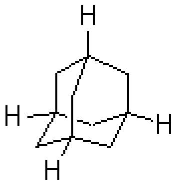
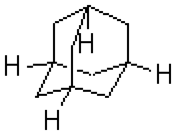
INVERTED ADAMANTANE

There is a mystique surrounding chemical torture. Just how much strain can one subject a poor old carbon atom to? We construct such tortured molecules as cubane and cyclopentyne and *trans*-fused bicyclo[4.1.0]heptane. Inverted carbons – think of propellanes – are also a fruitful arena for torturing hydrocarbons. Now, Irikura has examined inverted adamantane **inv-1**.[1]

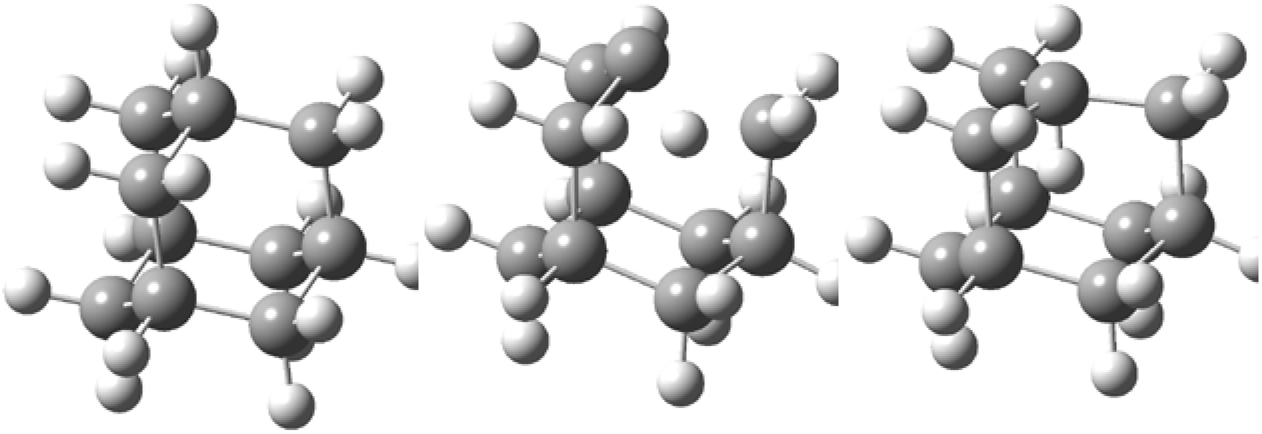


1



inv-1

The MP2/6-31G(d) optimized geometries of **1** and **inv-1** and the transition state separating them are displayed in Figure 1. The inverted structure is a local energy minimum, lying 105 kcal mol^{-1}above **1**.[2] The barrier for rearrangement of the inverted adamantane into adamantane, which involved a cleave of a C-C bond, is 17 kcal mol^{-1}, which implies a half-life of 30 ms at 298K and and 2 days at 195 K. The perfluoro isomer has a higher barrier (32 kcal mol^{-1}) and a longer half-life (110 years at 298K).



1 **TS-1** **inv-1**

Table 1. MP2/6-31G(d) optimized geometries of **1**, **inv-1**, and the transition state connecting them.[1]

So, **inv-1** has some kinetic stability. It also has little computed reactivity with water, oxygen, or a second molecule of **inv-**1. Irikura, however, did not compute reactions that might lead to loss of a hydride from **inv-1**, which would give a non-classical cation.

As might be expected, the spectroscopic properties of **inv-1** are unusual. The C-H vibrational frequency for the inverted hydrogen is 3490 cm^{-1} and the C-C-H bend is also 300 cm^{-1} higher than in **1**. The NMR shifts for the inverted methane group are 7.5 ppm for the hydrogen and 21 ppm for the carbon atom.

Irikura ends the article, “Experimental verification (or refutation) of [inv-1] presents a novel synthetic challenge.” Let’s hope someone picks up the gauntlet!

Source: http://comporgchem.com/blog/?p=97