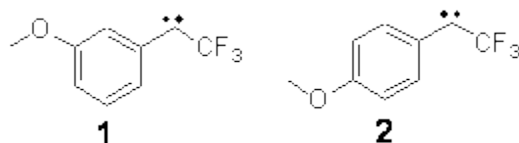


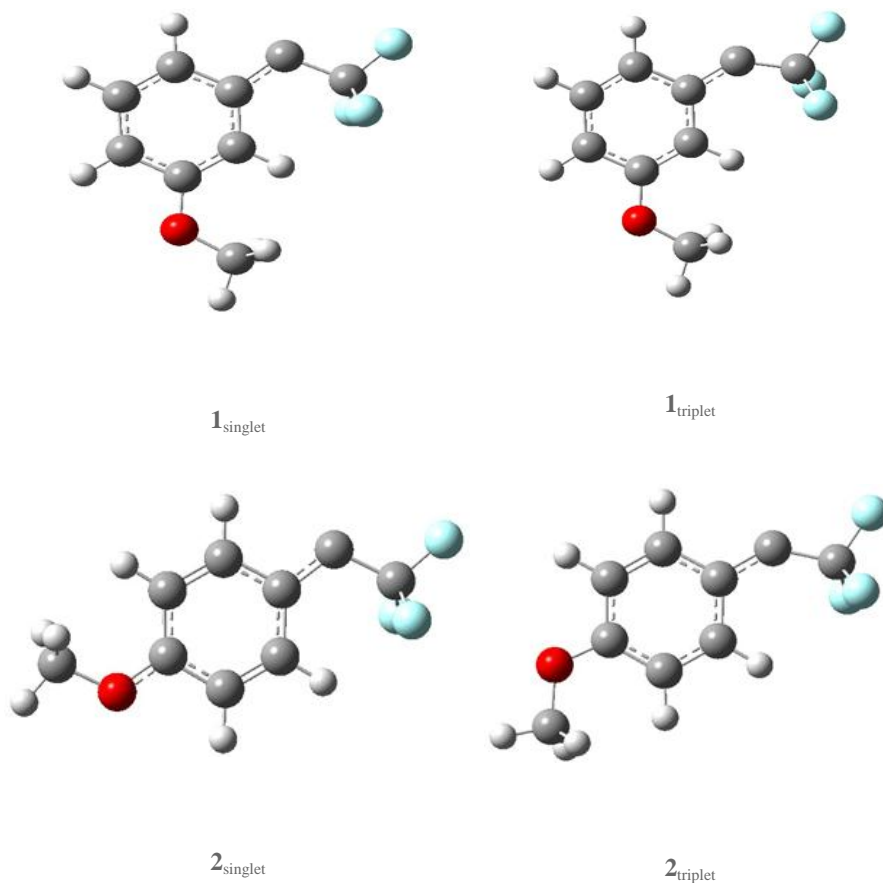
# SINGLET-TRIPLET CARBENE GAP AND REMOTE SUBSTITUENTS

Can a remote substituent affect the singlet-triplet spin state of a carbene?

Somewhat surprisingly, the answer is yes. Sheridan has synthesized and characterized the *meta* and *para* methoxy-substituted phenyl(trifluoromethyl)carbenes **1** and **2**.<sup>1</sup> The UV-Vis spectrum of **1** is consistent with a triplet as its EPR and reactivity with oxygen. However, the *para* isomer **2** gave no EPR signal and failed to react with oxygen or hydrogen, suggestive of a singlet.



The conformations of **1** and **2** were optimized at B3LYP/6-31+G(d,p) and the lowest energy singlet and triplet conformers are shown in Figure 1. The experimental spectral features of **1** match up best with the computed features of the triplet, and the same is true for the singlet of **2**.

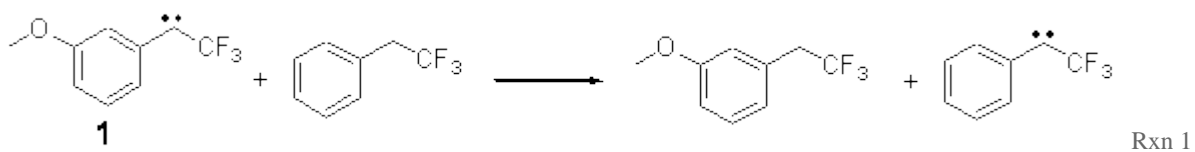


**Figure 1.** B3LYP/6-31+G(d,p) optimized geometries of **1** and **2**.

The triplet of **1** is estimated to be about  $4 \text{ kcal mol}^{-1}$  below that of the singlet – larger than the general overestimation of the stability of triplets that beleaguer B3LYP. For **2**, B3LYP predicts a singlet ground state.

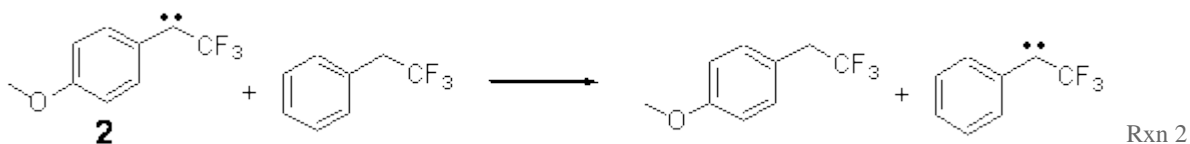
The isodesmic reactions 1 and 2 help understand the strong substituent effect. For **1**, the *meta*substituent destabilizes both the singlet and triplet by a small amount. For **2**, the *para* methoxy group stabilizes the triplet slightly, but stabilizes the singlet by a large amount.

This stabilization is likely the result of the contribution of a second resonance structure **2b**. A large rotational barrier for both the methyl methyl and the trifluoromethyl groups supports the participation of **2b**.



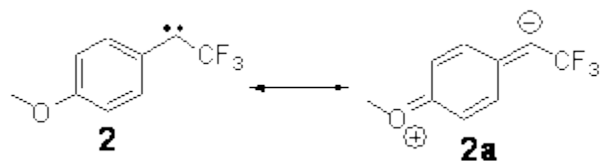
$$\Delta E_{\text{singlet}} = -0.8 \text{ kcal mol}^{-1}$$

$$\Delta E_{\text{triplet}} = -0.6 \text{ kcal mol}^{-1}$$



$$\Delta E_{\text{singlet}} = -5.8 \text{ kcal mol}^{-1}$$

$$\Delta E_{\text{triplet}} = -1.1 \text{ kcal mol}^{-1}$$



Source: <http://comporgchem.com/blog/?p=2013>