

Molecular Modeling of Anti-Bredt Compounds

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The molecular structure and thermochemical stability of 40 bicyclic alkenes and imines containing between five and eight heavy atoms has been investigated computationally by high-level G3/B3LYP method. The same method was also used to study their building blocks: monocyclic alkenes and imines. The relative stability of isomers, standard enthalpies of formation and strain energies are discussed and compared. Our results suggest that molecular mechanics provides an unsatisfactory description of strain energies in bridgehead alkenes. Some bridgehead alkene and imine species represent structures which are not local minima on the potential energy surface and are hence unlikely to be isolated. Furthermore, some bicyclic alkenes and imines have open-shell 1,2-diradical character.

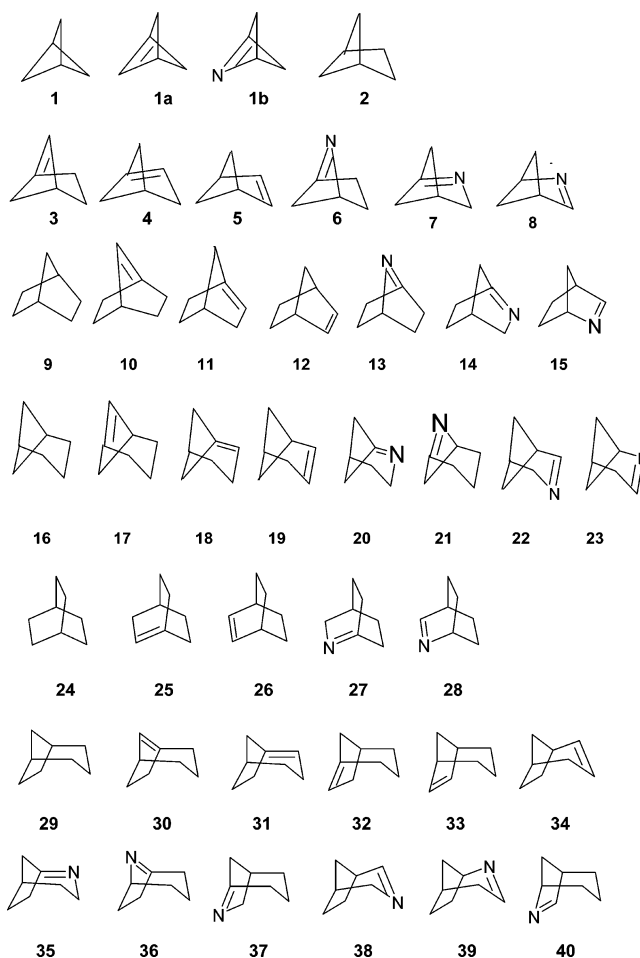
1. INTRODUCTION

Compounds with bridgehead double bonds are of considerable interest and have been studied by methods of synthetic and physical organic chemistry. The issues of C=C bond twisting and the resultant bridgehead atom rehybridization have been reviewed in some detail.¹ However, the important question of relative stabilities and enthalpies of compounds containing bridgehead double bonds has not been properly addressed. In the early work, Maier and Schleyer² used molecular mechanics (MM1 model) to study energetics (enthalpies of formation, hydrogenation, strain energies) and geometries of a large set of bridgehead olefins. In the same work olefinic strain energy (OS) was introduced as a quantifier of stability, reactivity and synthesizability for these compounds. Maier and Schleyer² suggested that if $OS < 17$ kcal/mol the compounds should be isolable, if 17 kcal/mol $< OS < 21$ kcal/mol the compound should be observable and if $OS > 21$ kcal/mol the compounds are unlikely to be isolated. Nonetheless, it was pointed out in the same work² that MM is not parametrized for bridgehead type double bonds. We are therefore interested in reexamining this class of compounds by more rigorous computational methods. The lack of MM parametrization is not surprising in view of relative instability (under standard conditions) of many bridgehead alkenes and imines which are either prepared in matrices at low temperatures^{3,4} or need to be stabilized by incarceration with the appropriate host.⁵ There is scarcity of thermochemical and structural data not only on bridgehead imines and alkenes but also on imines generally.⁶ We therefore used computational modeling to predict properties not only of bridgehead alkenes and imines but also of the related monocyclic alkenes and imines. Monocyclic derivatives are also used in calculation of standard enthalpies for the title compounds.

2. MOLECULAR MODELING METHODOLOGY

The bicyclic compounds studied are shown in Chart 1. The total electron energies were calculated with the Gaussian

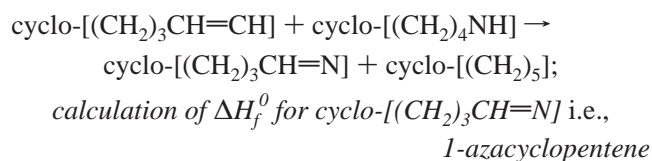
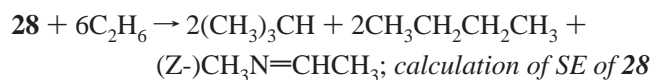
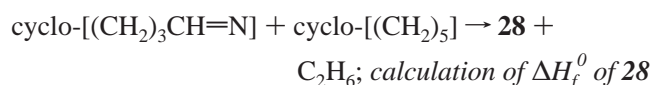
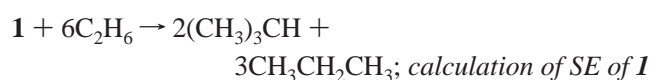
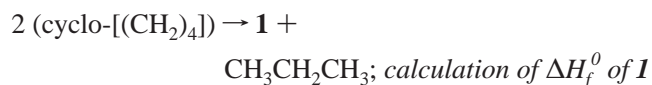
Chart 1



03 program⁷ using G3/B3LYP method.⁸ The method was shown to provide an accurate description of properties of strained hydrocarbons.⁹ Maximum average deviation of G3/B3LYP enthalpy from the experiment is 8 kJ/mol.⁸ Full geometry optimization for each molecule was performed at the B3LYP/6-311G** level in order to get accurate molecular geometries. Also, the harmonic vibrational analysis was used to check the number of imaginary frequencies and ensure

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that the obtained structures correspond to true minima on the potential energy surface. The strain energies (SE) and standard enthalpies of formation for the molecules in Chart 1 were deduced from enthalpies of isodesmic reactions based on group equivalent reaction schemes.¹⁰ The choice of isodesmic reactions was governed by the availability of experimental enthalpies for “reactants” and “products” in such reactions. The standard enthalpies of formation were also calculated independently using atomization reactions where atomic enthalpies were taken from the NIST source.¹¹ All isodesmic reactions used in the calculations of enthalpies and strain energies are listed explicitly in the Supporting Information. Nonetheless, a few isodesmic reactions are listed below as illustrative examples:



3. RESULTS AND DISCUSSION

The results of our calculations are summarized in Tables 1 and 2 and compared with MM1 results and with a few reported experimental enthalpies. The discussion shall be organized according to the classes of molecules which have similar structures or are isomeric.

Compound 1. In this class only compound **1** was calculated to be a true minimum. The related molecules **1a** and **1b** do not correspond to minima on the potential energy surfaces and are hence unlikely to be isolated. The levels of theory which were used to probe the existence of **1a** and **1b** were B3LYP/6-311G** and MP2/6-311G**. Their predicted lack of stability is contrary to the MM results, which indicate that the bicyclo[1.1.1]pentene may be observable.^{2,12} G3/B3LYP results often show considerable discrepancies in enthalpies and SE with regards to the MM results (Table 1). The MM values were generally lower than G3/B3LYP, which may explain the MM prediction about stability of **1a** and **1b**. In molecules with bridgehead double bonds we expect the G3/B3LYP results to be more consistent and reliable than MM because of the lack of MM parametrization for the anti-Bredt systems.

Compounds 2–8. In this class we find species **3**, **4**, **6** and **7** which contain bridgehead double bonds and the molecules **2**, **5** and **8** which do not. We shall outline the basic principles of our analysis in this section and apply them throughout the rest of this work. The insertion of nominal

CC/CN double bond into highly strained bicyclic systems such as **3–8** raises the possibility that such a bond may have a 1,2-diradical rather than double bond character. The 1,2-diradicals have unpaired electrons on neighboring, singly bonded atoms. Their spins may be either antiparallel (singlet diradical) or parallel (triplet diradical). The diradical character permits lengthening of a normally short CC/CN double bond and thus a reduction in SE. To investigate this possibility, we compared the calculated C=C/C=N bond lengths for **3–8** (Table 2) with experimental C=C/C=N bond lengths in norbornene¹³ and strained bicyclic imines.¹⁴ C=C bond length in norbornene is 1.336 Å, while imine C=N bond lengths are in the range of 1.286–1.292 Å, as determined by single-crystal X-ray diffraction.¹⁴ The species whose CC/CN bond lengths were much longer than these values were investigated for possible diradical character. This was achieved by UB3LYP/6-311G** method. Even though this is not a multideterminant method like CASSCF, it was demonstrated that it can provide results on diradicals which are in qualitative and quantitative agreement with a more sophisticated and computationally more demanding CASSCF method.¹⁵ The initial geometries in diradical calculations had bridgehead CC/CN bond lengths which were close to single bond values in e.g. azetidine (1.473 Å) or norbornene (1.566 Å). Starting geometries were then fully optimized at the UB3LYP/6-311G** level in order to detect possible diradical character and Wiberg bond indices¹⁶ calculated for singlet and triplet states pertaining to an open shell system. The results are presented in Table 3. For species **3**, **4**, **6** and **7** the triplet state is either lower in energy or very close to singlet energy. We thus conclude that these species are likely to have 1,2-diradical character and that bridgehead double bonds are unlikely in this class i.e., the Bredt rule is valid. The calculated CC/CN bond orders for open shell species (Table 3) show how in the triplet state, nominal CC/CN double bond lengths become comparable to single bonds which leads to the relaxation of molecular strain.

The comparison between total energies allows one to calculate strain energies. Maier and Schleyer² defined “olefinic strain” (OS) as the difference between SE of the most stable conformer of the saturated parent bicyclic hydrocarbon and SE of the corresponding bicyclic alkene derivative e.g. OS (**5**) = SE (**5**) – SE (**2**). The OS values reported previously² and in this work are compared in the Table 1 and show that the previous values² are considerably smaller than ours. In this work we have calculated SE for a closed shell, classically bonded species even when they have diradical character (Table 1) so as to make possible the comparison with Maier and Schleyer.² Our SE values for **3**, **4**, **6** and **7** are much higher than the MM values which are consistent with their diradical character. We predict that certain compounds in this group are much less stable and more difficult to isolate than suggested previously.²

Compounds 9–23. The class contains isomeric pairs e.g. [**9**, **16**], [**10**, **17**]. Bicyclo[2.2.1] group comprises **9–15** and bicyclo[3.1.1] group molecules **16–23**. Molecules **10**, **11**, **13**, **14**, **17**, **18**, **20** and **21** contain bridgehead double bonds, while the reference molecules **9**, **12**, **15**, **19**, **22** and **23** do not. SE and OS values have been derived as discussed previously and are shown in Table 1.

The most interesting observation concerns relative stability and SE of isomeric pairs. For instance, within the [**9**, **16**]

Table 1. Standard Enthalpies of Formation ($\Delta H_f^\circ/\text{kJ mol}^{-1}$), Strain Energies (SE/kJ mol⁻¹) and Olefinic Strain Energies (OS/kJ mol⁻¹) for Alkenes and Imines^{a-c}

compound	ΔH_f° isod	ΔH_f° atom	ΔH_f° (ref 2) or exp.	SE	SE (ref 2) or exp.	OS	OS (ref 2)
1	195.7	203.3	286.4	277.4	358.4		
2	52.0	60.2	76.7	154.9	172.1		
3*	473.9	480.1	324.8	460.9	311.1	306	138.9
4*	489.7	495.9	290.5	476.2	276.8	321.3	104.6
5	225.4	231.6	(251) ¹¹	206.0		51.1	
6*	502.2	514.1		447.9			
7*	556.5	568.4		501.6			
8	241.1	253.0		171.2			
9	-62.1	-54.4	-55.5 (-53.6) ¹⁸	60.9	63.2		
10*	381.9	388.7	214.5	390.1	224.2	329.2	161.1
11	273.3	280.1	199.5	281.0	209.1	220.1	146
12	75.6	82.4	(90 ± 30) ¹¹	77.3		16.4	
13*	456.1	468.6		422.9			
14	308.0	320.5		274.4			
15	93.6	106.2		44.8			
16	10.9	18.5	25.0	133.7	143.8		
17	304.4	311.1	297.9	312.3	307.6	178.6	163.6
18	301.6	308.3	254.9	309.3	264.5	175.6	120.9
19	122.2	128.9		123.4		-10.3	
20	330.2	343		296.8			
21	311.3	324.1		278.3			
22	159.5	172.3		110.1			
23	153.3	166.1		103.8			
24	-100.0	-92.7	-99.4 (-99.04) ¹¹	43.3	42.7		
25	209.6	216.0	178.7	237.5	211.7	194.2	169
26	20.0	24.6	(20.8) ¹¹	40.1		-3.2	
27	240.2	253.5		227.9			
28	39.8	53.2		12.5			
29 (endo)	-108.2	-100.0	-98.9	35.8	43.3		
29 (exo)	-81.3	-73.1	-70.3	64.4	70.2		
30 (endo/exo)	198.7	206.0	163.9	227.9	196.9	192.1	153.6
31 (Z)	127.1	134.4	129.8	155.8	162.8	91.5	119.7
31 (E)	207.0	214.3	186.8	235.7	219.9	199.9	119.7
32 (exo)	145.4	151.6	132.1	172.9	165.1	108.5	113.8
32 (endo)	147.5	153.7	124.0	175.0	157	139.2	113.8
33 (exo)	46.0	52.2		62.1		-2.3	
33 (endo)	23.5	29.7		39.6		3.8	
34	9.1	16.4		31.4		-4.4	
35 (Z)	154.0	165.9		140.3			
35 (E)	242.3	254.2		228.6			
36 (endo only stable)	213.8	225.8		200.6			
37 (exo)	164.7	176.7		151.0			
37 (endo)	165.6	177.5		151.8			
38	51.8	63.8		22.1			
39	43.2	55.2		13.5			
40 (endo)	44.1	56.1		15.3			
40 (exo)	64.0	75.1		34.3			
cyclobutane		30.8	(26.3) ¹¹				
cyclobutene		165.9	(157) ¹¹				
azetidine		102.8					
1-azetine		196.7		101.5			
cyclopentane		-71.3	(-76.4) ¹¹				
cyclopentene		39.2	(36.0) ¹¹				
pyrrolidine		1.4	(-3.4) ¹¹				
1-azacyclopentene	69.0	71.8	(63.0) ¹¹	-2.8			
cyclohexane		-118.6	(-123.1) ¹¹				
cyclohexene		6.5	(-4.32) ¹¹				
piperidine		-41.9	(-47.2) ¹¹				
1-piperidine cyclo-[(CH ₂) ₄ CH=N]	42.6	47.1					
cycloheptane		-113.0	(-117.9) ¹¹				
cycloheptene		-1.6	(-4.3) ¹¹				
azacycloheptane		-37.1	(-45.0) ¹¹				
tetrahydro-azepine cyclo-[(CH ₂) ₅ CH=N]	43.0	48.7					

^a The numbers in brackets followed by superscripts correspond to experimental enthalpies and the matching literature sources, respectively.^b Superscripts indicate sources of experimental enthalpies which were used to calculate SE via isodesmic reactions. ^c Structures in this table refer to closed-shell species. Those with possible diradical character are indicated by an asterisk and their open-shell structures and energies are given in Table 3.

and [12, 19] pairs, the isomers **9** and **12** are more stable. This can be expected, because **16** and **19** contain a highly

strained four-member ring. However, within the [10, 17] and [13, 21] pairs, **17** and **21** isomers are more stable. One can

Table 2. Molecular Structure Parameters for Closed Shell Species of Bridgehead Alkenes and Imines^{a,b}

compound	r _{C=C=N}	Θ	χ ₁	χ ₂	<CCC	<CNC
3*	1.387	46.8	69.5	53.3	107.3	
4*	1.382	39.2	87.9	49.3	88.5	
5	1.336					
6*	1.325	60.9				71.3
7*	1.312	53				93.3
8	1.283					
10*	1.380	39.2	61.1	55.7	112.2	
11	1.355	51.3	65.2	37.2	104.0	
12	1.337					
13*	1.297	68.1				85.4
14	1.293	49				102.6
15	1.282					
17	1.363	46.8	55.3	38.3	117.6	
18	1.353	57.2	76	41.7	90.7	
19	1.337					
20	1.287	47.6				108.7
21	1.316	49.4				84.4
22	1.276					
23	1.275					
25 ⁵	1.358	48.4	50.5	46.3	112.3	
26	1.335					
27 ⁴	1.293	56.1				108.4
28	1.279					
30	1.358	45.9	47.4	44.4	62.7	
31 ⁵	1.342	39.7	52.7	26.6	104.6	
32	1.343	33.8	44.5	23.1	113.5	
33	1.334					
34	1.338					
35 ⁴	1.279	28.3				111.5
36	1.294	56.5				101.0
37	1.283	30.9				105.2
38	1.274					
39	1.274					
40	1.278					

^a Asterisk indicates that the species have open-shell, diradical character (see Table 3). ^b Superscripts indicate references describing closed shell species isolated under special conditions.

rationalize this “anomaly” by suggesting that the strain originating in the bridgehead double bond in **17** and **21** can be efficiently relieved by two large, flexible, six-member

rings. In **10** and **13** this is impossible, because the bridgehead bond is not part of a six-member ring so both species have a diradical character (Table 3). Similar arguments apply to [**11**, **18**] and [**14**, **20**] pairs, where **11** and **14** are the more stable isomers. This can be rationalized by suggesting that while six-member rings efficiently relieve bridgehead strain in all four isomers, **18** and **20** retain highly strained four-member rings. Analogously, the presence of a four-member ring makes **22** and **23** less stable than isomer **15**.

We note at this point that the possibility of devising general, qualitative rules for the stability of bridgehead alkenes had been questioned.¹ However, the consideration of ring sizes and the location of a double bond within the molecule offer generally valid and useful insights. The introduction of nitrogen does not lead to inversion of relative stabilities of imines vs their alkene counterparts.

Besides energy considerations, the structure of the bridgehead double bond is also of interest. Structural parameters obtained from geometry optimization at B3LYP/6-311G** level are given in Table 2.

The calculated bridgehead C=C/C=N bond lengths are longer than in nonbridgehead counterparts, e.g. C=C bond lengths in **17** and **18** are longer than in **19**. Two other structural parameters, bond twist (θ) angle and degree of rehybridization of bridgehead π-centers, are also of interest.¹ These parameters are defined in the Appendix and follow the conventions used in the previous work.^{1,17} The conclusion which can be drawn from parameters in Table 2 is that twisting and rehybridization of the C=N bridgehead bond is larger than the corresponding distortion of its C=C counterpart.

Compounds 24–40. In this class we analyze the following sets of isomers: [**24**, **29**], [**25**, **30**, **31**, **32**], [**26**, **33**, **34**], [**27**, **35**, **36**, **37**], [**28**, **38**, **39**, **40**]. The principles of analysis are the same as above. One general characteristic of the compounds in this class is that there are no four-member rings. We could thus expect differences in relative isomer stability to be much reduced compared to the previous classes.

Table 3. UB3LYP/6-311G** Energies (au), Relative Triplet State Energy (ΔST/kJ mol⁻¹), ZPE (au), Bridgehead Bond Lengths and Bond Indices for Bicyclic Alkenes and Imines with Diradical Character

species	UB3LYP/6-311G** (ΔST)	ZPE (au)	C=C–C/C=N–C bond lengths (Å)	Wiberg bond indices
3-singlet	–233.324942	0.119985	1.386	1.73
3-triplet	–233.316802 (21.4)	0.119285	1.514	1.02
4-singlet	–233.3150442	0.119894	1.379	1.80
4-triplet	–233.3271493 (–31.8)	0.118417	1.482	1.02
6-singlet	–249.3759489	0.107078	1.326, 1.585	1.57, 0.84
6-triplet	–249.3744926 (3.8)	0.108267	1.449, 1.510	1.04, 0.96
7-singlet	–249.3547688	0.106848	1.312, 1.517	1.65, 0.95
7-triplet	–249.3760272 (–55.8)	0.108199	1.406, 1.494	1.13, 0.98
10-singlet	–272.6707241	0.149763	1.380	1.81
10-triplet	–272.6818173 (–29.1)	0.149040	1.495	1.03
13-singlet	1 Imag.freq.			
13-triplet	–288.7372461	0.138177	1.485, 1.425	0.98, 1.07
17-singlet	–272.7103934	0.150471	1.363	1.77
17-triplet	–272.6584166 (136.4)	0.148021	1.512	1.02
21-singlet	–288.7651605	0.138914	1.316, 1.495	1.72, 0.98
21-triplet	–288.7162875 (128.3)	0.137271	1.441, 1.509	1.05, 0.96
30-singlet	–312.0640405	0.180466	1.358	1.79
30-triplet	–312.0249063 (102.7)	0.178118	1.478	1.05
36-singlet	–328.11731628	0.168523	1.295, 1.468	1.76, 0.99
36-triplet	–328.07909882 (100.3)	0.167260	1.478, 1.410	1.478, 1.410

This expectation is clearly born out in e.g. [24, 29] set. The stability of **24** is intermediate between the stabilities of the two conformers of **29** (Table 1).

Calculated enthalpies in the set [25, 30, 31, 32] show that **25** and **30** are less stable than **31** or **32**. This can be rationalized by noting that the C=C bond in the first two isomers lies within a six-member ring, while in the last two isomers it lies within the more flexible seven-member ring. The same arguments and conclusions apply to the isomeric set of imines i.e., the [27, 35, 36, 37].

In the [26, 33, 34] set, **34** is the most stable isomer and **26** the least stable one. This can be attributed to the location of C=C bond. In **34** the bond is located within six- and seven-member rings, while in **26** the location of the same bond is within two six-member rings. Nonetheless, the differences in relative stabilities of compounds in this class are small and approach the limits of the accuracy range of the G3/B3LYP method. The relative stabilities of isomers in the last set [28, 38, 39, 40] are also close to the limits of the computational method used.

We have also noticed large differences in stabilities of geometrical isomers of **29**, **31** and **35**. In both **31** and **35**, the exo conformers are more stable. This prediction agrees with the experimental study⁴ performed on **35** which has shown that the exo form (Z-form) is 20 times more abundant than the endo form (E-form) in an argon matrix at 12K. This comparison between a very rare experimental observation and our modeling results demonstrates the usefulness of the latter. Many bridgehead compounds can only be prepared in a matrix from suitable precursors e.g. by photolysis. In such cases the identification of anti-Bredt products is made spectroscopically, but the interpretation of spectra is complicated by the presence of many species including the precursor. Our modeling results provide useful guidance regarding which species are likely to predominate on the basis of their relative stabilities. Our results are relevant for the gas phase with little interaction between molecules. This environment approximates well the inert argon matrix which is used for generation of these compounds in the laboratory.

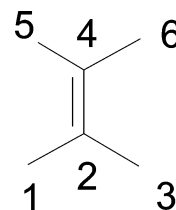
4. CONCLUSION

The modeling of structure, stability and strain energy of bicyclic, bridgehead alkenes and imines has shown that ring size and location of the C=C/C=N bond are general factors which describe and rationalize the thermodynamic stability of anti-Bredt compounds. Some of the bicyclic imines were found to have 1,2-diradical character i.e., they are devoid of classical double bond.

The fact that experimental data for the compounds studied are very scarce and that some species have diradical character makes devising a MM parametrization scheme impractical.

APPENDIX

Geometrical parameters of a bridgehead double bond:



Twist angles: $\Phi_1 = \angle 3245$; $\Phi_2 = \angle 1246$; $\theta = (\Phi_1 + \Phi_2)/2$; out-of-plane bending angles: $\chi_1 = \angle 1243$; $\chi_2 = \angle 5426$; $\omega = (\chi_1 + \chi_2)/2$; in bridgehead imines: $\theta = \Phi_1$ or Φ_2 ; $\Phi = \angle \text{CNC}$ valence angle.

Supporting Information Available: List of isodesmic reactions, calculated total energies, optimized geometries and zero point energies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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