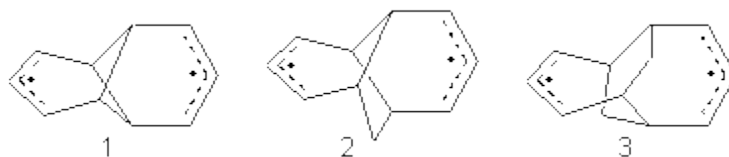
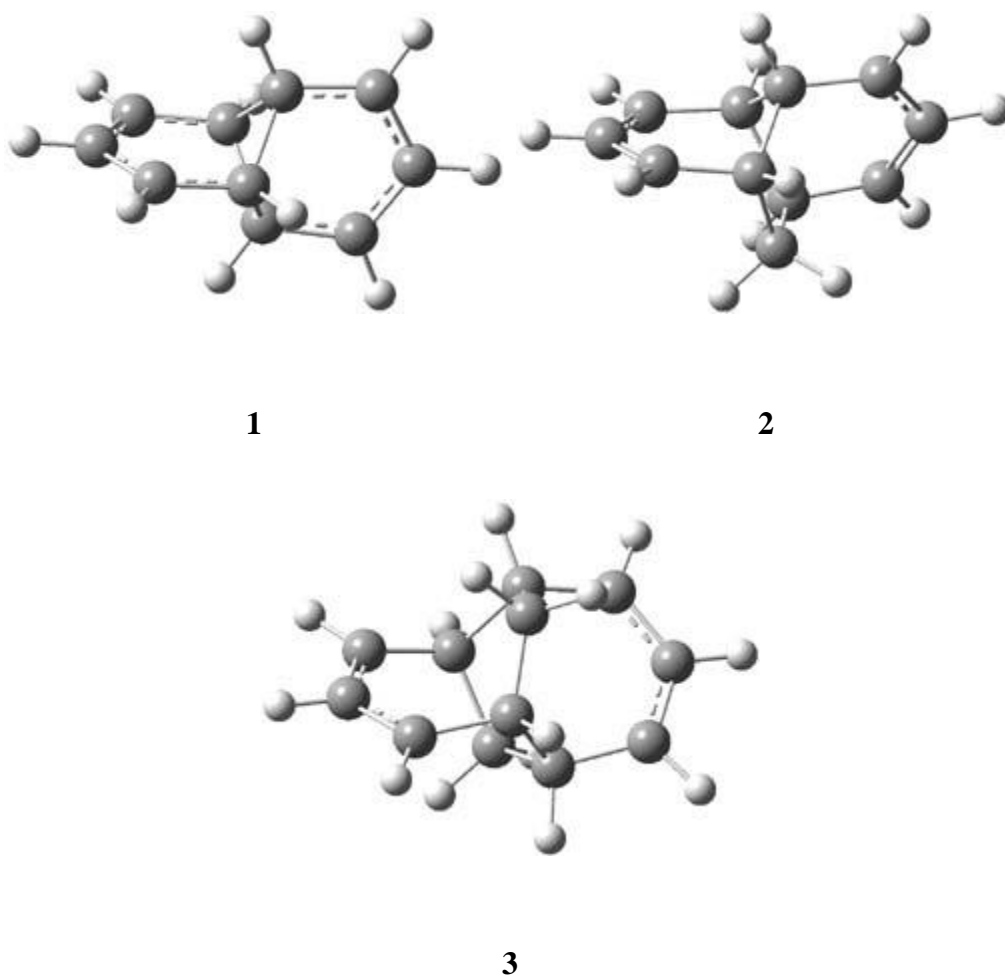


# INTERACTING BIS-ALLYL DIRADICALS

Interacting bis-allyl radicals are the topic of a computational study by Gleiter and Borden.<sup>1</sup> The new twist is to have the two allyl groups interact through a cyclobutyl, cyclopentyl or cyclohexyl ring, as in **1-3**.



The degree of interaction of the radical electrons is evaluated with a number of metrics. First, the singlet-triplet energy gap is computed at CASSCF(6,6)/6-31G(d) and UB3LYP/6-31G(d). A larger gap is suggestive of strong interaction between the two allyl radicals. Next, the  $\langle S^2 \rangle$  value of the UB3LYP wavefunction will be 0 for a pure singlet, which occurs when the radicals are strongly interacting. A value near 1 suggests an electron localized into each allyl fragment. Lastly, the natural orbital occupation numbers (NOON) of the two highest lying orbitals would be 2 and 0 for the pure interacting state and each would be 1 for the non-interacting state. The B3LYP/6-31G(d) optimized geometries of **1-3** are shown in Figure 1. The values of each metric are listed in Table 1.



**Figure 1.** B3LYP/6-31G(d) optimized geometries of **1-3**.

**Table 1.** Metrics for evaluating the allyl interaction in **1-3**.

Diradical	$\Delta E_{ST}$ (DFT) <sup>a</sup> [kcal/mol]	$\Delta E_{ST}$ (CAS) <sup>a</sup> [kcal/mol]	$\langle S^2 \rangle$	NOON
<b>1</b>	21.4	25.5	0.0	1.62, 0.38
<b>2</b>	3.7	5.9	0.85	1.31, 0.69
<b>3</b>	1.6	2.4	0.96	1.20, 0.80

The different metrics are all consistent. The allyl radicals are strongly interacting in **1**, with a low lying singlet state. The interaction is significantly lessened in **2** and smaller still in **3**. The authors argue these differences in terms of the molecular orbital interactions between the allyl fragments and the central ring fragment.

Source: <http://comporgchem.com/blog/?p=1238>