experimental data.

Calculations

Geometry optimizations and frequency calculations were carried out with the *Gaussian 03* program.[9] The geometry optimizations were performed at the MP2/6-311G* level. Vibrational frequencies at the MP2/6-311G*//MP2/6-311G* level were used to characterize stationary points as minima (number of imaginary frequency (NIMAG) = 0). The MP2/6-311G* geometries were further optimized at the higher MP2/cc-pVTZ and MP2/cc-pVQZ levels. NMR chemical shifts were calculated by the GIAO (Gauge Invariant Atomic Orbitals) method[16] using MP2/cc-pVTZ geometries. GIAO−CCSD(T), GIAO−MP2, and GIAO−SCF calculations using tzp/dz (tzp is used for carbon and dz is used for hydrogen) and qzp/tzp (qzp is used for carbon and tzp is used for hydrogen) basis sets[17,18] have been performed with the ACES II program.[10] The ^{13}C NMR chemical shifts were computed using tetramethylsilane

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TABLE 1: Calculated[a] and Experimental ^{13}C NMR Chemical Shifts

no	atom	GIAO−SCF/tzp/dz//MP2/cc-pVTZ	GIAO-MP2/tzp/dz//MP2/cc-pVTZ	GIAO−CCSD(T)/tzp/dz//MP2/cc-pVTZ	GIAO−CCSD(T)/qzp/tzp//MP2/cc-pVTZ	exptl
cyclopropene[b]	C(H)	120.8	107.9	107.4	108.7	108.9
	C(H2)	−0.2	2.7	2.0	2.6	2.3
cyclobutene[b]	C(H)	147.0	137.4	135.5	136.9	137.2
	C(H2)	28.4	32.0	31.8	33.4	31.4
cyclopentene[b]	C(H)	140.4	133.2	129.9	132.0	130.2
	C(H2)[c]	24.2	35.3	33.2	34.5	32.3
	C(H2)	29.6	28.0	26.4	28.0	22.7
1	C1	69.2	142.8	*d*	69.4	
	C2	57.8	64.9		48.5	
2	C1	325.9	143.5	207.7	212.4	
	C2	30.3	31.5	30.2	31.8	
	C5	77.7	38.9	50.4	51.6	
3[e]	C1	182.6	163.7	162.9	164.7	163.5
	C2	40.4	47.4	44.4	46.1	43.7
4[f]	C1	165.7	152.8	150.7		150.2
	C2	28.9	35.0	32.7		32.1
	C3	27.2	31.0	29.4		28.5
	C6	26.1	30.3	28.8		27.3
5[g]	C1	157.9	150.9	147.4		146.0
	C2	27.8	33.0	30.9		29.2
	C3	28.4	33.4	31.4		28.4
6	C1	205.4	177.1	172.5		
	C2	49.5	58.1	53.9		
	C3	67.3	80.7	73.0		
	C4	34.2	40.9	38.7		
7	C1	227.2	173.3	187.4		
	C2	73.6	85.7	77.9		
	C3	32.5	47.3	43.5		

[a] ^{13}C NMR chemical shifts were referenced to TMS; for numbering scheme, please see Scheme 1 and Figure 1. [b] Exptl values of cyclopropene, cyclobutene, and cyclopenetene were taken from ref 22. [c] Methylene carbons adjacent to the double bond. [d] Did not converge at this level of GIAO−CCSD(T) calculations. [e] Exptl values taken from ref 3. [f] Exptl values taken from ref 5. [g] Exptl values taken from ref 23.

(TMS) (calculated absolute shift, i.e., σ(C), tzp/dz = 193.9 (GIAO−SCF), 199.6 (GIAO−MP2), 197.9 (GIAO−CCSD(T), and σ(C), qzp/tzp = 196.1 (GIAO−CCSD(T)) as reference.

TABLE 2: Calculated and Experimental[a] C−C Bond Distances (in Å)

	r(C−C)	MP2/cc-pVTZ	MP2/cc-pVQZ	exptl
cyclopropene	C1−C3	1.299	1.295	1.293(1)
	C1−C2	1.508	1.505	1.505(1)
cyclobutene	C1−C4	1.345	1.342	1.342(4)
	C1−C2	1.513	1.510	1.517(3)
	C1−C2	1.565	1.562	1.566(3)
cyclopentene	C1−C5	1.338	1.336	1.341(10)
	C1−C2	1.506	1.504	1.519(30)
	C2−C3	1.540	1.537	1.544(35)
1	C1−C3	1.406	1.400	
	C1−C2	1.489	1.486	
2	C1−C4	1.384	1.380	
	C1−C2	1.541	1.538	
	C2−C3	1.536	1.533	
	C1−C5	1.499	1.496	
3	C1−C4	1.326	1.323	
	C1−C2	1.528	1.526	
	C2−C3	1.597	1.594	

[a] Exptl data were taken from the following: cyclopropene, ref 19; cyclobutene, ref 20; cyclopenetene, ref 21.

Results and Discussion

The structures of the studied olefins were calculated at the ab initio MP2/cc-pVTZ level. ^{13}C NMR chemical shift calculations were carried out by the GIAO−CCSD(T) method (Table 1). To check reliability of the method, the structures and ^{13}C NMR chemical shifts of the parent cyclopropene, cyclobutene, and cyclopentene were also calculated. Computed structures of cyclopropene,[19] cyclobutene,[20] and cyclopentene[21] agree extremely well with the experimental structures (Table 2). The MP2/cc-pVTZ calculated C═C distances of cyclopropene, cyclobutene, and cyclopentene are 1.299, 1.345, and 1.338 Å, respectively. They are only 0.006, 0.003, and 0.003 Å deviated from those of the experimental values of 1.293, 1.342, and 1.341 Å, respectively. The calculated other C−C bond distances are also very close to those of experimental values (Table 2). However, we would like to emphasize that the close agreement between calculated and experimental values is somewhat fortuitous especially in the case of the geometry of cyclopentene, which has an uncorrected r_g geometry from electron diffraction and is almost certainly too long.

^{13}C NMR chemical shifts of cyclopropene, cyclobutene, and cyclopentene were calculated by the GIAO−coupled cluster method at the GIAO−CCSD(T)/tzp/dz level using MP2/cc-pVTZ geometries (Table 1). Chemical shifts were also computed at the higher GIAO−CCSD(T)/qzp/tzp level using the same MP2/cc-pVTZ geometries. The calculated ^{13}C NMR chemical shifts of the olefins agree extremely well with the available experimental values. Thus, the GIAO−CCSD(T)/tzp/dz calculated δ^{13}C of the olefinic carbons of cyclopropene, cyclobutene, and cyclopentene of 107.4, 135.5, and 129.9, respectively, are slightly deviated from the experimental values[22] of 108.9, 137.2, and 130.2 ppm. The GIAO−CCSD(T)/qzp/tzp calculated δ^{13}C of cyclopropene and cyclobutene (108.7, 136.9, and 132.0) also agree very well with the experimental values (Table 1).

MP2/cc-pVTZ geometries of smaller olefins were further optimized at the higher MP2/cc-pVQZ level. However, optimizations of the structures at the MP2/cc-pVQZ level changed the geometries very little (Table 2), For instance, calculated C═C distances of cyclopropene, cyclobutene, and cyclopentene are 1.295, 1.342, and 1.336 Å, respectively. These are only 0.004, 0.003, and 0.002 Å shorter than those of the MP2/cc-pVTZ values of 1.299, 1.345, and 1.338 Å. Furthermore, to check the

TABLE 3: Calculated[a] and Experimental[b] ^{13}C NMR Chemical Shifts

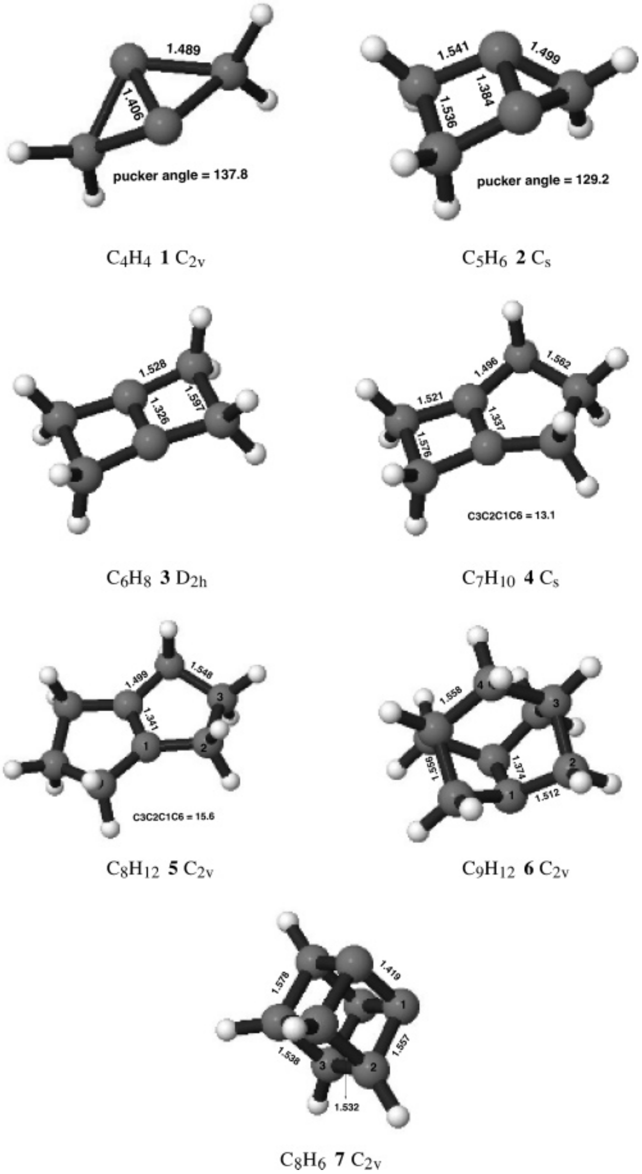
no	atom	GIAO−CCSD(T)/tzp/dz//MP2/cc-pVQZ	GIAO−CCSD(T)/qzp/tzp//MP2/cc-pVQZ	exptl
cyclopropene	C(H)	107.2	108.3	108.9
	C(H2)	1.9	2.4	2.3
cyclobutene	C(H)	135.3	136.6	137.2
	C(H2)	31.7	33.1	31.4
cyclopentene	C(H)	129.8	131.9	130.2
	C(H2)[c]	33.2	34.4	32.3
	C(H2)	26.3	27.9	22.7
2	C1	206.3	210.8	
	C2	30.7	32.2	
	C2	50.1	51.2	
3	C1	162.7	164.3	163.5[d]
	C2	44.2	45.7	43.7[d]

[a] ^{13}C NMR chemical shifts were referenced to TMS (calculated absolute shift, i.e., σ(C), tzp/dz = 198.2 and qzp/tzp = 196.3). [b] Exptl values were taken from ref 22. [c] Methylene carbons adjacent to the double bond. [b] Exptl value was taken from ref 3.

reliability of the calculated geometry, the ^{13}C NMR chemical shifts of the olefins were also calculated at the GIAO−CCSD(T)/tzp/dz and GIAO−CCSD(T)/qzp/tzp levels using the MP2/cc-pVQZ geometries, and the data are listed in Table 3. However, changes in the ^{13}C NMR chemical shifts are very little (Table 3).

Experimental ^{13}C NMR chemical shifts of the bicyclic olefins **3**,[3] **4**,[5] and bicyclo[3.3.0]octa-1(5)-ene **5**[23] are known. The structures of these bicyclic olefins were also calculated at the MP2/cc-pVTZ level and are given in Figure 1. The C═C distances of **3**, **4**, and **5** are 1.326, 1.337, and 1.341 Å, respectively, reflecting a gradual decrease in ring strain in this series. ^{13}C NMR chemical shifts were computed at the GIAO−CCSD(T)/tzp/dz level. Calculated δ^{13}C of the olefinic carbons of **3**, **4**, and **5**, are 162.9, 150.7, and 147.4, respectively, are also very close to the experimental values of 163.5, 150.2, and 146.0 ppm. Decreasing order of both calculated and experimental ^{13}C NMR chemical shifts are also reflecting a gradual decrease in ring strain in this series. As seen from Table 1, the GIAO−MP2/tzp/dz calculated values are little more deshielded than those of the corresponding GIAO−CCSD(T)/tzp/dz values. The GIAO−SCF/tzp/dz calculated values are, however, significantly more deshielded than those of the GIAO−CCSD(T)/tzp/dz values. These results again show that electron correlation contributions are important to obtain reliable ^{13}C NMR chemical shifts of these types of olefins. The good agreement between GIAO−SCF/tzp/dz and GIAO−CCSD(T)/tzp/dz calculated values of **1** appears to be fortuitous. Excellent correlation between GIAO−CCSD(T) calculated ^{1}H NMR chemical shifts and the available experimental data was also found (Table 4).

Highly strained pyramidalized olefins **1**, **2**, tricyclo[3.3.1.0^{3,7}]non-3(7)-ene **6**, and cubene **7** are not yet characterized experimentally. The MP2/cc-pVTZ computed structures are shown in Figure 1. The puckering angles (the angle between the two rings) of **1** and **2** were found to be 137.8° and 129.2°. The pyramidalization angles[6] (Φ) of **6** and **7** were found to be 54.3° and 86.2°, respectively. The C═C distances of **1**, **2**, **6**, and **7** are 1.406, 1.384, 1.374, and 1.419 Å, respectively. Vibrational frequencies of the experimentally unknown olefins **1** and **2** were calculated at the MP2/6-311G*//MP2/6-311G* level and are given in Table 5. ^{13}C NMR chemical shifts were computed at the GIAO−CCSD(T)/tzp/dz level. Calculated δ^{13}C of the olefinic carbons of **2**, **6,** and **7** are 212.4, 172.5, and 187.4, respectively. GIAO−CCSD(T)/tzp/dz calculated values of 172.5 and 187.4 for **6** and **7** are remarkably close to the GIAO−DFT calculated[7] (at the MPW1PW91/6-31G* level) values of 178.2 and 189.6, respectively. This indicates that the GIAO−DFT method is certainly reliable and affordable for much larger olefins. The high deshielding of the olefinic carbons in these strained olefins can be rationalized by the HOMO−LUMO energy gap. In fact, the olefinic carbon become increasingly deshielded with the decrease of the HOMO−LUMO gap.[7]



C_4H_4 **1** C_{2v} C_5H_6 **2** C_s

C_6H_8 **3** D_{2h} C_7H_{10} **4** C_s

C_8H_{12} **5** C_{2v} C_9H_{12} **6** C_{2v}

C_8H_6 **7** C_{2v}

Figure 1. MP2/cc-pVTZ structures of **1**−**7**.

It was not possible to compute the ^{13}C NMR chemical shifts of **1** at the GIAO−CCSD(T)/tzp/dz level (did not converge at

TABLE 4: Calculated[a] and Experimental[b] ^{1}H NMR Chemical Shifts

no	atom	GIAO−CCSD(T)/ tzp/dz//MP2/ cc-pVTZ	GIAO−CCSD(T)/ qzp/tzp//MP2/ cc-pVTZ	exptl
cyclopropene	H(CH)	6.60	7.00	7.06
	H(CH2)	0.94	0.94	0.93
cyclobutene	H(CH)	5.79	6.00	6.03
	H(CH2)	2.48	2.59	2.57
cyclopentene	H(CH)	5.58	5.72	5.60
	H(CH2)[c]	2.12	2.10	2.28
	H(CH2)	1.70	1.62	
3	H(CH2)	3.22	3.40	3.24[d]

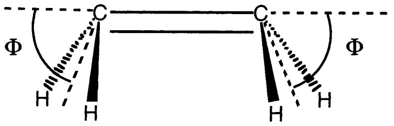
[a] ^{13}C NMR chemical shifts were referenced to TMS (calculated absolute shift, i.e., σ(H), tzp/dz = 31.92 and qzp/tzp = 32.08). [b] Exptl values were taken from ref 22. [c] Methylene carbons adjacent to the double bond. [d] Exptl value was taken from ref 3.

TABLE 5: MP2/6-311G* Calculated Frequencies[a] and IR Intensities of 1 and 2

no	frequencies in cm^{-1} (IR intensities in km/mol)
1	353 (4), 594 (133), 806 (0), 906 (13), 1022 (7), 1094 (1), 1119 (0), 1133 (4), 1147 (1), 1189 (0), 1313 (4), 1371 (22), 1549 (4), 1577 (1), 3089 (59), 3092 (54), 3243 (1), 3244 (8)
2	208 (0), 326 (1), 471 (66), 710 (5), 738 (4), 859 (14), 895 (1), 946 (2), 1014 (0), 1069 (6), 1088 (4), 1137 (1), 1175 (2), 1197 (1), 1223 (2), 1246 (1), 1247 (3), 1430 (6), 1487 (5), 1504 (1), 1527 (3), 3104 (35), 3105 (20), 3110 (27), 3175 (1), 3188 (20), 3245 (4)

[a] Not scaled.

TABLE 6: Calculated C═C Length, Relative Energies,[a] and δ^{13}C[b] with Respect to Pyramidalization Angle (Φ) of Ethylene



Φ in deg	r(C═C) in Å	energy in kcal/mol	δ^{13}C
0	1.330	0.0	121.2
18	1.335	4.4	124.9
36	1.352	17.3	136.7
54	1.385	38.3	157.7
72	1.446	66.8	188.7
90	1.545	99.2	222.1

[a] At the MP2/cc-pVQZ//MP2/cc-pVQZ level. [b] At the GIAO−CCSD(T)/qzp/tzp//MP2/cc-pVQZ level. [b] Exptl value is 123.3.

this level). However, it was possible to calculate them at the GIAO−CCSD(T)/qzp/tzp level. The computed δ^{13}C of the olefinic carbon of **1** is 69.4. Interestingly, the δ^{13}C of 69.4 is not that of a very deshielded peak as predicted[8] (455.6) by IGLO calculations. This again indicates the importance of electron correlation to obtain reliable ^{13}C NMR chemical shifts in this kind of an unusual system. The shielding of the olefinic carbon of **1** compared to that of **2** can be rationalized by the length of the C═C (1.406 Å) and hybridization (high p-character due to Walsh orbitals).

To check the structure−energy and the structure−chemical shift relationships of these pyramidalized olefins, we have calculated the ^{13}C NMR chemical shifts (at the GIAO−CCSD(T)/qzp/tzp//MP2/cc-pVQZ level) of the parent olefin (ethylene) at different C_{2v} geometries with different pyramidalization angles (Φ) from 0° to 90° (Table 6). At each point, we fully optimized the geometry at the MP2/cc-pVQZ level by keeping the pyramidalization angle constant. The resulting change in energies and ^{13}C NMR chemical shifts with respect to pyramidalization angles is plotted in Figure 2. As the pyramidalization angle increased from 0° to 90°, the MP2 energies and ^{13}C NMR chemical shifts of these conformers also systematically increased almost in a similar fashion. As a result, the relative energies of these conformers also correlated extremely well with the ^{13}C NMR chemical shifts, reflecting the linear dependence of the ^{13}C NMR chemical shifts with the internal strain of the molecules. As expected, with the increase the pyramidalization

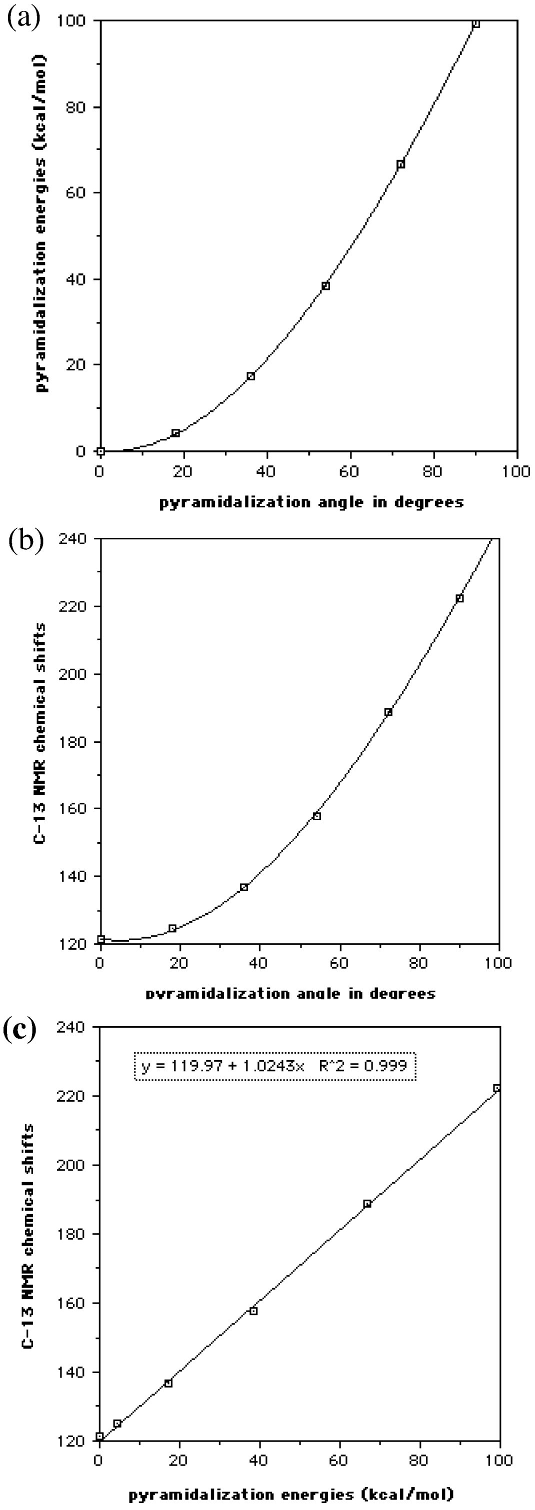


Figure 2. (a) MP2/cc-pVQZ calculated pyramidalization energies in ethylene. (b) GIAO−CCSD(T)/qzp/tzp//MP2/cc-pVQZ calculated ^{13}C NMR chemical shifts of ethylene with respect to pyramidalization. (c) ^{13}C NMR chemical shifts with respect to pyramidalization energies in ethylene.

angles, the C═C length of ethylene is increasingly becoming longer.

Conclusion

The ^{13}C NMR chemical shifts of bicyclic and related strained olefins were calculated using the ab initio/GIAO−CCSD(T) method. The calculated ^{13}C NMR chemical shifts of the olefins agree extremely well with the available experimental values. The δ^{13}C of the olefinic carbons of the yet unknown bicyclo[1.1.0]but-1,3-ene **1** and bicyclo[2.1.0]pent-1(4)-ene **2** were computed to be 69.4 and 212.4, respectively, at the GIAO−CCSD(T)/qzp/tzp//MP2/cc-pVTZ level. The δ^{13}C of the olefinic carbon of the intriguing (also yet unknown) cubene **7** was calculated to be 187.4 at the GIAO−CCSD(T)/tzp/dz//MP2/cc-pVTZ level. In a systematic study, the relative energies of the various conformers of ethylene were found to correlate extremely well with the ^{13}C NMR chemical shifts, reflecting the linear dependence of the ^{13}C NMR chemical shifts with the internal strain of the molecules.

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