

SOLVENT EFFECT ON CARBENE SPIN STATE

Carbenes remain an active area of interest for computational chemists, as seen in Chapter 5 of my book. For many carbenes, the triplet is the ground state, and that is true of diphenylcarbene **1**. Can solvent play a role in the stability of carbene spin states? Surprisingly, the answer, provided in a recent paper by Sander,¹ is *yes!*

In the gas phase, the singlet-triplet gap of **1** is computed to be 5.62 kcal mol⁻¹ at (U)B3LYP/6-311++G(d,p) (and this reduces to 5.06 at (U)B3LYP+D3/6-311++G(d,p)) with the ground state as a triplet. If a single methanol molecule is allowed to approach **1**, then the complex involving the singlet has a short hydrogen bond distance of 1.97 Å but the triplet has a much longer distance of 2.33 Å. These structures are shown in Figure 1. This manifests in a dramatic change in the relative stability, with the singlet complex now 0.26 kcal mol⁻¹ (0.44 with the D3 correction) *lower in energy than the triplet*.

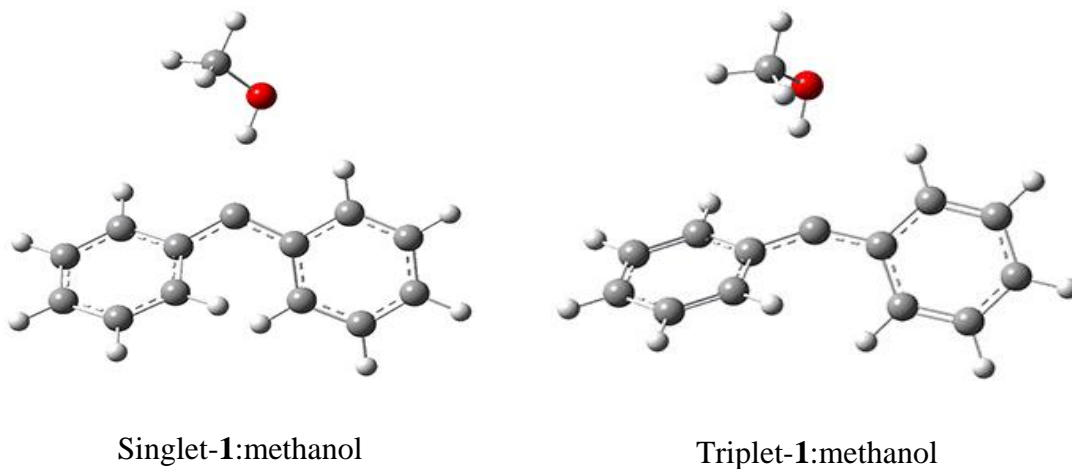


Figure 1. (U)B3LYP/6-311++G(d,p) optimized geometries of the complexes of methanol with singlet or triplet **1**.

IR spectroscopy of **1** in an argon matrix doped with a small amount of methanol confirms the presence of the singlet carbene, and detailed description of the difference in the reactivities of the singlet and triplet are provided.

Source: <http://comporgchem.com/blog/?p=3138>