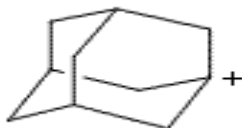


1-ADAMANTYL CATION – PREDICTING ITS NMR SPECTRA

What is required in order to compute *very* accurate NMR chemical shifts? Harding, Gauss and Schleyer take on the interesting spectrum of 1-adamantyl cation to try to discern the important factors in computing its ^{13}C and ^1H chemical shifts.¹

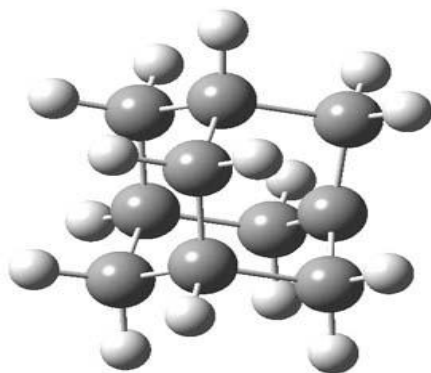


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To start, the chemical shifts of 1-adamantyl cation were computed at B3LYP/def2-QZVPP and MP2/qz2p//MP2/cc-pVTZ. The root means square error (compared to experiment) for the carbon chemical shifts is large: 12.76 for B3LYP and 6.69 for MP2. The proton shifts are predicted much more accurately with an RMS error of 0.27 and 0.19 ppm, respectively.

The authors speculate that the underlying cause of the poor prediction is the geometry of the molecule.

The structure of **1** was optimized at HF/cc-pVTZ, MP2/cc-pVTZ and CCSD(T)/pVTZ and then the chemical shifts were computed using MP2/tzp with each optimized geometry. The RMS error of the ^{12}C chemical shifts are HF/cc-pVTZ: 9.55, MP2/cc-pVTZ: 5.62, and CCSD(T)/pVTZ: 5.06. Similar relationship is seen in the proton chemical shifts. Thus, a better geometry does seem to matter. The CCSD(T)/pVTZ optimized structure of **1** is shown in Figure 1.



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Figure 1. CCSD(T)/pVTZ optimized structure of **1**.

Unfortunately, the computed chemical shifts at CCSD(T)/qz2p//CCSD(T)/cc-pVTZ are still in error; the RMS is 4.78ppm for the carbon shifts and 0.26ppm for the proton shifts. Including a correction for the zero-point vibrational effects and adjusting to a temperature of 193 K to match the experiment does reduce the error; now the RMS for the carbon shifts is 3.85 ppm, with the maximum error of 6 ppm for C3. The RMS for the proton chemical shifts is 0.21ppm.

The remaining error they attribute to basis set incompleteness in the NMR computation, a low level treatment of the zero-point vibrational effects (which were computed at HF/tz2p), neglect of the solvent, and use of a reference in the experiment that was not dissolved in the same media as the adamantyl cation.

So, to answer our opening question – it appears that a very good geometry and treatment of vibrational effects is critical to accurate NMR shift computation of this intriguing molecule. Let the computational chemist beware!

Source: <http://comporgchem.com/blog/?p=1631>