

UNUSUAL CARBENE GROUND STATES

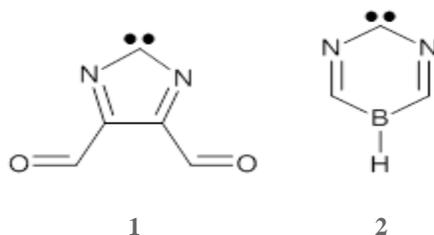
The singlet and triplet carbene is the topic of Chapter 4, especially sections 1 and 2. The ground state of methylene is the triplet, with one electron in the σ -orbital and one electron in the π -orbital, with the spins aligned. The lowest singlet state places the pair of electrons in the σ -orbital, and this state is about 9 kcal mol⁻¹ higher in energy than the triplet. The next lowest singlet state has one electron in each of the σ - and π -orbitals, with the spins aligned. The singlet state with both electrons in the π -orbital is the highest of these four states, some 60 kcal mol⁻¹ above the ground state triplet.

Hoffmann and Borden now pose the question “Can the doubly occupied π carbene ($^1A_1-\sigma^0\pi^2$) be the ground state with appropriate substitution?” The answer they find is yes!¹

The trick is to find a combination of substituents that will raise the energy of the σ -orbital and lower the energy of the π -orbital. The latter effect can be enhanced if the π -orbital can be a part of an aromatic ($6e^-$) ring.

Two of the best possibilities for identifying a ground state $^1A_1-\sigma^0\pi^2$ carbene are **1** and **2**. The CASSCF/6-31G(d) optimized geometries of these two are shown in Figure 1. In **1**, the nitrogen lone pairs act to destabilize the σ -orbital, while the

aldehyde group acts as a withdrawing group to stabilize the π -orbital. The result is that the $^1A_1-\sigma^0\pi^6$ state of **1** is predicted to be about 8 kcal mol⁻¹ more stable than the triplet state, as per CASPT2 and CCSD(T) computations.



An ever greater effect is predicted for **2**. Here the nitrogen lone pairs adjacent to the carbene act to destabilize the σ -orbital. The empty π -orbital on B lowers the energy of the carbene π -orbital by making it part of the 6-electron aromatic ring. The $^1A_1-\sigma^0\pi^6$ state of **2** is predicted to be about 25 kcal mol⁻¹ more stable than its triplet state!

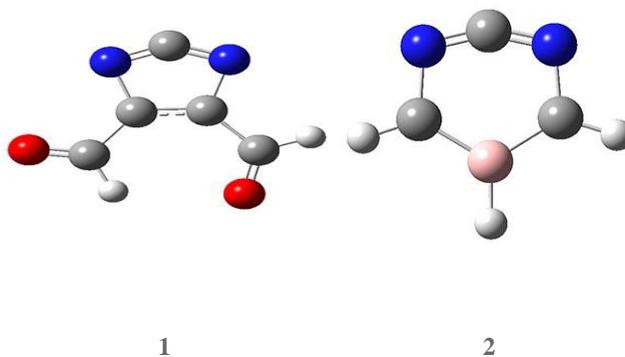


Figure 1. CASSCF/6-31G(d) optimized geometries of the $^1A_1-\sigma^0\pi^6$ states of **1** and **2**.

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