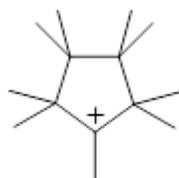


NONAMETHYLCYCLOPENTYL CATION

The nine methyl groups of nonamethylcyclopentyl cation **1** all interconvert with a barrier of 7 kcal mol⁻¹. However, at low temperature only partial scrambling occurs: there are two sets of methyl groups, one containing five groups and the other containing four methyl groups. The barrier for this scrambling is only 2.5 kcal mol⁻¹. While this behavior was found more than 20 years ago, Tantillo and Schleyer¹ only now have offered a complete explanation.



1

The ground state structure of **1** is shown in Figure 1 and has C_1 symmetry. The two pseudo-axial methyl groups adjacent to the cationic center show evidence of hyperconjugation: long C-C bonds and Me-C-C⁺ angles of 100°.

The transition state **TS1**, also in Figure 1, is of C_s symmetry. This transition state leads to interchange of the pseudo-axial methyls, and interchange of the pseudo-equatorial methyls, but no exchange between the members of these two groups. The M06-2x/6-31+G(d,p) and mPW1PW91/6-31+G(d,p) estimate of this barrier is 1.5 and 2.5 kcal mol⁻¹, respectively. This agrees well with the experiment.

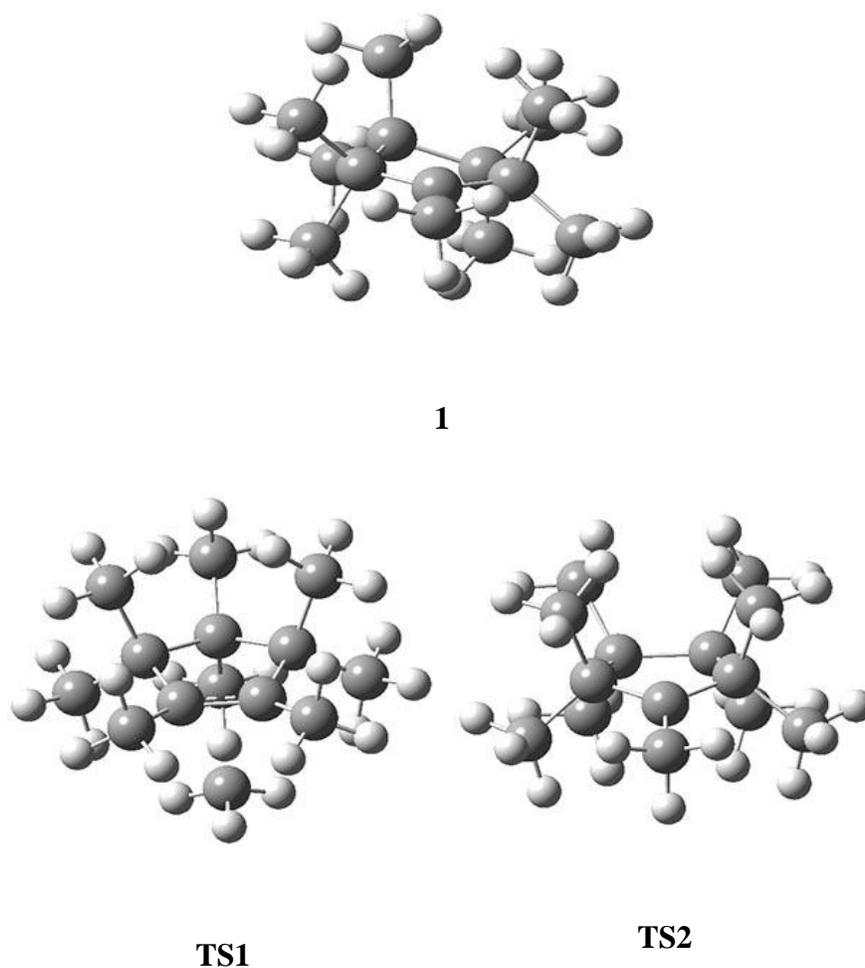


Figure 1. B3LYP/6-3+G(d,p) optimized geometries.

A second transition state **TS2** was found and it corresponds with a twisting motion that interconverts an axial methyl with an equatorial methyl.

This TS has C_s symmetry (shown in Figure 1) and the eclipsing interaction give rise to a larger barrier: 7.3 (M06-2x/6-31+G(d,p)) and 6.7 kcal mol⁻¹ (mPW1PW91/6-31+G(d,p)). So twisting through **TS2** and scrambling through **TS1** allows for complete exchange of all 9 methyl groups.

An interesting point also made by these authors is that these three structures represent the continuum of cationic structure: a classical (localized) cation in **TS2**, a bridged structure in **TS1** and hyperconjugated cation in **1**.

Source: <http://comporgchem.com/blog/?p=2759>