of acetylene and fulminic acid. FMO analysis predicts the transition-state HOMO to be formed from the interaction of the acetylene HOMO with the LUMO of fulminic acid, suggesting little p-type density on oxygen and large p-type density on the carbon and nitrogen of the fulminic acid fragment. The projected electron density of the transition-state HOMO is given in Figure 10. The HOMO shows large oxygen and nitrogen p-type densities and very little density on carbon. The acetylene HOMO actually interacts with a linear combination formed by the addition of the fulminic acid HOMO and LUMO. This prototypical 1,3-cycloaddition certainly involves significant HOMO–HOMO interaction.

Additionally, the involvement of the HOMO–HOMO interaction explains a peculiarity noted by Komornicki et al. They performed a force constant analysis of the transition state and noted the force constant along the forming C–O bond to be about 10 times as large as the force constant along the forming C–C bond.[16] The electron density map of the transition-state HOMO (Figure 10) clearly indicates considerable density in the region forming a bond between carbon and oxygen but little density in the region forming the C–C bond. FMO theory predicts a stronger C–C interaction than C–O on the basis of the coefficients in the fulminic acid LUMO. This is obviously invalid and is corrected by adding in the HOMO of fulminic acid to create a sizable oxygen coefficient while significantly reducing the carbon coefficient.

Conclusion

Evidently, the FMO approximation of HOMO–LUMO interactions dominating the transition state is too severe. The HOMO–HOMO interaction must be included to obtain adequate description. The HOMO of the transition state is determined primarily from the HOMO–HOMO interaction of the reactants. The *energy* of the transition state is determined by LUMO interactions as well.

Acknowledgment. This work was supported in part by USPH NIH Grant GM-30369. We are also indebted to Prof. Paul v. R. Schleyer for discussions and exchange of information in advance of publication. A. S. also thanks the Humboldt Stiftung, Bonn, DFR, for travel support that made possible these discussions.

Registry No. H_2CO, 50-00-0; LiH, 7580-67-8; CH_3CHO, 75-07-0; HCCH, 74-86-2; HCNO, 506-85-4.

---

[16] Some controversy exists concerning the definition of the force constants in the transition state of this reaction; see: Hiberty, P. C.; Ohanessian, G.; Schlegel, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 719.

Hyperstable Olefins: Further Calculational Explorations and Predictions

Alan B. McEwen[†] and Paul von Ragué Schleyer*

Contribution from the Institut für Organische Chemie, Universität Erlangen—Nürnberg, D-8520 Erlangen, Federal Republic of Germany. *Received October 15, 1985*

Abstract: Although olefins at bridgehead positions are generally destabilized by strain, such locations may actually be preferred in larger polycyclic systems. A large number of such hyperstable bridgehead olefins have been explored by using Allinger's MM2 force field to calculate heats of formation and strain energies. In addition to monoolefins, systems with two double bonds at bridgeheads and tetracyclic olefins are predicted to be hyperstable. "In" rather than "out" pyramidalization of saturated bridgehead carbons in both bridgehead olefins and in the parent hydrocarbons is favored in several instances. The most stable bridgehead olefin (*E* isomer of out bicyclo[4.4.3]trideca-1-ene) and double bridgehead diene (*EE* isomer of bicyclo[4.4.3]-trideca-1,6-diene) studied have olefin strains of −16.8 and −31.7 kcal/mol, respectively. Two tetracyclic olefins (tetracyclo[8.4.4.4^{3,8}.0^{2,9}]docosan-2(9)-ene, and tetracyclo[9.5.5.5^{3,9}.3^{2,10}]hexacosan-2(10)-ene) are predicted to have *endothermic* cis heats of hydrogenation.

Bridgehead olefins have fascinated chemists ever since Bredt noted that double bonds avoid the ring junctions in camphane and pinane systems.[1,2] Recently, Maier and Schleyer recognized that the reverse can be expected in medium-size polycyclic ring systems where bridgehead double bonds may actually be preferred.[3] These "hyperstable olefins" have *negative* olefin strain energies (OS): the strain energy of the olefin is *less* than that of its parent hydrocarbon. A qualitative correlation was found between calculated (MM1 force field) OS values, which measure the thermodynamic driving force toward reaction, and experimentally observed stabilities and reactivities.[3a] Due to their negative OS values, hyperstable bridgehead olefins have heats of hydrogenation ΔH_{hyd} lower than normal (i.e., the values found for acyclic olefins with the same degree of substitution); these ΔH_{hyd} are even lower than those of medium size ring cycloalkenes (Table I).[5,6]

Several hyperstable bridgehead olefins were reported shortly after Maier and Schleyer's paper appeared. The predicted hyperstability of bridgehead olefins in medium size ring systems[3a] was first experimentally corroborated by de Meijere et al.'s ob-

---

[†] Present address: Department of Chemistry, University of California, Berkeley, Berkeley, CA 94720.

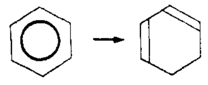
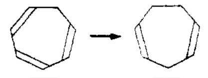
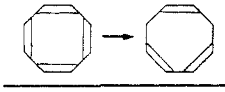
[1] Bredt, J.; Thoret, H.; Schmitz, J. *Liebigs Ann. Chem.* **1924**, *437*, 1.

[2] Reviews: (a) Buchanan, G. L. *Chem. Soc. Rev.* **1974**, *3*, 41. Liebman, J. F.; Greenberg, A. *Strained Organic Molecules*; Academic: New York, 1978. (b) Shea, K. J. *Tetrahedron* **1980**, *36*, 1683. (c) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311. (d) Szeimies, G. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1983; Vol. III, Chapter 5, p 299. Also see ref 9.

[3] (a) Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1891. (b) Warner, P. M.; Peacock, S. *J. Comput. Chem.* **1982**, *3*, 417. (c) Precedents are found in the enhanced stability of planar bridgehead centers in medium size polycyclic ring systems in carbocations: Parker, W.; Trouter, W. C.; Watt, C. I. F.; Chang, L. W. K.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 7121. The flattened bridgehead position of bicyclo[3.3.3]undecane (Manxane) system: Murray-Rust, P; Murray-Rust, J.; Watt, C. I. F. *Tetrahedron* **1980**, *36*, 2799. Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1975**, *97*, 4136. Coll, J. C.; Crist, D. R.; Barrio, M. d. C. G.; Leonard, N. J. *J. Am. Chem. Soc.* **1972**, *94*, 7092. And flattened amine groups at bridgehead positions (ref 4). Also see: Bly, R. S.; Hossain, H. M.; Leboida, L. *J. Am. Chem. Soc.* **1985**, *107*, 5549.

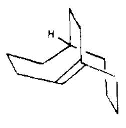
0002-7863/86/1508-3951$01.50/0

Table I.[a] Heats of Hydrogenation and Olefin Strain (OS) for Selected Cycloalkenes

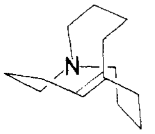
alkene	ΔH_{hyd}[b]		OS[c]		
cis-cyclopentene	26.9[d]	(26.0)[e]	−0.7	(−0.6)	[−0.6][f]
cis-cyclohexene	28.6	(27.1)	1.0	(0.5)	[0.9]
cis-cycloheptene	26.5	(25.8)	−1.1	(−0.8)	[−0.7]
trans-cycloheptene					[19.6]
cis-cyclooctene	23.5	(23.0)	−4.1	(−3.6)	[−2.7]
trans-cyclooctene		(32.2)		(5.6)	[6.3]
cis-cyclononene		(23.6)		(−3.0)	
trans-cyclononene		(26.5)		(−0.1)	
cis-cyclodecene	21.7	(20.7)	−5.9	(−5.9)	[−5.4]
trans-cyclodecene		(24.0)		(−2.6)	[−4.0]
cis-cyclododecene		(26.3)		(−0.3)	
trans-cyclodecene		(26.8)		(0.2)	
	−5.6		−33.2		
		(14.6)		(−12.0)	
		(18.1)		(−8.5)	

[a] Energies in kcal/mol. [b] See: Jensen, J. L. *Prog. Phys. Org. Chem.* **1976**, *12*, 189. [c] OS defined here as the difference in experimental heat of hydrogenation from that of *trans*-2-butene (−27.6 gas, −26.6 in AcOH) taken as reference. [d] Gas phase. [e] Solution (AcOH). [f] Calculated values using the cycloalkane analogue as the reference (MM1).[6a]

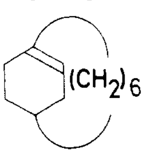
servations that bicyclo[4.4.2]dodeca-1-ene (**1**) resists hydrogenation.[7] The hyperstable bridgehead olefin 1-azabicyclo[4.4.4]tetradeca-5-ene (**2**), which showed an intramolecular N-olefin interaction by photoelectron spectroscopy, was calculated by Alder et al. to have a heat of hydrogenation of only 7.6 kcal/mol (MM2).[8] Bicyclo[6.2.2]dodeca-1(9)-ene (**3**) also was shown to be a hyperstable bridgehead olefin by two groups.[9,10] Roth was unable to determine the heat of hydrogenation of **3** experimentally due to the slow rate of hydrogenation but reported a calculated OS value of −14.2 kcal/mol (MM2).[9] Two other bridgehead olefins, bicyclo[8.2.2]tetradeca-1(12)-ene (**4**)[11] and "in" bicyclo[4.4.4]tetradeca-1-ene (**5**),[12] also were found to resist hydrogenation.



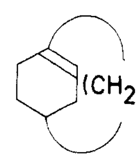
1



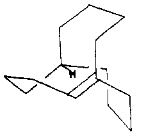
2



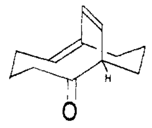
3



4

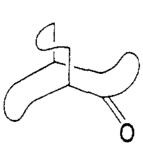


5

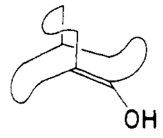


6

Hyperstable enols with bridgehead double bonds have been implied by several studies.[13,14] For example, the observed facile base-catalyzed deuterium exchange of the bridgehead proton in ketone **6** can be attributed to the formation of a hyperstable enol with the double bond at the bridgehead position.[14]



ketone



bridgehead enol

Some medium ring bridgehead and polycyclic olefins are of biological interest.[2b] An important class of antileukemic and tumor agents contain the bridgehead olefin bicyclo[5.3.1]undeca-1(10)-ene moiety.[15] Difficulties in hydrogenating tetrasubstituted double bonds in steroids and other natural products typically have been attributed to steric hindrance inhibiting approach to the metal catalyst surface.[16] This kinetic factor certainly may contribute to such problems, but there have been scattered reports of difficulties in effecting the hydrogenation of "exposed" olefins. This can now be attributed to reduced thermodynamic driving force (i.e., hyperstability).

Dienes with two bridgehead olefins, double anti-Bredt compounds, recently have been prepared[10,14,17] and have been proposed as reactive intermediates.[18] In fact, as Warner and Peacock have shown, double bridgehead dienes with both *trans*-olefin units in nine-membered rings may be hyperstable (MM2).[19] Of several double bridgehead dienes synthesized by Tobe et al., **7**–**9** are thermally persistant.[10,17a] The two isomers of diene **10** were isolated by Engel et al. from the triplet-sensitized irradiation of 1,4-dicyclopropyl-2,3-diazabicyclo[2.2.2]octa-2-ene.[17b] Shea et

---

(4) (a) Alder, R. W. *Acc. Cem. Res.* **1983**, *16*, 321. (b) Alder, R. W.; Arrowsmith, R. J. *J. Chem. Res. Synap.* **1980**, *163*; *J. Chem. Res., Miniprint* **1980**, 2301. (c) Alder, R. W.; Arrowsmith, R. J.; Casson, A.; Sessions, R. B.; Heilbronner, E.; Kovac, B.; Huber, H.; Taagepera, M. *J. Am. Chem. Soc.* **1981**, *103*, 6137. Alder, R. W.; Moss, R. E.; Sessions, R. B. *J. Chem. Soc., Chem. Commun.* **1983**, 997, 1000. Alder, R. W.; Orpen, A. G.; Sessions, R. B. *J. Chem. Soc., Chem. Commun.* **1983**, 999.

(5) Conn, J. B.; Kistiakowsky, G. B.; Smith, E. A. *J. Am. Chem. Soc.* **1939**, *61*, 1868. Prelog, V. *J. Chem. Soc.* **1950**, 420. Turner, R. B.; Goebel, P.; Mallon, B. J.; Doering, W. v. E.; Coburn, J. F.; Pomerantz, M. *J. Am. Chem. Soc.* **1968**, *90*, 4315.

(6) (a) Allinger, N. L.; Spraque, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 5734. (b) Osawa, E.; Musso, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1. Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, DC, 1982.

(7) Kukuk, H.; Proksch, E.; De Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 306.

(8) Alder, R. W.; Arrowsmith, R. J.; Boothby, C. S. J.; Heilbronner, E.; Zhong-zhi, Y. *J. Chem. Soc., Chem. Commun.* **1982**, 940.

(9) Roth, W. R. *Nachr. Chem. Tech. Lab.* **1983**, *31*, 964.

(10) Tobe, Y.; Kishimura, T.; Kakiuchi, K.; Odaira, Y. *J. Org. Chem.* **1983**, *48*, 551. Tobe, Y.; Ueda, Y.; Matsumoto, M.; Sakai, Y.; Odaira, Y. *Tetrahedron Lett.* **1982**, *23*, 537.

(11) Hopf, H., private communication.

(12) McMurry, J. E.; Hodge, C. N. *J. Am. Chem. Soc.* **1984**, *106*, 6450.

(13) Maier, W., private communication.

(14) Doering, W. v. E.; Schmidhauser, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 5025.

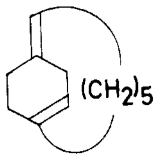
(15) Wani, M. C.; Taylor, H. L.; Wall, M. E.; Coggon, P.; McPhail, A. T. *J. Am. Chem. Soc.* **1971**, *93*, 2325. Miller, R. W.; Powell, R. G.; Smith, C. R., Jr.; Arnold, E.; Clardy, J. *J. Org. Chem.* **1981**, *46*, 1469. Shea, K. J.; Gilman, J. W. *Tetrahedron Lett.* **1984**, *25*, 2451.

(16) Akhorem, A. A.; Titov, Y. A. *Total Steroid Synthesis*; Plenum: New York, 1970. Fieser, L.; Fieser, M. *Steroids*; Reinhold: New York, 1959.

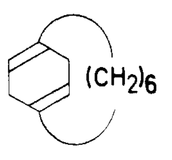
(17) (a) Tobe, Y.; Fukuda, Y.; Kakiuchi, K.; Odaira, Y. *J. Org. Chem.* **1984**, *49*, 2012. (b) Engel, P. S.; Keys, D. E.; Kitamura, A. *J. Am. Chem. Soc.* **1985**, *107*, 4964. (c) Shea, K. J.; Burke, L. D.; Doedens, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 5305. (d) Shea, K. J.; Burke, L. D. *J. Org. Chem.* **1985**, *50*, 725. (e) Warner, P.; Chu, I.-S.; Boulanger, W. *Tetrahedron Lett.* **1983**, *24*, 4165. Shea, K. J.; Greeley, A. C.; Nguyen, S.; Beauchamp, P. D.; Wise, S. *Tetrahedron Lett.* **1983**, *24*, 4173. (f) Wiseman, J.; Vanderbilt, J. *J. Am. Chem. Soc.* **1978**, *100*, 7730. (g) Rastetter, W. H.; Richard, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 3893. Rastetter, W. H.; Richard, T. J.; Jones, N. D.; Chaney, M. O. *J. Chem. Soc., Chem. Commun.* **1978**, 377. Rastetter, W. H.; Richard, T. J.; Bordner, J.; Hennessee, G. L. A. *J. Org. Chem.* **1979**, *44*, 999.

(18) Warner, P.; Boulanger, W. *Tetrahedron Lett.* **1980**, *21*, 123. Shea, K. J.; Wise, S. *Tetrahedron Lett.* **1978**, 2283. Turkenburg, L. A. M.; Van Straten, J. W.; De Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1980**, *102*, 3256.

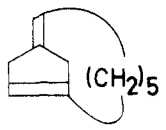
(19) Warner, P.; Peacock, S. *Tetrahedron Lett.* **1983**, *24*, 4169.



7

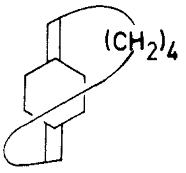


8

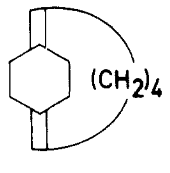


9

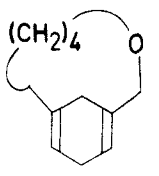
al. prepared **11** enroute to the metacyclophane analogue.[17c] Each of the double bonds in **7**–**11** is contained in *trans*-cycloalkene ring fragments larger than nine-membered. Less stable double bridgehead dienes with smaller *trans*-cycloalkene moieties also have been prepared, notably the thermally labile bicyclo[4.2.2]-deca-1,6-diene (**12**)[17f] and the two bicyclo[4.3.2]deca-1,5-diene systems **13**[17d] and **14**.[17c] Both **15a** and **15b** are stable due to ring constraints; however 15c rapidly undergoes a Cope rearrangement.[17g] Furthermore, the double bridgehead diene bicyclo[5.3.2]dodeca-1,6,11-triene (**16**) was synthesized to investigate orthogonal double bonds.[14] Bridged annulenes and similar conjugated bicyclic systems (e.g., cyclophanes) also contain double bridgehead diene moieties.[20]



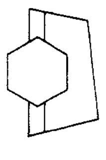
(*E*)-**10**



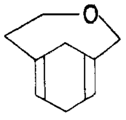
(*Z*)-**10**



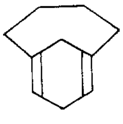
11



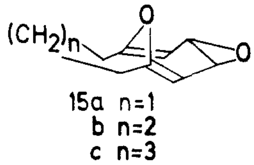
12



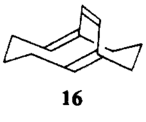
13



14



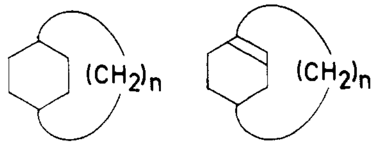
15a n=1
b n=2
c n=3



16

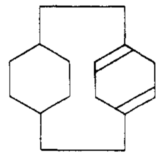
Several cyclophanes undergo only partial hydrogenation to polycyclic olefins, which resist further reduction.[11,21] Hydrogenation of [2.2](1,4)cyclophane forms a diene (proposed to be **17**) which takes up hydrogen much slower.[21a] Both [2.2.2]-(1,2,4)cyclophane and [2.2.2](1,2,4)(1,2,5)cyclophane do not hydrogenate completely, leading to the polycyclic olefin **18**[21b] and diene **19**,[11] respectively. Hyperstability is now recognized to be the cause of this behavior.[22]

Chart I. Bicyclo[*n*.2.2] Bridgehead Olefins and Saturated Hydrocarbons Investigated

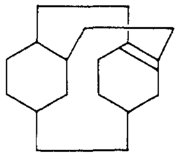


X Xa

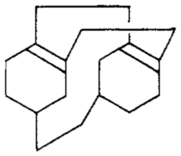
n = 1–10



17



18



19

The importance of strain in helping determine reactivity is well recognized.[2c,22] In polycyclic systems much of the strain often is associated with the bridgehead positions. Bridgehead groupings in certain medium size ring bicyclic compounds prefer to flatten,[3c] thus favoring sp^2 centers. In other cases, sp^3 bridgehead groups prefer to pyramidalize inward. This behavior has been exploited extensively by Alder to study intrabridgehead interactions.[4a] Inward orientations also are a basis for cryptand chemistry.[24]

We now have investigated additional bridgehead olefins in bicyclic and in tetracyclic systems calculationally. We predict a number of presently unknown compounds to be hyperstable. Two unconjugated olefins are predicted to have *endothermic* cis heats of hydrogenation, previously only associated with the partial reduction of benzene and aromatic compounds.

Method

The MM2 empirical force-field program[25] was used to optimize all structures and to calculate the heats of formation and strain energies. Great care was taken to find the global minimum for each molecule. Many starting geometries were employed, and only the lowest energy conformations are reported here. However, this is a trial-and-error process, and particularly in large ring systems, it is impossible to ensure that the absolute lowest energy conformations have been found. The accuracy of energies and geometries calculated by such method is well documented.[6] The OS values were determined as previously described.[3a] In order to evaluate the OS values, we used the saturated hydrocarbon resulting from "out" hydrogenation of the olefin since this is the stereochemistry expected experimentally (at least initially) from catalytic reduction.

Geometries of the minimum energy conformations are available in the supplementary material. These conformations are represented roughly in the structural drawings.

Results and Discussion

I. Bridgehead Olefins. We investigated olefin stability at bridgehead positions in a number of bicyclic ring systems: the

---

[20] For a discussion of double bridgehead dienes, see ref 2b and 2c.

[21] (a) Cram, D. J.; Allinger, N. L. *J. Am. Chem. Soc.* **1955**, *77*, 6289. (b) Aalbersberg, W. G. L.; Vollhardt, K. P. C. *Tetrahedron Lett.* **1979**, *22*, 1939. Murad, A. E.; Hopf, H. *Chem. Ber.* **1980**, *113*, 2358. (c) Boekelheide, V. *Top. Curr. Chem.* **1983**, *113*, 87. Brosz, C., unpublished observations, Erlangen.

[22] McEwen, A. B., unpublished results, Erlangen.

[23] Stirling, C. J. *Tetrahedron* **1985**, *41*, 1613. Schneider, H.-J.; Schmidt, G.; Thomas, F. *J. Am. Chem. Soc.* **1983**, *105*, 3556.

[24] Dietrich, B. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic: London, 1984; Vol. 2, and references cited therein.

[25] Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

Table II. MM2 Optimized Energies (kcal/mol) and Derived Values[a] for Bicyclo[*n*.2.2] Systems (Chart I)

x	*n*	ΔH_t	strain *E*	OS	ΔH_{hyd}
21	1	47.7[b]	50.0	34.9	-61.0
21a		-13.3[b]	15.1		
22	2	42.7[b]	50.6	40.4	-66.5
22a		-23.8[b]	10.2		
23	3	22.2[b]	35.6	20.6	-46.8
23a		-24.6[b]	14.9		
24	4	9.19[b] (9.35)[c]	28.2 (32.3)	7.9 (7.4)	-34.0 (-33.0)
24a		-24.8[b] (-23.6)[c]	20.4 (24.9)		
25	5	-1.91	26.8	-6.3	-19.3
25a		-21.2	33.1		
3	6	-11.1	23.4	-10.6	-14.9
3a		-26.0	34.0		
26	7	-17.2	23.0	-12.2	-13.4
26a		-30.6	35.2		
4	8	-26.0	20.0	-9.8	-15.8
4a		-41.8	29.8		
27	9	-34.6	17.1	-5.3	-20.4
27a		-55.0	22.4		
28	10	-40.3	17.2	-5.6	-20.1
28a		-60.4	22.8		

[a] Strain energies given by the MM2 program are derived via strain free group increments: OS = (olefin strain - alkane strain). $\Delta H_{hyd} = \Delta H_f(\text{alkane}) - \Delta H_f(\text{olefin})$. [b] MM1 data.[3a] [c] MM2 data.[3b]

set of bicyclo[*n*.2.2]alkanes (*n* = 5-10), bicyclo[5.4.3]tetradecane, bicyclo[4.4.4]tetradecane, bicyclo[4.4.3]tridecane, bicyclo[4.4.2]dodecane, and bicyclo[5.3.2]dodecane. In addition, several double bridgehead dienes in these systems were examined. The possible saturated bridgehead configurations, with the hydrogens pointed into ("in") or out of ("out") the cage were calculated for the larger bridgehead olefins and bicyclic alkanes.

Section A presents data for a simple series of homologous bridgehead olefins which reveal the role of *trans*-cycloalkene moieties in helping to determine the stability of these systems. Data in section B provide evidence for the generality of hyperstable bridgehead olefins and several examples of hyperstable dibridgehead dienes.

(A) Bicyclo[*n*.2.2]-1(*n* + 4)-ene System (*n* = 5-10). The bicyclo[*n*.2.2] series, *n* = 5-10, depicted in Chart I were found to be quite different than the smaller systems (*n* = 1-4). These smaller bridgehead olefins have been studied by using the MM1 force field[3a] (*n* = 4 more recently with MM2[3b]) and were found to be strained. All bridgehead olefins in this [n.2.2] set have a cis-cyclohexene moiety and a trans double bond in a second ring fragment. The smaller bicyclic systems suffer from the presence of unfavorable trans double bonds in five-to eight-membered ring units. However, *trans*-cycloalkenes in medium rings with nine or more carbons have negative OS values (Table I). Larger bicyclic [*n*.2.2] systems (*n* = 6-10) incorporating such moieties have enhanced stability, as observed experimentally for two members of this series (*n* = 6 and 8).[9-11]

The results for the *n* = 1-10 set of compounds are summarized in Table II and in Figure 1. Indeed, all the new bicyclo[*n*.2.2]-1(*n* + 4)-enes (*n* = 5-10) investigated are hyperstable bridgehead olefins in contrast to the lower homologues (*n* = 1-4). Bicyclo[7.2.2]trideca-1(11)-ene (**26**) has the lowest OS value (-12.2 kcal/mol) in this series.

It is useful to consider bridgehead bicyclic olefins as being comprised of three ring moieties. One of these fragments will have a trans and another a cis double bond. The third ring moiety contains one sp^2 center associated with an exocyclic double bond. The size of the *trans*-cycloalkene ring is a useful criterion for the qualitative assessment of the stability of these larger bridgehead olefins, as was the case for smaller bridgehead olefins.[26] Thus, bicyclo[4.2.2]deca-1(8)-ene (**24**) has an OS = 7.9 kcal/mol, largely due to the strain of the *trans*-cyclooctene ring. The next compound in this series (**25**) is the first to exhibit hyperstability in accordance with the decrease in the relative strain of the *trans*-cyclononene ring. The compound in this series with the lowest OS value, **26**, has a favorable *trans*-cycloundecene ring.[2c] The OS values increase in the higher homologues (Figure 1) because olefins in the larger ring systems (>12-membered) are relatively strain free.

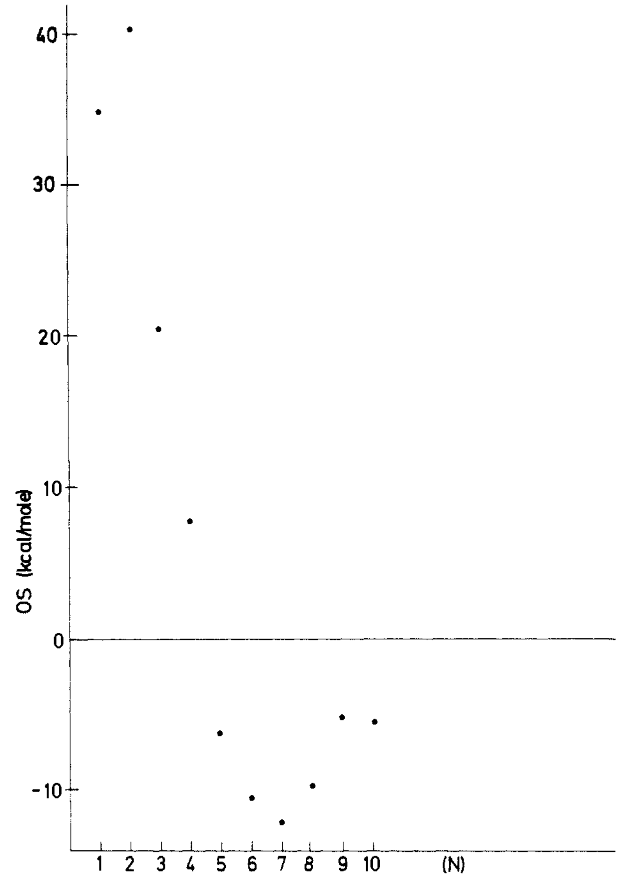
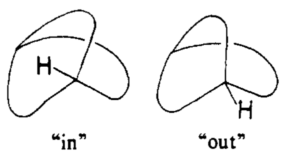


Figure 1. OS value vs. chain size (*N*) for bicyclo[*n*.2.2]-1(*n* + 4)-enes (Chart 1).

(B) Bicyclo[5.4.3]tetradeca, -[4.4.4]tetradeca, -[4.4.3]trideca, -[4.4.2]dodeca, and -[5.3.2]dodeca Systems. Bridgehead olefins and double bridgehead dienes in five medium size bicyclic systems containing 7- to 10-membered ring fragments were explored and found to be hyperstable. We also examined the effect of inward vs. outward pyramidalization of the bridgehead CH groups in the bridgehead olefins and the parent hydrocarbons. Several prior studies demonstrate the importance of such in-out configurations with regard to the chemistry of cyclic and bicyclic systems.[4,8,12,27] Our results for the compounds depicted in Charts II and III are summarized in Table III.



The smaller saturated bicyclic systems favor the out,out configurations due to ring size constraints. Both out,out isomers of bicyclo[4.4.2]dodecane (**57**) and bicyclo[5.3.2]dodecane (**63**) are 7.5 and 3.5 kcal/mol more stable, respectively, than the corresponding out, in isomers (**58** and **64**). Larger bicycloalkanes favor

---

[26] Wiseman, J. R.; Pletcher, W. A. *J. Am. Chem. Soc.* **1970**, *92*, 956. Burkert, U. *Chem. Ber.* **1977**, *110*, 773.

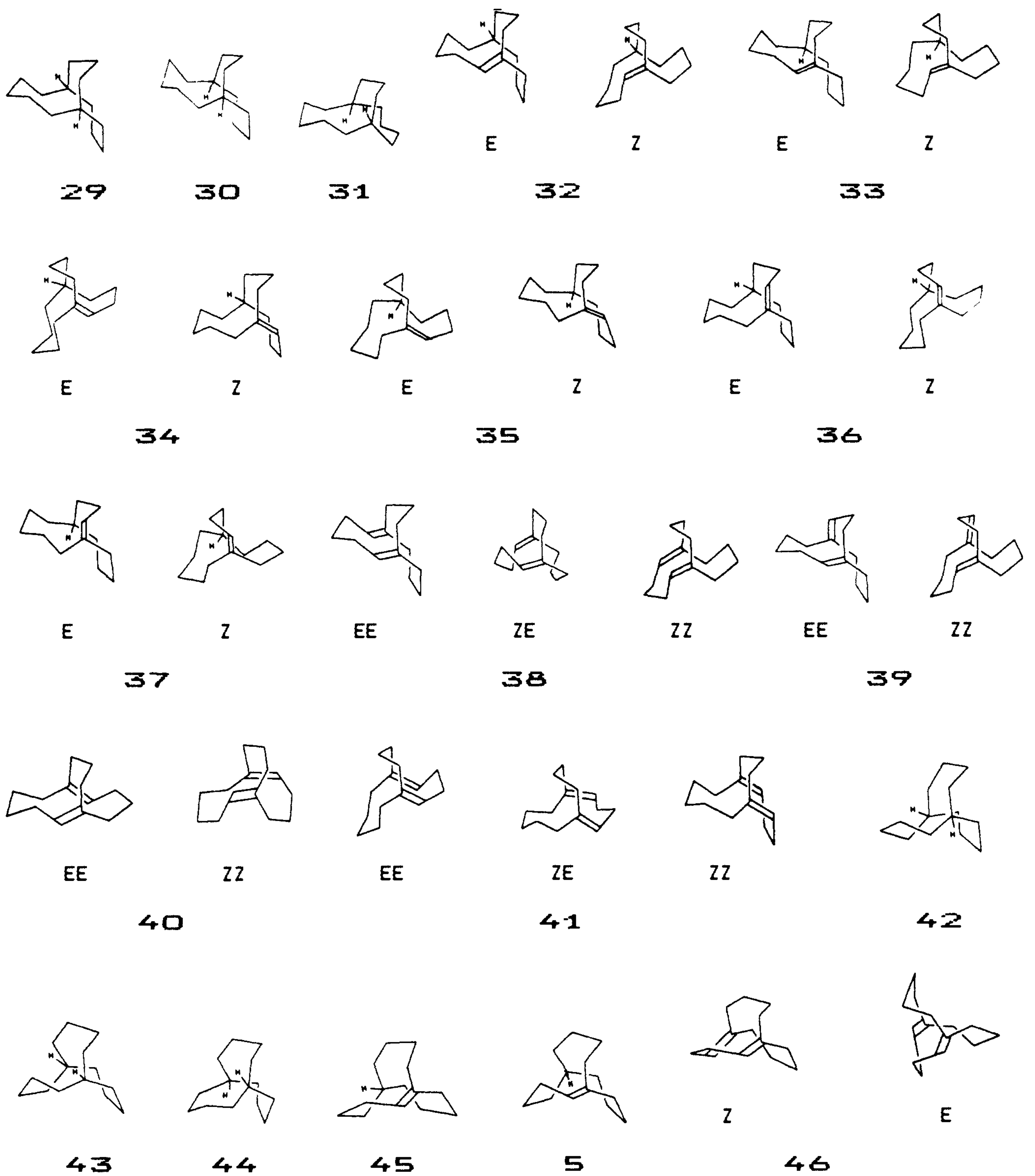
[27] Bicyclic systems: Gassman, P. G.; Thummel, R. P. *J. Am. Chem. Soc.* **1972**, *94*, 7183. Park, C. H.; Simmons, H. E. *J. Am. Chem. Soc.* **1972**, *94*, 7184. Wipff, G.; Kollman, P. *Nouv. J. Chim.* **1985**, *9*, 457. (b) Cyclic systems with *μ*-hydride bridging: Kirchen, R. P.; Ranganayakulu, K.; Rauk, A.; Aingh, B. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1981**, *103*, 588. Kirchen, R. P.; Okazawa, N.; Ranganayakulu, K.; Rauk, A.; Sorensen, T. S. *J. Am. Chem. Soc.* **1981**, *103*, 588. (c) The propellanes are bicyclic systems with bonding between the two in-pyramidalized bridgeheads.

Table III. MM2 Calculated Energies (kcal/mol) and Derived Values for Molecules in Charts II and III[a]

molecule		ΔH_f	strain *E*	OS[b]	OS/DB[c]
			Bicyclo[5.4.3]tetradeca-		
29		-22.1	49.5		
30		-27.2	44.4		
31		-8.4	63.2		
32	(*E*)	-11.2	34.8	-14.7	
	(*Z*)	-8.1	37.9	-11.6	
33	(*E*)	-12.1	33.9	-10.5	
	(*Z*)	-11.0	35.0	-9.4	
34	(*E*)	-6.3	39.7	-9.8	
	(*Z*)	0.8	46.8	-2.6	
35	(*E*)	-12.6	33.3	-11.0	
	(*Z*)	-4.8	41.2	-3.2	
36	(*E*)	-7.4	38.6	-10.9	
	(*Z*)	-1.7	44.3	-5.2	
37	(*E*)	-0.6	45.4	1.0	
	(*Z*)	-2.3	43.7	-0.7	
38	(*EE*)	1.7	22.1	-27.4	-13.7
	(*ZE*)	4.9	25.3	-24.2	-12.1
	(*ZZ*)	2.4	22.7	-26.7	-13.4
39	(*EE*)	6.8	27.2	-22.2	-11.1
	(*ZZ*)	13.4	33.8	-15.7	-7.8
40	(*EE*)	3.6	24.0	-25.5	-12.7
	(*ZZ*)	16.0	36.4	-13.1	-6.5
41	(*EE*)	8.2	28.63	-20.9	-10.4
	(*EZ*)	15.2	35.6	-13.9	-6.9
	(*ZZ*)	29.9	50.3	0.8	0.4
			Bicyclo[4.4.4]tetradeca-		
42		-12.2 (-7.0)[d] [-9.6][e]	59.4 (60.5)		
43		-24.4 [-21.9][e]	47.2		
44		-8.9	62.7		
45		-2.6 (5.0)[d]	43.4 (46.4)	-16.0 (-14.1)	
5		-10.0	36.0	-11.2	
46	(*Z*)	19.1	39.5	-19.9	-10.0
	(*E*)	19.9	40.3	-19.2	-9.6
47	(*E*)	9.6	30.0	-29.4	-14.7
	(*Z*)	15.2	35.6	-23.8	-11.9
			Bicyclo[4.4.3]trideca-		
48		-12.6	53.2		
49		-19.0	46.8		
50	(*E*)	-3.3	36.4	-16.8	
	(*Z*)	1.0	40.7	-12.5	
51	(*E*)	0.8	40.6	-6.3	
	(*Z*)	6.3	46.0	-0.8	
52		4.0	44.3	-8.9	
53		1.2	40.9	-5.9	
54	(*EE*)	12.3	25.9	-27.4	-14.7
	(*ZZ*)	19.5	33.1	-20.2	-11.1
55	(*EE*)	13.2	26.7	-31.7	-16.9
	(*ZE*)	14.3	27.9	-25.3	-13.7
	(*ZZ*)	18.2	31.7	-21.5	-11.8
56		17.6	31.2	-21.9	-12.0
			Bicyclo[4.4.2]dodeca-		
57		-23.9 (-17.8)[d] [-20.7][f]	36.2 (38.6) [39.4]		
58		-16.4	43.7		
59	(*E*)	-7.8 (-4.7)[d]	26.1 (25.5)	-10.1 (-13.0)	
	(*Z*)	4.6	38.6	2.4	
60	(*E*)	7.0	41.4	-2.3	
	(*Z*)	18.8	52.8	9.1	
61	(*EE*)	17.7	25.5	-10.6	-5.3
	(*ZZ*)	40.3	48.1	12.0	6.0
62	(*EE*)	16.8	24.6	-11.6	-5.8
	(*ZE*)	28.5	36.3	0.1	0.1
	(*ZZ*)	35.6	43.4	7.3	3.6
			Bicyclo[5.3.2]dodeca-		
63		-23.0	37.0		
64		-19.5	40.6		
65	(*E*)	-7.8	26.7	-10.4	
	(*Z*)	0.4	34.9	-2.2	
66	(*E*)	4.8	38.7	-1.8	n
	(*Z*)	13.9	47.8	7.3	
67	(*EE*)	12.6	20.4	-15.4	-7.7
	(*ZZ*)	18.3	26.1	-9.7	-4.8

[a] See Table I for definition of terms. [b] All OS values use the saturated hydrocarbon resulting from "out" hydrogenation. [c] Olefin strain per double bond. [d] MM1 data.[3a] [e] MM1 data.[4b] [f] MM2 data.[3b]

Chart II. Bridgehead and Dibridgehead Olefins Investigated[a]

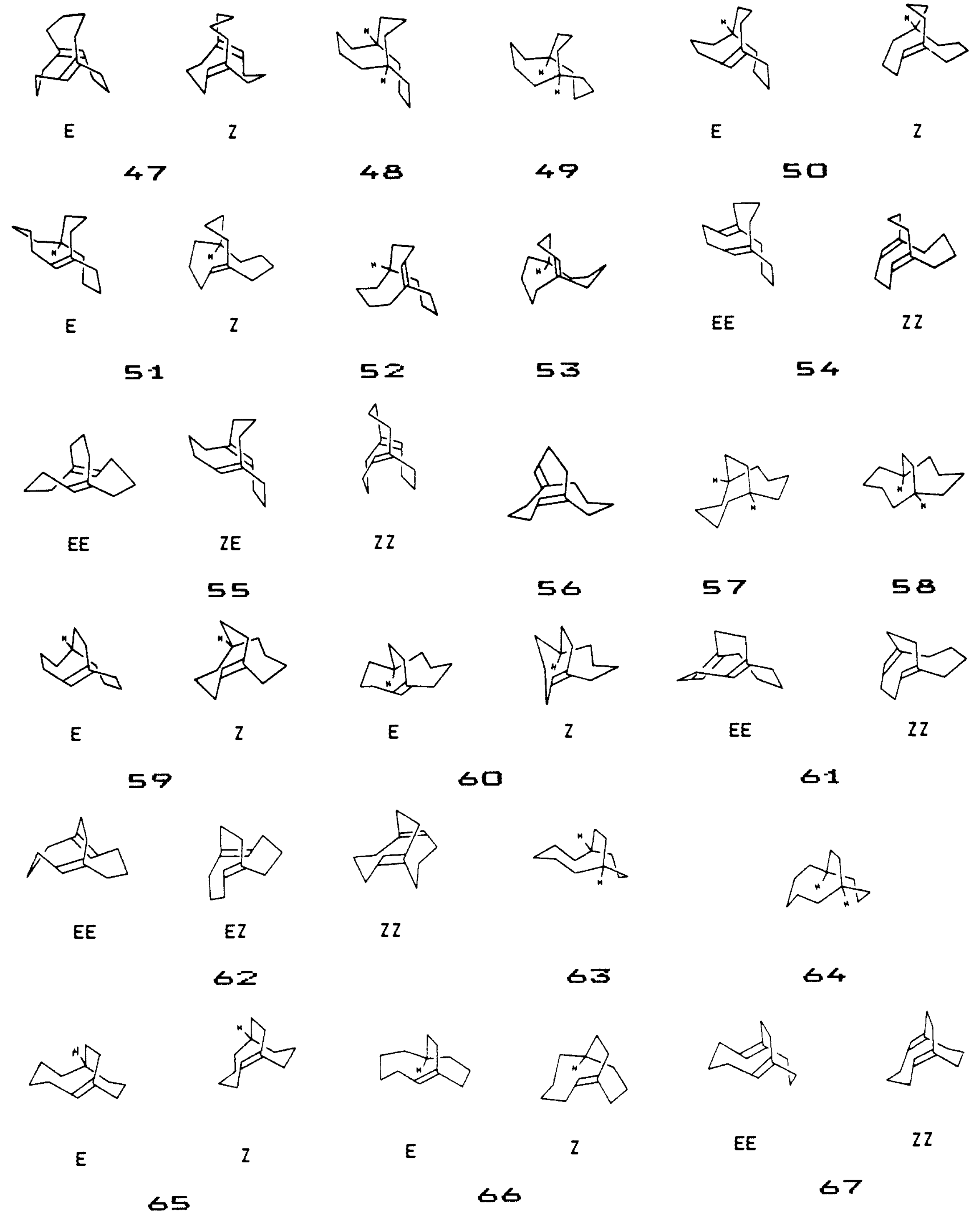


[a] The drawings are schematic rather than exact and are meant to represent, in general, the minimum energy conformations found. All details of the calculated geometries are given in the supplementary material.

the out,in configuration. The out,in configuration of bicyclo[4.4.3]tridecane, bicyclo[4.4.4]tetradecane, and bicyclo[5.4.3]tetradecane (**49**, **43**, and **30**) are the most stable (by 6.4, 12.2, and 6.3 kcal/mol, respectively, relative to the out,out isomers). The in,in alkane configurations of bicyclo[4.4.4]tetradecane (**44**) and bicyclo[5.4.3]tetradecane (**31**) are the least stable, but they are only 3.3 and 3.7 kcal/mol higher in energy than the out,out isomers (**42** and **29**). As recognized by Alder, this flattening and increased preference for in-pyramidalized bridgehead groups in medium size bicyclic alkanes contribute to the stability of the corresponding bridgehead olefin compounds.[4a]

Bicyclic systems can provide substantial stability to bridgehead olefins. This is emphasized by the large hyperstability of bicyclo[4.4.3]trideca-1-ene [(*E*)-**50**] (OS = -16.8 kcal/mol, III). The lowest energy bridgehead olefin isomers in all bicyclic systems studied are hyperstable and generally incorporate the *trans*-cycloalkene moiety in the larger ring (i.e., *E* isomers). Many of the *Z* isomers are hyperstable as well, especially in the larger tetradecyl and tridecyl bicyclic systems. The in configurations of the less stable *Z* isomers in the smaller dodecyl systems are strained;

Chart III. Bridgehead and Dibridgehead Olefins Investigated[a]



[a] The drawings are schematic rather than exact and are meant to represent, in general, the minimum energy conformations found. All details of the calculated geometries are given in the supplementary material.

however, even these should be readily isolable since their OS values are less than 10 kcal/mol.[3a]

The OS values in these systems are related to the ring size of the cycloalkene moieties. All the hyperstable bridgehead olefins that have been calculated, their OS values, and the sizes of the various ring fragments are summarized in Table IV. Stability of the cycloalkene components is important in determining the overall stability of bicyclic systems. *cis*-Cycloalkenes with 7-membered or larger rings are hyperstable; however, *trans*-cycloalkenes in only 9- to 12-membered rings exhibit hyperstability

Table IV. Hyperstable Bridgehead Olefins

bicyclic system	OS,[a] kcal/mol	ring size of fragments[b]			pyramidalization[c]
		trans	cis	other	
[4.4.3] (*E*)-**50**	−16.8	10	9	9	out
[4.4.4] **45**	−16.0	10	10	10	out
[5.4.3] (*E*)-**32**	−14.7	11	10	9	out
[4.4.3] (*Z*)-**50**	−12.5	9	10	9	out
[7.2.2] **26**	−12.2	11	6	11	out
[5.4.3] (*Z*)-**32**	−11.6	10	11	9	out
[4.4.4] **5**	−11.2	10	10	10	in
[5.4.3] (*E*)-**35**	−11.0	11	9	10	in
[5.4.3] (*E*)-**36**	−10.9	10	9	11	out
[6.2.2] **3**	−10.6	10	6	10	out
[5.4.3] (*E*)-**33**	−10.5	11	10	9	in
[5.3.2] (*E*)-**64**	−10.4	10	9	7	out
[4.4.2] (*E*)-**59**	−10.1	10	8	8	out
[5.4.3] (*E*)-**34**	−9.8	11	9	10	out
[8.2.2] 4	−9.8	12	6	12	out
[5.4.3] (*Z*)-**33**	−9.4	10	11	9	in
[4.4.3] **52**	−8.9	9	9	10	out
[4.3.2][d]	−7.2	9	7	8	out
[5.2.2] **25**	−6.3	9	6	9	out
[4.4.3] (*E*)-**51**	−6.3	10	9	9	in
[4.4.3] **53**	−5.9	9	9	10	in
[10.2.2] **28**	−5.6	14	6	14	out
[4.3.2][d]	−5.4	9	8	7	out
[9.2.2] **27**	−5.3	13	6	13	out
[5.4.3] (*Z*)-**36**	−5.2	9	10	11	out
[4.4.2] (*E*)-**60**	−5.1	10	8	8	in
[5.5.2][e]	−4.5	9	9	12	out
[4.3.3][e]	−4.2	9	9	8	out
[5.4.3] (*Z*)-**35**	−3.2	9	11	10	in
[5.4.3] (*Z*)-**34**	−2.6	9	11	10	out
[5.3.2] (*Z*)-**65**	−2.2	9	10	7	out
[5.3.2] (*E*)-**66**	−1.8	10	9	7	in
[4.4.1][d]	−1.5	10	7	7	out
[4.4.3] (*Z*)-**51**	−0.8	9	10	9	in
[5.4.3] (*Z*)-**37**	−0.7	9	10	11	in

[a] Olefin strain. [b] Trans: size of *trans*-cycloalkene moiety. Cis: size of *cis*-cycloalkene moiety. Other: size of third non-olefin ring fragment. [c] Pyramidalization of the saturated bridgehead position: "out" refers to hydrogen pointing out of the cage, "in" into the cage. [d] MM1 data.[3a] [e] MM2 data.[3b]

(Table I).[28] The only out bridgehead olefins studied which are not hyperstable are those with *trans*-cycloalkene rings smaller than nine-membered. For example, (*Z*)-**59** and (*Z*)-**60** have a *trans*-cyclooctene moiety and positive OS values.

Although at least a nine-membered *trans*-cycloalkene unit seems to be necessary for hyperstability in out bridgehead olefins, this feature does not guarantee negative OS values. The other ring fragments are also important. *cis*-Cyclohexene the smallest moiety found occurring in the examples of Table IV, has an OS of 1.0 kcal/mol. Cyclopentene with an OS of −0.6 kcal/mol might be expected to contribute favorably to the hyperstability of bridgehead olefins. However, bicyclo[5.2.1]deca-1(9)-ene, containing the five-membered *cis*-cycloalkene and nine-membered *trans*-cycloalkene moieties, has an OS of 1.6 kcal/mol.[3b] This positive value probably is due to the constraints imposed by the cyclopentene ring on the bicyclic system. The seven-membered non-olefin-containing ring moiety is the smallest present in the hyperstable olefins listed in Table IV. In principle, the sum of the strains due to each of the three ring moieties might give the total strain. If this additivity were to hold, the smallest possible hyperstable bridgehead olefin should be comprised of the minimum-sized fragments found in Table IV: a nine-membered *trans*-cycloalkene, a four-membered *cis*-cycloalkene, and a seven-membered non-cycloalkene. This is not the case. Bicyclo[4.3.1]deca-1(9)-ene has an OS of 3.2 kcal/mol.[3b] While no quantitative additivity relationship connects the OS values of Tables I and IV, there is a general correlation between the fragment energies and the degree of hyperstability of bridgehead olefins. The constraints afforded by the bicyclic systems prevent each of the fragments from assuming the lowest energy conformations.

Table V. Hyperstable Bridgehead Olefins That Are More Stable "In" Than "Out"

olefin		$\Delta\Delta H_f$,[a] kcal/mol	ring size of fragments[b]		
in	out		trans	cis	other
5	**45**	7.4	10	10	10
(*E*)-**35**	(*E*)-**34**	6.3	11	9	10
(*Z*)-**35**	(*Z*)-**34**	5.6	9	11	10
53	**52**	2.9	9	9	10
(*Z*)-**33**	(*Z*)-**32**	2.9	10	11	9
(*E*)-**33**	(*E*)-**32**	0.9	11	10	9
(*Z*)-**37**	(*Z*)-**36**	0.6	9	10	11

[a] $\Delta\Delta H_f = \Delta H_f$ "in" isomer $-\Delta H_f$ "out" isomer. [b] Trans: size of *trans*-cycloalkene moiety. Cis: size of *cis*-cycloalkene moiety. Other: size of third non-olefin ring fragment.

Increasing the size of the bicyclic system does not increase the hyperstability of the out bridgehead olefins proportionally. The increase in bridgehead C–C–C bond angles disfavors the larger bicyclic systems. On the other hand, pyramidalizing the saturated bridgeheads inward decreases strain in the parent hydrocarbons and in the bridgehead olefins as well. In several of the larger bridgehead olefin systems, the in isomers have lower heats of formation than the out (Table V). However, enhanced stability of in bridgehead olefins is not reflected in decreased OS values due to the greater stability of the reference in,out hydrocarbon as compared to the out,out.

The extensively studied bicyclo[4.4.4]tetradecyl system[8,12] will be used to illustrate several points. While the in bridgehead olefin bicyclo[4.4.4]tetradeca-1-ene (**5**) isomer is more stable than the out, **45**, the degree of hyperstability is greater in the latter (−11.2 vs. −16.0 kcal/mol). This results from the greater strain (12.2 kcal/mol) of the out,out alkane isomer (**42**) as compared to the in,out (**43**). Inward pyramidalization of one bridgehead atom stabilizes the bridgehead aza- and diazabicyclo[4.4.4]tetradecyl systems as well.[4,8] The "in" conformation of the bridgehead olefin 1-azabicyclo[4.4.4]tetra-deca-5-ene (**2**) is more stable than the "out" (by more than 10 kcal/mol) and has a heat of hydrogenation of only 7.6 kcal/mol (MM2).[8] The bridgehead olefins are favored over nonbridgehead locations. The heat of formation of **5** is 4.4 and 11.8 kcal/mol less than other nonbridgehead isomers in the "out" and "in" systems.[22] In addition, **2** is more stable than the nonbridgehead isomer, 1-azabicyclo[4.4.4]tetradeca-4-ene, by 17.7 kcal/mol (MM2).[8] McMurry et al. recently synthesized **5** (OS = −11.2 kcal/mol); its hydrogenation to give the "in,out" alkane isomer **43** proceeded unusually slowly.[12]

Double Bridgehead Dienes. Introduction of a second double bond at the other bridgehead position also can result in hyperstability in bicyclic systems.[19] All low energy configurations of the double bridgehead dienes in Table III are hyperstable. The degree of hyperstability due to the second bridgehead olefin is not as large as that of the first; however, an additional effect is provided in relation to both the monobridgehead and saturated molecules. For example, the most stabilized double bridgehead diene (*EE*)-**55** has a total OS of −31.7 kcal/mol. The OS relative to the monobridgehead olefin (**50**) is −9.7 kcal/mol, a significantly negative value. Not all double bridgehead dienes are hyperstable with respect to the monobridgehead olefin. Similar to the monobridgehead olefins, dienes incorporating a *trans*-cyclooctene ring are destabilized (e.g., (*ZZ*)-**61**, (*ZE*)-**62**, and (*ZZ*)-**62**.) Incorporating the two double bonds in the same ring moiety is unfavorable compared to the isomer with the double bonds in separate ring fragments; however, the presence of two olefins in the same ring unit does not preclude hyperstability.

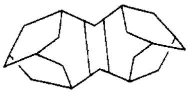
In summary, the lowest energy configurations of all bridgehead olefins in Table III are predicted to be hyperstable. Many of the less favorable configurations also fall into this category. The large number of possible hyperstable bridgehead olefins is emphasized

---

[28] Although the heat of hydrogenation has not been determined, we assume that the OS value for *trans*-cycloundecene is similar to the 10- and 12-membered ring analogues.

Chart IV. Tetracyclic Olefins Investigated

X = $(CH_2)_n$
n = 2–6
(Y = **69**–**73**)



74

by Table IV. This list is certainly not complete. Hyperstability also can be expected when a second olefin is present at the other bridgehead position. We predict several double bridgehead dienes to be hyperstable relative both to the monobridgehead olefins and to the saturated hydrocarbons.

Bicyclo[n.2.2] bridgehead olefins are accessible through hydrogenation of [n]paracyclophanes[29] and by direct synthesis (Sakai et al.).[30] Other bridgehead olefins also should be easy to prepare.[2b,12,17,27] Experimental determination of the predicted heats of hydrogenation should be possible in some instances, but the slow rates of hydrogenation of hyperstable bridgehead olefins may cause difficulties.[9] Determination of the differences in the heats of combustion of olefins and the corresponding saturated hydrocarbons may be necessary in such instances.

II. Tetracyclic Olefins. Intrigued by the possibility that unconjugated olefins might be so favorable as to have a lower heat of formation than their saturated analogue (and a positive heat of hydrogenation!), we investigated the olefinic systems depicted in Chart IV. These systems were chosen because medium size rings are strained due to repulsive hydrogen transannular interactions. Placing a double bond in a medium size ring relieves some strain by removing two hydrogens and rehybridizing two carbons to sp^2.[5,6] When the double bond is common to two rings, as in hyperstable bicyclic systems, the gain in stability is even greater. Therefore, a double bond common to several medium size rings should afford maximum stabilization. The systems in Chart IV fulfill this requirement. By varying the chain length (n = 2–6), the double bond can be common to four rings, 6- to 10-membered. Bis(homoadamantene) (**74**) was also investigated; by placing two methylene bridging into the n = 3 system, unfavorable transannular interactions are removed.[31]

The results are summarized in Table VI. As is apparent from the magnitude of the negative OS values, a double bond is stabilized by the tetracyclic ring arrangement. In fact, all the olefins in Table VI are hyperstable. Both **71** and **72** have *endothermic* cis hydrogenations of 4.5 and 1.7 kcal/mol, respectively.

Several factors affect the thermodynamics of cis and trans hydrogenation in these systems. In the lower homologues (n = 2, 3), ring constraints prevent twisting around the central bond, thus favoring cis hydrogenation. The higher homologues (n = 4–6), on the other hand, favor trans hydrogens in the reduction product. The anti arrangement of these hydrogens is not adverse energetically, but repulsive interactions between the ring systems which are forced together impair cis hydrogenation. For example, the currently most hyperstable olefin known (**72**) has a heat of formation only 3.6 kcal/mol higher than that of the parent hydrocarbon; however, the ΔH_f of **72** is 4.5 kcal/mol *lower* than that of its cis-hydrogenated analogue. The double bond in **72** is common to *four cis*-cyclononaene fragments. The OS value of **72** (−20.1 kcal/mol) is 8.1 kcal/mol less than that expected from the additivity of four *cis*-cyclononaene (OS = −3.0 kcal/mol) units.

The degree of hyperstability of bis(homoadamantene) (**74**) is less than the similar nonbridged molecule (**70**). As expected, incorporation of two methylene bridges into **70** to form **74** reduces the strain. However, the strain of the saturated molecule is reduced more than that of the olefin, and the degree of hyperstability decreases.

Table VI.[a] MM2 Calculated Energies (kcal/mol) and Derived Values for the Tetracyclic Olefins in Chart IV[a]

(n)		ΔH_f	strain	OS	ΔH_{hyd}
2	(**69**)	0.3	35.0		
	69a (cis)[b]	−22.3	36.1	−1.1	−22.0
	69a (trans)	−6.3	52.1	−17.1	−6.0
3	(**70**)	−14.7	43.0		
	70a (cis)	−23.4	58.1	−15.1	−8.7
	70a (trans)	−17.2	64.3	−21.3	−2.5
	(**74**)	−18.6	37.4		
	74a (cis)	−30.1	49.6	−12.2	−11.5
	74a (trans)	−28.9	50.9	−13.5	−10.3
4	(**71**)	−7.1	73.7		
	71a (cis)	−5.3	99.1	−25.4	+1.7
	71a (trans)	−15.4	89.1	−15.4	−8.35
5	(**72**)	−10.0	93.8		
	72a (cis)	−5.5	122.0	−28.2	+4.5
	72a (trans)	−13.6	113.9	−20.1	−3.6
6	(**73**)	−21.3	105.6		
	73a (cis)	−38.8	111.7	−6.1	−17.5
	73a (trans)	−40.3	110.3	−4.7	−19.0

[a] See Table I for definition of terms. [b] Ya is the saturated hydrocarbon resulting from cis hydrogenation (cis) or trans hydrogenation (trans) of Y.

The predicted thermodynamic stability of these tetracyclic olefins toward hydrogenation merits experimental confirmation. The synthesis of these systems and their hydrogenation should be interesting. The total strain in these molecules is large (Table VI) but no prohibitive. For instance, the strain in **72** is only 3.9 kcal/mol per carbon atom.

Conclusion

Our results indicate that a large number of bridgehead olefins should be hyperstable. Hyperstable double bridgehead dienes also are to be expected in medium size ring systems. The incorporation of a double bond common to four medium size rings can result in an even greater degree of hyperstability.

Bridgehead groups in medium size bicyclic systems flatten or prefer to pyramidazole inward. Flattening at the bridgehead positions occurs in the bicyclo[3.3.3]undecane (manxane) system[3c] where the bridgehead olefin is only slightly destabilized.[3a] Bicyclo[4.3.3]dodeca-1-ene, the next larger bridgehead bicyclic system, is a hyperstable olefin.[3b] The first manifestation of flattening and enhanced stability of planar arrangements at bridgehead positions to be recognized was the increased solvolysis rate for middle ring polycyclic bridgehead systems.[3c]

Hyperstability of bridgehead olefins can be related to the stability of the cyclic moieties, the *trans*-cycloalkene unit in particular. Qualitatively, as the systems become larger, hyperstability of bridgehead olefins begins when both a *trans*-cyclononaene ring and a *cis*-cyclohexene ring are present. Increasing the size of the bicyclic system further does not necessarily increase the degree of hyperstability of the bridgehead olefin. With larger size bicyclic systems, in pyramidalization is favored. In bridgehead olefins have lower heats of formation than the out isomers when the bicyclic system contains a 10- and two 9-membered rings. Hyperstable double bridgehead dienes result when both bridgehead positions prefer to be sp^2 hybridized.

Tetracyclic olefins with a double bond common to four medium size rings, such as those studied in Chart IV, have substantially lower strain energies than the parent hydrocarbons. This is exemplified by **72**, where the cis hydrogenation is *endothermic* by 4.5 kcal/mol. This value, comparable to the endothermic first heat of hydrogenation of benzene, shows that the thermochemical resistance provided to an olefin by aromaticity (Table I) can also be achieved by geometrical effects in unconjugated systems.

Acknowledgment. We thank J. E. McMurray, H. Hopf, and R. Alder for suggestions and C. Schade and W. Maier for their

---

[29] [5]Paracyclophane was isolated at reduced temperature; this can provide access to **18**: Jenneskens, L. W.; De Kanter, F. J. J.; Kraakman, P. A.; Turkenburg, L. A. M.; Koolhaas, W. E.; De Wolf, W. H.; Bickelhaupt, R. *J. Am. Chem. Soc.* **1985**, *107*, 3716. van Zijl, P. C. M.; Jenneskens, L. W.; Bastiaan, E. W.; MacLean, C.; deWolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1986**, *108*, 1415.

[30] For preparation of the n = 4–6 compounds, see: Sakai, Y.; Toyotani, S.; Ohtani, M.; Matsumoto, M.; Tobe, Y.; Odaira, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1474.

[31] The radical cation derived from this olefin has been investigated: Nelsen, S.; Nelsen, S. F.; Kapp, D. L. *J. Org. Chem.* **1985**, *50*, 1339.

interest. This work was supported by the Fonds der Chemischen Industrie.

Note Added in Proof. R. Alder has called attention to this study,[32] both calculational and experimental, of double bridgehead dienes in bicyclo[4.4.4]tetradecane systems. That some of the energies do not always agree perfectly with those we have calculated independently for the same molecules emphasizes the difficulty in ensuring that the most stable conformation was found in each case.

Registry No. 3, 36532-38-4; **3a**, 79312-79-1; **4**, 284-51-5; **4a**, 89507-04-0; **21**, 279-23-2; **21a**, 21810-44-6; **22**, 280-33-1; **22a**, 3618-06-2; **23**, 283-19-2; **23a**, 25048-48-0; **24**, 284-26-4; **24a**, 67152-31-2; **25**, 53974-82-6; **25a**, 79312-78-0; **26**, 24504-36-7; **26a**, 101999-73-9; **27**, 284-53-7; **27a**, 101999-74-0; **28**, 284-67-3; **28a**, 101999-75-1; **29**, 101999-76-2; **30**, 102046-62-8; (*E*)-**32**, 101999-77-3; (*Z*)-**32**, 101999-78-4; (*E*)-34, 101999-79-5; (*Z*)-**34**, 101999-80-8; (*E*)-**36**, 101999-81-9; (*Z*)-**36**, 101999-82-0; (*EE*)-**38**, 101999-83-1; (*ZE*)-**38**, 101999-84-2; (*ZZ*)-**38**, 101999-85-3; (*EE*)-**39**, 101999-86-4; (*ZZ*)-**39**, 101999-87-5; (*EE*)-**40**, 101999-88-6; (*ZZ*)-**40**, 101999-89-7; (*EE*)-**41**, 101999-90-0; (*EZ*)-**41**, 102046-63-9; (*ZZ*)-**41**, 101999-91-1; **42**, 54101-79-0; **45**, 77159-19-4; (*Z*)-**46**, 102046-64-0; (*EZ*)-**47**, 101999-92-2; (*ZZ*)-**47**, 102046-65-1; **48**, 88671-93-6; (*E*)-**50**, 101999-93-3; (*Z*)-**50**, 101999-94-4; **52**, 101999-95-5; (*EE*)-54, 102046-66-2; (*ZZ*)-**54**, 101999-96-6; (*EE*)-**55**, 101999-97-7; (*ZE*)-**55**, 101999-98-8; (*ZZ*)-**55**, 101999-99-9; **56**, 102000-00-0; **57**, 7490-33-7; (*E*)-**59**, 102000-01-1; (*Z*)-**59**, 102000-02-2; (*EE*)-**61**, 88816-29-9; (*ZZ*)-**61**, 102000-03-3; (*EE*)-**62**, 102000-04-4; (*EZ*)-**62**, 102000-05-5; (*ZZ*)-**62**, 102000-06-6; **63**, 34401-00-8; (*E*)-**65**, 102000-07-7; (*Z*)-**65**, 102000-08-8; (*EE*)-**67**, 102000-09-9; (*ZZ*)-**67**, 102000-10-2; **69**, 88656-03-5; *cis*-**69a**, 102000-11-3; *trans*-**69a**, 102000-12-4; **70**, 102000-13-5; *cis*-**70a**, 102000-14-6; *trans*-**70a**, 102000-15-7; **71**, 102000-18-0; *cis*-**71a**, 102000-19-1; *trans*-**71a**, 102000-20-4; **72**, 102000-21-5; *cis*-**72a**, 102000-22-6; *trans*-**72a**, 102129-59-9; **73**, 102000-23-7; *cis*-**73a**, 102000-24-8; *trans*-**73a**, 102130-34-7; **74**, 30614-34-7; *cis*-**74a**, 102000-16-8; *trans*-**74a**, 102000-17-9; cyclopentene, 142-29-0; cyclohexene, 110-83-8; *cis*-cycloheptene, 628-92-2; *cis*-cyclooctene, 931-87-3; *trans*-cyclooctene, 931-89-5; *cis*-cyclononene, 933-21-1; *trans*-cyclononene, 3958-38-1; *cis*-cyclodecene, 935-31-9; *trans*-cyclodecene, 2198-20-1; *cis*-cyclododecene, 1129-89-1; *trans*-cyclododecene, 1486-75-5; benzene, 71-43-2; 1,3,5-cycloheptatriene, 544-25-2; 1,3,5,7-cyclooctatetraene, 629-20-9.

Supplementary Material Available: Geometries of minimum energy conformations (111 pages). Ordering information is given on any current masthead page.

---

[32] Alder, R. W.; Arrowsmith, R. J.; Bryce, M. R.; Eastment, P.; Orphen, A. G. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1519.

Dimerization of Borirene to 1,4-Diboracyclohexadiene. Structures and Stabilities of (CH)$_4$(BH)$_2$ Molecules

Peter H. M. Budzelaar,[†1a] **Sies M. van der Kerk,**[1b] **Karsten Krogh-Jespersen,**[1c] **and Paul von Ragué Schleyer***[1a]

Contribution from the Institut für Organische Chemie, Universität Erlangen—Nürnberg, D-8520 Erlangen, Federal Republic of Germany, the Laboratory of Organic Chemistry, Agricultural University, 6703 BC Wageningen, The Netherlands, and the Department of Chemistry, Rutgers—The State University of New Jersey, New Brunswick, New Jersey 08903.

Received October 29, 1985

Abstract: Possible pathways for the dimerization of borirene (**1**) to 1,4-diboracyclohexa-2,5-diene (**3**) (DBCH) and to the more stable isomer 2,3,4,5-tetracarba-*nido*-hexaborane(6) (**5**) were studied by semiempirical and ab initio MO theory. Two possible paths of C_2 and C_i symmetry, respectively, were found for the dimerization of **1** to **3**; both involve highly nonplanar four-center transition states in which the boron acceptor orbitals play a crucial role. The low activation energy, ca. 11 kcal/mol for the C_2 path, indicates that borirenes will easily dimerize to DBCH's unless π-donor groups at boron or bulky substituents are present. Despite extensive searches, no low-energy pathway was found for the dimerization of **1** to **5**. Two paths were found for the "disproportionation" of two borirene molecules into 1,3-diboretene (**2**) and acetylene. This disproportionation reaction is nearly thermoneutral, and the activation energy (ca. 15 kcal/mol) is so low that we expect this reaction to occur for borirenes without π-donor substituents attached to boron. Several additional (CH)$_4$(BH)$_2$ isomers were also examined. The energies increase in the order carborane **5** < 1,4-diboracyclohexadiene (**3**) < 2,6-diborabicyclo[3.1.0]hexene (**7**) ~ 1,2,3,5-tetracarba-*nido*-hexaborane(6) (**6**) ~ 1,2-diboracyclohexa-3,5-diene (**4**) < 5,6-diborabicyclo[2.1.1]hexene (**8**).

The aromaticity of borirene (**1**) was first predicted by Volpin[2] and later discussed more extensively and quantified by Schleyer et al.[3,4] Several groups have recently reported the synthesis of borirene derivatives;[5-8] all of these have bulky substituents or a π-donor group at boron (Chart I). It has been suggested that borirenes carrying small substituents could readily dimerize to 1,4-diboracyclohexa-2,5-dienes (DBCH's, **3**).[5,9] Such facile dimerization could explain the formation of DBCH's from the reactions of acetylenes with MeBBr$_2$ and C$_8$K.[9-11] Derivatives of 2,3,4,5-tetracarba-*nido*-hexaborane(6) (**5**), a valence isomer of DBCH, were also obtained from these reactions,[9,12] and their formation could conceivably also involve the dimerization of borirenes.

We have now investigated computationally several possible reactions of two borirene molecules, viz., the dimerization to **3**

[†] Present address: Koninklijke/Shell Laboratorium, 1003 AA Amsterdam, The Netherlands.

(1) (a) Erlangen. (b) Wageningen. (c) New Jersey.

(2) Volpin, M. E.; Koreskov, Y. D.; Dulova, V. G.; Kursanov, D. N. *Tetrahedron* **1962**, *18*, 107.

(3) Krogh-Jespersen, K.; Cremer, D.; Dill, J. D.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 2589.

(4) Budzelaar, P. H. M.; Kos, A. J.; Clark, T.; Schleyer, P. v. R. *Organometallics* **1985**, *4*, 429.

(5) Van der Kerk, S. M.; Budzelaar, P. H. M.; Van der Kerk-van Hoof, A.; Van der Kerk, G. J. M.; Schleyer, P. v. R. *Angew. Chem.* **1983**, *95*, 61.

(6) Pues, C.; Berndt, A. *Angew. Chem.* **1984**, *96*, 306.

(7) Pachaly, B.; West, R. *Angew. Chem.* **1984**, *96*, 444.

(8) Habben, C.; Meller, A. *Chem. Ber.* **1984**, *117*, 2531.

(9) Van der Kerk, S. M.; Budzelaar, P. H. M.; Van Eekeren, A. L. M.; Van der Kerk, G. J. M. *Polyhedron* **1984**, *3*, 271.

(10) Van der Kerk, S. M.; Van Eekeren, A. L. M.; Van der Kerk, G. J. M. *J. Organomet. Chem.* **1980**, *190*, C8.

0002-7863/86/1508-3960$01.50/0