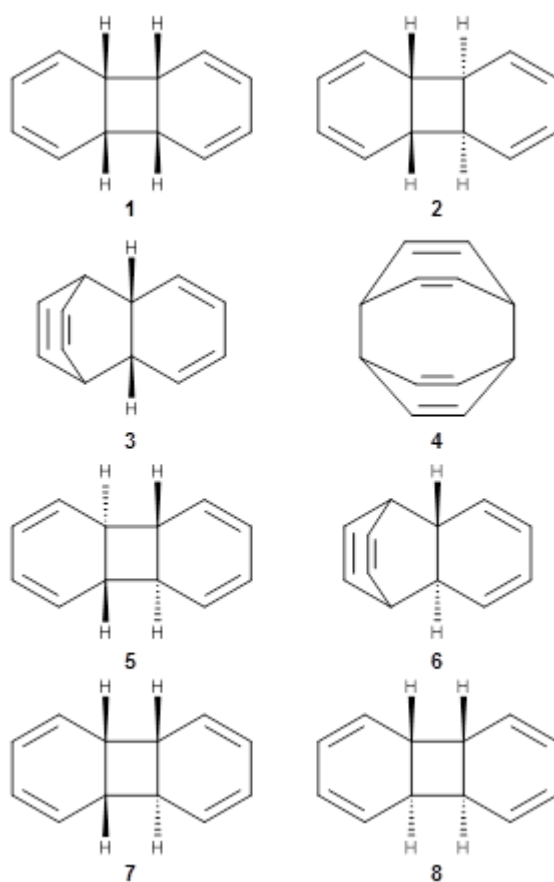
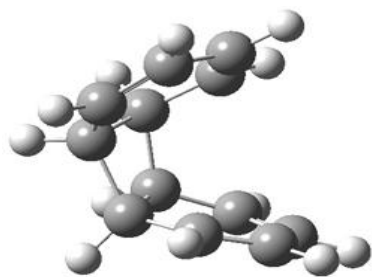


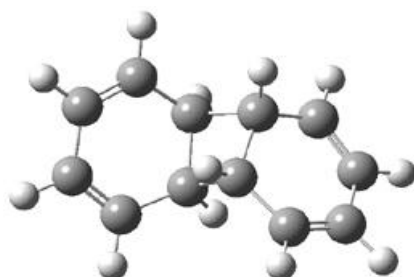
# BENZENE DIMERS – [2+2] AND [4+2]

Hoffmann<sup>1</sup> reports on a number of new benzene dimer structures, notably **5-8**, whose RIJCOSX-MP2/cc-pVTZ<sup>2</sup> structures are shown in Figure 1. A few of these new dimers are only somewhat higher in energy than the known dimers **1-4**. The energies of these dimers, relative to two isolated benzene molecules, are listed in Table 1.

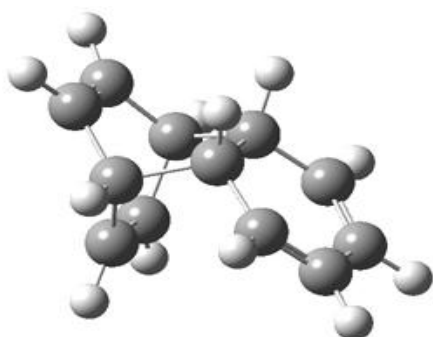




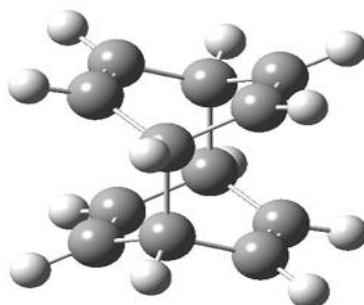
**1**



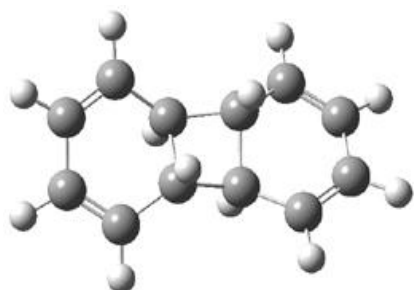
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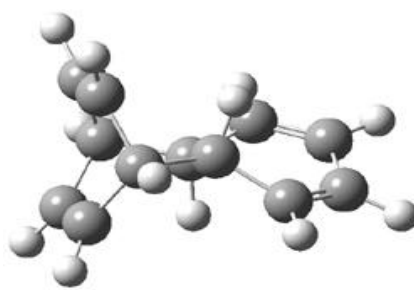
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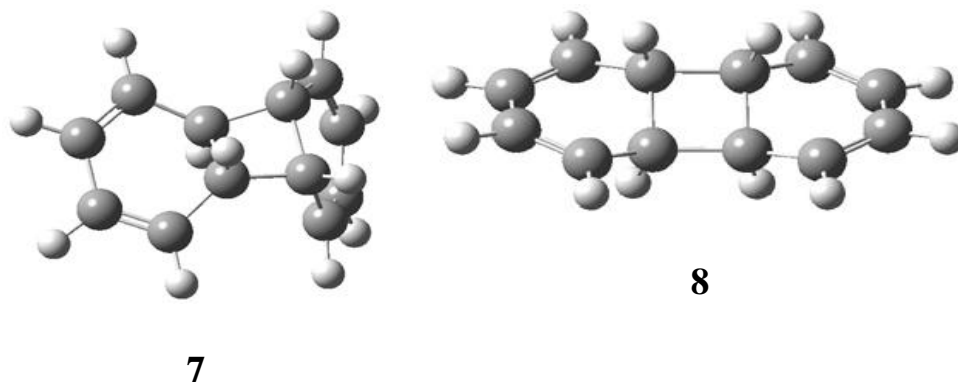
**4**



**5**



**6**



**Figure 1.** RIJCOSX-MP2/cc-pVTZ optimized geometries of **1-8**.

**Table 1.** Energy ( $\text{kcal mol}^{-1}$ ) of the dimers relative to two benzene molecules and activation energy for reversion to two benzene molecules.

Compound	$E_{\text{rel}}$	$E_{\text{act}}$
<b>1</b>	50.9	29
<b>2</b>	49.9	
<b>3</b>	38.2	9
<b>4</b>	58.7	19
<b>5</b>	71.9	30
<b>6</b>	49.9	36
<b>7</b>	60.8	27
<b>8</b>	98.8	28

The energy for reversion of the isomers **5-8** to two isolated benzene molecules is calculated to be fairly large, and so they should be stable relative to that decomposition mode. They also examined a series of other decomposition modes, including [1,5]-hydrogen migration, all of which had barriers of 21 kcal mol<sup>-1</sup> or greater, retrocyclization ([2+2]), for which they could not locate transition states, electrocyclic ring opening (Cope), with barriers of at least 17 kcal mol<sup>-1</sup> and dimerization – some of which had relatively small enthalpic barriers of 4-5 kcal mol<sup>-1</sup>. However, the dimerizations all have very unfavorable entropic activation barriers.

So, the conclusion is that all of the novel dimers (**4-8**) can be reasonably expected to hang around for some time and therefore are potential synthetic targets.

Source: <http://comporgchem.com/blog/?p=2258>