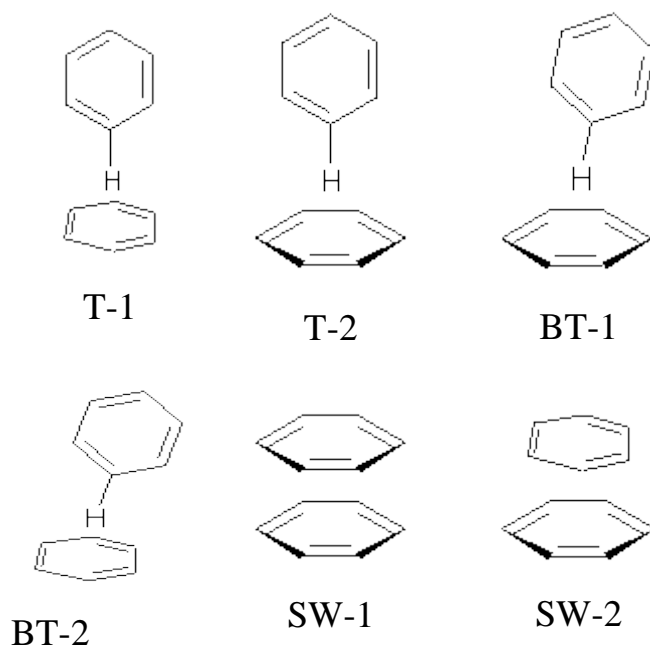
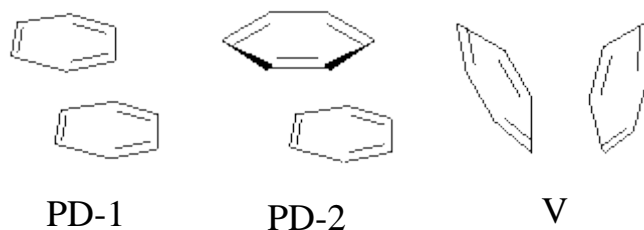


BENZENE DIMER AGAIN

Yet more on the benzene dimer. Lesczynski has optimized 9 different benzene dimer configurations, shown in Scheme 1.¹ There are two T-shaped isomers, where a hydrogen from one benzene interacts with the center of the π -cloud of the second. There are two bent versions of the T-shape, called Bent-T-shape. There are two sandwich configurations and two variants where the benzenes are parallel but displaced. Lastly, they report on a new variant, the V-shape configuration. (Once again, the author has not deposited the structures and so I can't produce interactive figures!)

Scheme 1





The structures were optimized at MP2/aug-cc-pVDZ and then single point energies computed at MP4(SDTQ)/aug-cc-pVDZ and corrected for basis set superposition error. I list these energies in Table 1. The authors note that in comparison with CCSD(T) computations one has to adjust the amount of BSSE correction – which just supports my long-held contention that the standard counterpoise correction overcompensates and that we really have no reliable way of correcting for BSSE.

Table 1. Dimerization energies (kcal mol⁻¹) at MP4(SDTQ)/aug-cc-pVDZ.¹

T-1	T-2	BT-1	BT-2	SW-1	SW-2	PD-1	PD-2	V
-2.15	-2.15	-2.21	-2.30	-1.25	-1.23	-2.13	-2.13	-0.83

The relative energies of the 9 configurations are similar, indicating a very flat potential energy surface. The lowest energy structure is BT-2, and the V-shape configuration is the least favorable of the nine geometries examined.

Source: <http://comporgchem.com/blog/?p=161>