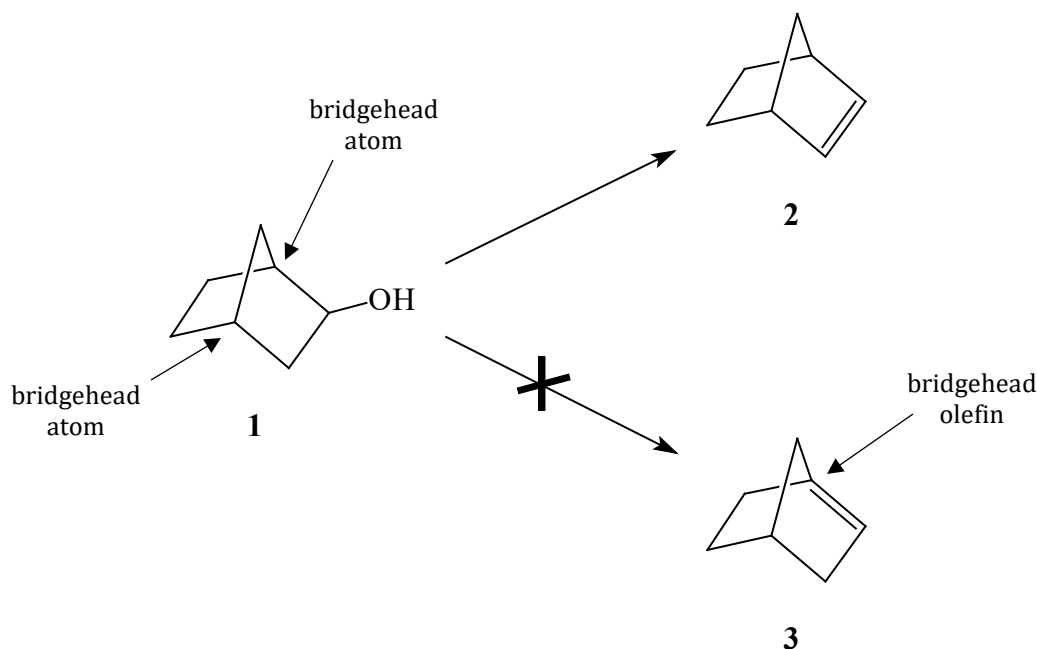


Bredt's Rule: The Relative Stabilities of Bridgehead Olefins

Bredt's Rule states that carbon-carbon double bonds cannot form at the bridgehead positions of a bridged bicyclic molecule. The rule can be demonstrated with a simple example. Dehydration¹ of the bicyclic alcohol **1** (named bicyclo[2.2.1]heptan-2-ol) gives **2** (bicyclo[2.2.1]hept-2-ene), an olefin² in which the double bond does not involve a bridgehead atom. The alternative compound **3** (bicyclo[2.2.1]hept-1-ene), a *bridgehead olefin*, is not produced in this reaction.



This behavior can be explained based on the relative stabilities—that is, the energy difference—of **2** and **3**. The molecular geometry of **2** exhibits a normal double bond with the $2p$ orbitals of the sp^2 -hybridized carbons aligned, resulting in favorable π interaction and strong stabilization. In contrast, the double bond of **3** is highly strained—a twisted double bond—with weak π interaction and limited stabilization. The reaction favors compound **2** because it is more stable than **3**.

The double bond of **3** exists in a five-membered ring. We might anticipate that by increasing the ring size of the bicyclic compound that the bridgehead carbon will become increasingly free to reorient its $2p$ orbital to strengthen the π interaction and stabilize the bridgehead double bond, thereby stabilizing the bridgehead olefin. Thus, *the tendency for dehydration reactions to avoid the bridgehead olefin product may diminish with increasing ring size*. In this exercise, we use electronic structure methods to test this "ring strain hypothesis."

¹ Dehydration is the loss of water, H-OH, from a reactant molecule. The hydroxyl group (OH) comes from the "alpha" C and the H atom from an adjoining "beta" C, yielding a $C_\alpha=C_\beta$ double bond.

² "Olefin" is the original term for an alkene, a hydrocarbon with at least one carbon-carbon double bond.

Calculations

Perform Gaussian calculations using WebMO. Build isomers **2** and **3** and optimize their geometries at the B3LYP/cc-pVDZ level. Perform a (vibrational) frequencies calculation on each optimized geometry to ensure that each is an equilibrium geometry. If not an equilibrium geometry, rebuild the molecule, reoptimize, and rerun the frequencies calculation until an equilibrium geometry is found.

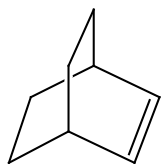
Record the energies (in Hartrees) of the equilibrium geometries for **2** and **3** to six places after the decimal point. Identify the more stable isomer and determine the relative energy ΔE of the higher energy form.

$$\Delta E = E(\text{higher energy isomer}) - E(\text{lower energy isomer})$$

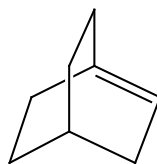
Energy differences (in kcal/mol) should only be reported to one place after the decimal point. Note that 1 Hartree = 627.51 kcal/mol.

Here are some questions to consider (but written responses are not expected): Do the results of your calculations for **2** and **3** support Bredt's Rule? Do you see any evidence for the instability of **3** in its equilibrium (optimized) geometry, particularly in the twisting of the double bond at the bridgehead atom?

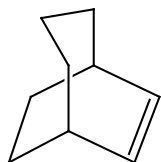
Repeat the calculations (geometry optimizations and frequencies) with the isomeric olefins **4** and **5**, **6** and **7**, and **8** and **9** that, respectively, place the double bond in six-, seven-, and eight-membered rings.



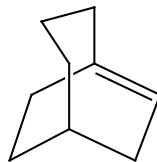
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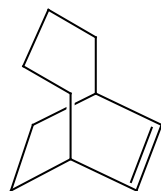
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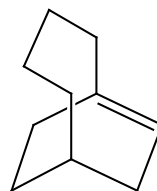
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7



8



9

Note that molecules **4-9** become increasingly flexible as the ring size increases from six to eight carbons. Increased flexibility in turn means that there are likely multiple equilibrium geometries (with differing energies) that Gaussian can identify. Build each of these molecules, especially **8** and **9**, multiple times in WebMO and optimize.

If multiple optimizations lead to the same geometry and energy, you have most likely identified the most stable form of the molecule. If multiple optimizations yield differing geometries and energies, continue building and optimizing until you have several calculations that give the same lowest energy geometry. You can only be confident that you have identified the lowest energy geometry of a molecule if multiple calculations give the same result.

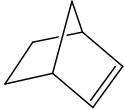

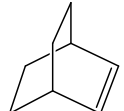
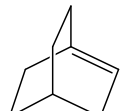
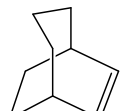
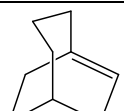
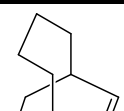
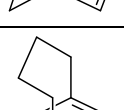
Only report results for the lowest energy geometries in the following. You can ignore any higher energy geometries that Gaussian may have optimized.

Report

Prepare a one-page report describing your calculations and summarizing your conclusions. Consider the following questions:

- (i) Are the relative energies of the bicycloalkene isomers consistent with Bredt's Rule?
- (ii) Are the trends in these energies in accord with the increasing stability of the bridgehead olefins with increasing ring size?
- (iii) Do the equilibrium geometries exhibit any features that support the ring strain hypothesis?

Justify your responses to each of these questions by referring directly to the data you report on the following table. Submit the report with a copy of the table.

Compound	B3LYP/cc-pVDZ <i>E</i> (Hartree)	B3LYP/cc-pVDZ <i>E</i> (kcal/mol)
2 		
3 		
ΔE		
4 		
5 		
ΔE		
6 		
7 		
ΔE		
8 		
9 		
ΔE		