# INVERTED CARBON GEOMETRIES: CHALLENGES TO EXPERIMENT AND THEORY

Inverted carbon atoms, where the bonds from a single carbon atom are made to four other atoms which all on one side of a plane, remain a subject of fascination for organic chemists. We simply like to put carbon into unusual environments! Bremer, Fokin, and Schreiner have examined a selection of molecules possessing inverted carbon atoms and highlights some problems both with experiments and computations.[1]

The prototype of the inverted carbon is propellane **1**. The C_{inv}-C_{inv} bond distance is 1.594 Å as determined in a gas-phase electron diffraction experiment.[2] A selection of bond distance computed with various methods is shown in Figure 1. Note that CASPT2/6-31G(d), CCSD(t)/cc-pVTZ and MP2 does a very fine job in predicting the structure. However, a selection of DFT methods predict a distance that is too short, and these methods include functionals that include dispersion corrections or have been designed to account for medium-range electron correlation.


1
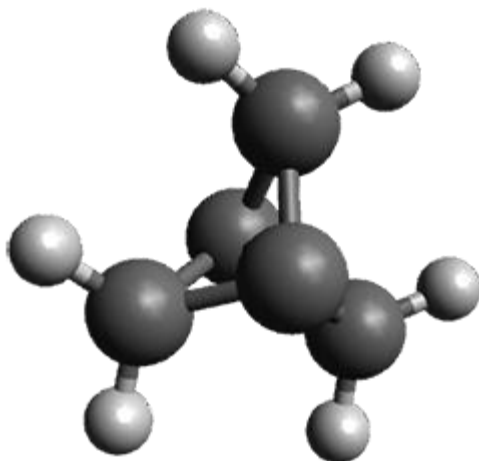
CASPT2/6-31G(d)	1.596
CCSD(T)/cc-pVTZ	1.595
MP2/cc-pVTZ	1.596
MP2/cc-pVQZ	1.590
B3LYP/6-311+G(d,p)	1.575
B3LYP-D3BJ/6-311+G(d,p)	1.575
M06-2x/6-311+G(d,p)	1.550

Figure 1. Optimized Structure of **1** at MP2/cc-pVTZ, along with C_{inv}-C_{inv} distances (Å) computed with different

methods.

Propellanes without an inverted carbon, like **2**, are properly described by these

DFT methods; the C-C distance predicted by the DFT methods is close to that

predicted by the post-HF methods.

2   NC 3
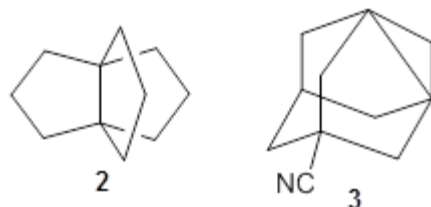
The propellane **3** has been referred to many times for its seemingly very long C_{inv}-C_{inv} bond: an x-ray study from 1973 indicates it is 1.643 Å.[3] However, this distance is computed at MP2/cc-pVTZ to be considerably shorter: 1.571 Å (Figure 2). Bremer, Fokin, and Schreiner resynthesized **3** and conducted a new x-ray study, and find that the C_{inv}-C_{inv} distance is 1.5838 Å, in reasonable agreement with the computation. This is yet another example of where computation has pointed towards experimental errors in chemical structure.
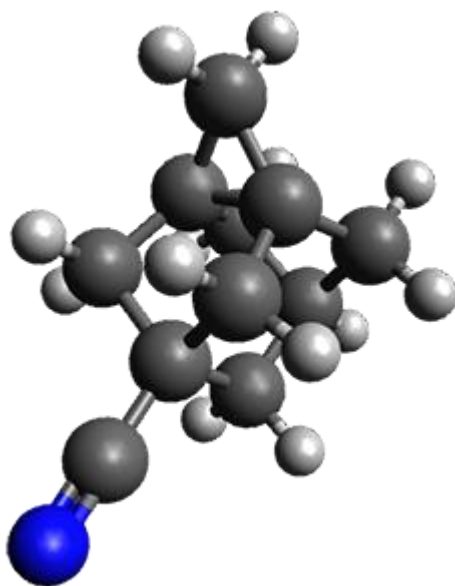
Figure 2. MP2/cc-pVTZ optimized structure of **3**.

However, DFT methods fail to properly predict the C_{inv}-C_{inv} distance in **3**. The functionals B3LYP, B3LYP-D3BJ and M06-2x (with the cc-pVTZ basis set) predict a distance of 1.560, 1.555, and 1.545 Å, respectively. Bremer, Folkin and Schreiner did not consider the ωB97X-D functional, so I optimized the structure of **3** at ωB97X-D/cc-pVTZ and the distance is 1.546 Å.

Inverted carbon atoms appear to be a *significant challenge for DFT methods*.