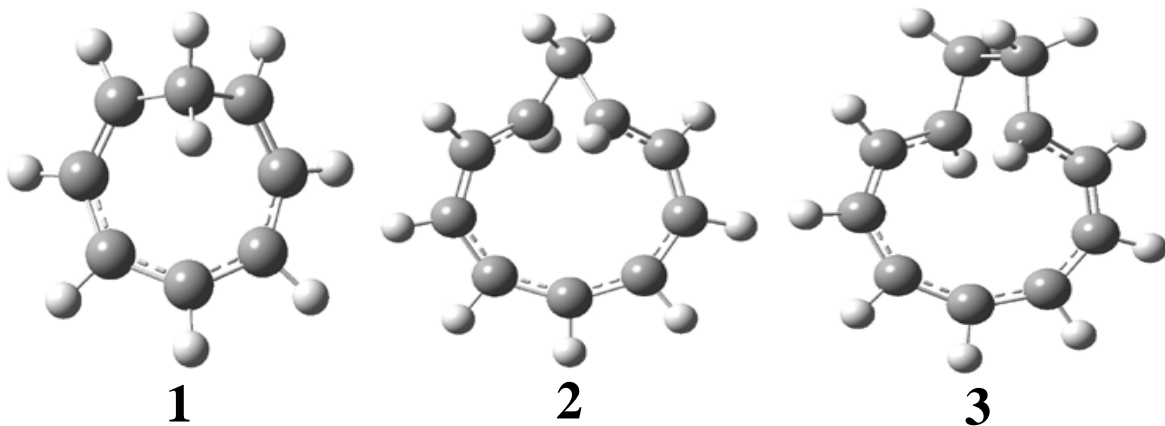


ASSIGNING THE STRUCTURE OF OBTUSALLENES USING COMPUTED NMR

Here's another interesting application of computed NMR spectra to resolve the structure of natural products. Braddock and Rzepa have examined obtusallenes V (1), VI (2) and VII (3).¹ The geometries were optimized at mPW1PW91/6-31G(d,p) and the chemical shifts were obtained at this level and using the aug-cc-pVDZ basis set. The larger basis reduces the error and no statistical correction need be applied. The coordinates of these compounds are available through this web-enhanced object of the paper.



The confusion in these structures relates to the position of the halide attachments.

For **1** and **2**, the problem is which halide (Br or Cl) is at C-7 and C-13.

The original structures proposed had these halogens switched from what I've drawn, and the correlation between the computed chemical shifts for these original structures and the experiment shows significant deviation: a mean deviation of 1.42 ppm for **1** and 1.67 ppm for **2**. Using the structures shown above, along with switching the assigned ^{13}C chemical shifts gives much better agreement between the computed and experimental values; the mean deviation is 1.15 ppm for both **1** and **2**. Unfortunately the stereochemistry about the allene cannot be determined using NMR – the two different isomers have similar chemical shifts. Similarly, the structure of **3** is predicted as shown above, though the experiment reported only some of the chemical shifts so some uncertainty remains.

Source: <http://comporgchem.com/blog/?p=63>