

PREDICTING KINETICALLY UNSTABLE C-C BONDS FROM THE GROUND-STATE PROPERTIES OF A MOLECULE

Can one identify a labile bond in a molecule without computing activation barriers? Markopoulos and Grunenberg suggest that examination of the bond length and its associated relaxed force constant might provide some guidance.¹

The relaxed force constant comes from identifying the force constant for some coordinate while allowing for other coordinates to relax. Badger's rule relates the (normal) force constant to bond distance ($k = a/(r_{eq} - d)^3$). For a series of 36 molecules, covering 71 C-C single bonds, Badger's rule fits the data well, except for a set of molecules which undergo rapid Cope rearrangements (like bullvalene and semibullvalene). For these molecules, the relaxed force constants are much lower than Badger's rule predicts, and indicates a weakened bond. This gives rise to their low activation barriers.

Another example is provided with the highly strained polycyclic hydrocarbon **1**. This compound is predicted (B3LYP/6-31G(d)) to undergo a [1,2]-shift to give the carbene **2** (see Figure 1), and this is extremely exothermic: $-105.7 \text{ kcal mol}^{-1}$, reflecting the enormous strain of **1**.

The barrier, through **TS1** (Figure 1), is only $6.7 \text{ kcal mol}^{-1}$. This rearrangement was predicted by examining the relaxed force constants which identified a very weak bond, despite a short bond distance of 1.404 \AA . It is unlikely that without this guidance, one would have predicted that this short bond is likely to rupture and produce this particular product.

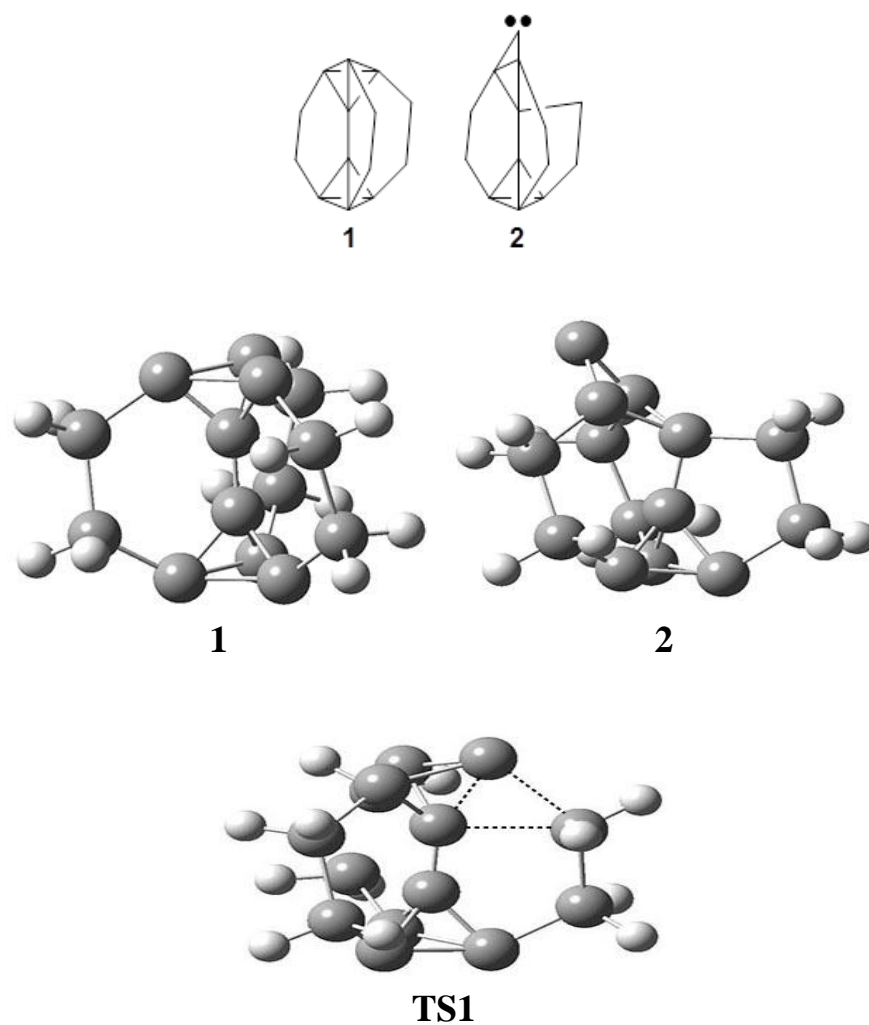


Figure 1. B3LYP/6-31G(d) optimized structures of **1**, **2**, and **TS1**.

Source: <http://www.compchemhighlights.org/2013/11/predicting-kinetically-unstable-c-c.html>