Bredt's Rule

Semi-empirical AM1 calculations and 3-21G ab initio calculations are used to verify Bredt's rule, "elimination to give a double bond in a bridged bicyclic system always leads away from the bridgehead".

Bredt observed that elimination of water from a bicyclic alcohol, such as 1, gave an alkene in which the double bond did not involve the bridgehead position, 2, rather than the bridgehead alkene, 3.

\[ \text{OH} \xrightarrow{-\text{H}_2\text{O}} 2 \]

The preference is known to diminish with increasing ring size, which suggests that its origin is ring strain associated with incorporation of a double bond into a bridgehead position.\(^1\) In this experiment, you will use semi-empirical and ab initio molecular orbital calculations to test this hypothesis by comparing the stabilities of several bridgehead and non-bridgehead alkenes.

**Procedure**

Build 2 and 3, and optimize their geometries using semi-empirical AM1 calculations. Perform single-point 3-21G ab initio calculations using the AM1 equilibrium geometries. Identify the more stable isomer and work out the relative energy of the higher energy form. Do your results support Bredt's rule? Examine the geometries of 2 and 3. Do you see any evidence of geometrical distortion that might explain their relative stabilities? (Hint: the C=C bond length in ethylene is 1.34 Å and the molecule is planar.) Calculate and display the highest-occupied molecular orbital for 2 and 3. What evidence do they provide for distortion of the alkene? Which alkene, if either, contains a distorted \( \pi \) orbital? Is this result consistent with your structure and energy results?

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Repeat the calculations with the isomeric alkenes 4 and 5, 6 and 7, and 8 and 9.

For the larger systems, try to choose conformers that minimize obvious steric interactions. Are the differences in energies and equilibrium structures for these compounds relative to those for 2 and 3 consistent with a ring strain origin for Bredt’s rule? Based on your calculations, above what ring size would Bredt’s rule not apply? Cite any experimental evidence for your speculation.

Optional

Electrostatic potential maps should be able to tell you whether or not bridgehead alkenes are also more reactive (kinetically less stable) than the corresponding non-bridgehead isomers. In particular, changes in potential on the π bond should signal changes in reactivity toward electrophiles. Pick one pair of isomers from the above systems (2-9) and, for each isomer, generate an electrostatic potential map. Simultaneously display the two on the same scale. According to this measure, is the π bond in the bridgehead alkene likely to be more or less reactive toward electrophiles than the π bond in the non-bridgehead system? Try to rationalize your result.