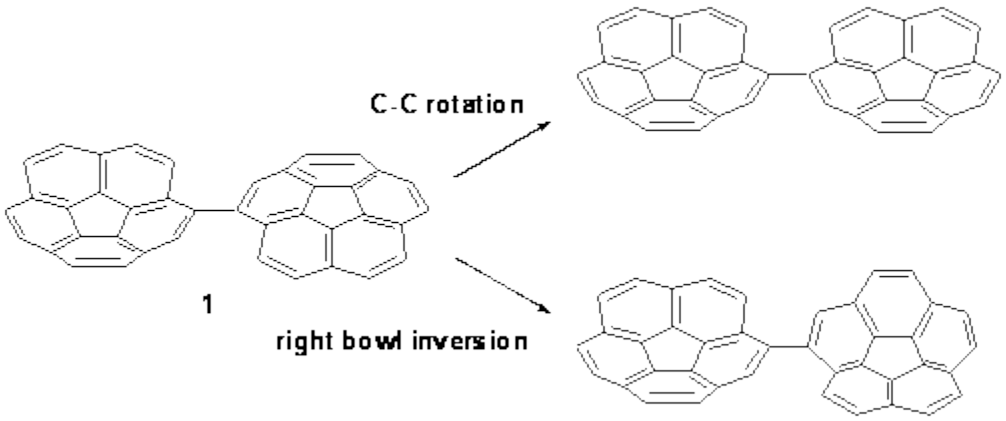
BISCORANNULENYL STEREOCHEMISTRY

Consider bicorannulenyl **1**. Each corranulene unit is a bowl and each is chiral due to being monosubstituted. Additional chirality is due to the arrangement of the bowls along the C_1-$C_{1'}$ bond, the bond where the two rings join. So both rotation about the C_1-$C_{1'}$ bond and bowl inversion will change the local chirality (Scheme 1 distinguishes these two processes.) One might anticipate that the stereodynamics of **1** will be complicated!

Scheme 1



Rabinovitz, Scott, Shenhar and their groups have tackled the stereodynamics of **1**.[1] (This is a very nice joint experimental and theoretical study and I wonder why it did not appear in *JACS*.) At room temperature and above, one observes a

single set of signals, a singlet and eight doublets, in the ^{1}H NMR. Below 200 K, there are three sets of signals, evidently from three different diastereomers.

Each ring can have either *P* or *M* symmetry. The authors designate conformations using these symbols for each ring along with the value of the torsion angle about the C_1-$C_{1'}$ bond. So, for example, a *PP* isomer is the enantiomer of the *MM* conformer when their dihedral angles are of opposite sign.

DFT computations help make sense of these results. PBE0/6-31G* computations reveal all local minima and rotational and inversion transition states of **1**. The lowest (free) energy structure isPP_{44} (see Figure 1). A very small barrier separates it from PP_{111}; this barrier is related to loss of conjugation between the two rings. Further rotation must cross a much larger barrier (nearly 17 and 20 kcal mol^{-1}). These barriers result from the interaction of the C_2 hydrogen of one ring with either the $C_{2'}$ or $C_{10'}$ hydrogen, similar to the rotational barrier in 1,1'-binaphthyl. However, the barrier is lower in **1** than in 1,1'-binaphthyl due to the non-planar nature of **1** that allows the protons to be farther apart in the TS. Once over these large barriers, two local minima, PP_{-45} and PP_{-137}, separated by a small barrier are again found.

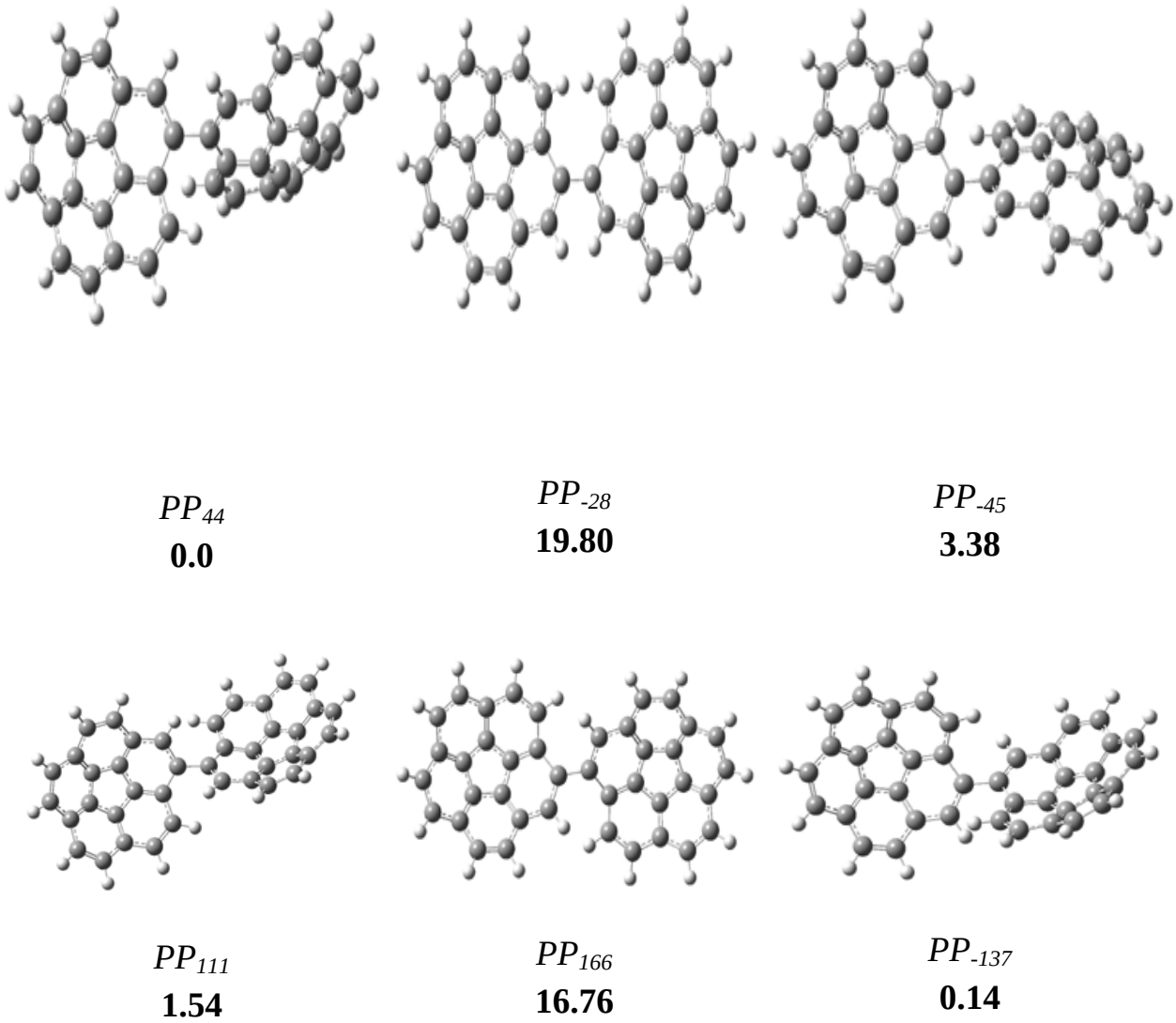
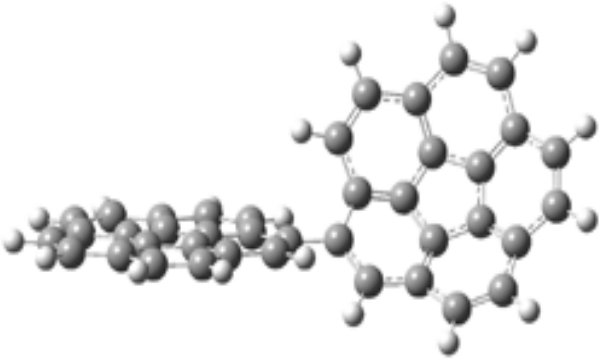


Figure 1. PBE0/6-31G* optimized geometries and relative free energies (kcal mol^{-1}) of the *PP* local minima (PP_{44}, PP_{111}, PP_{-45}, and PP_{-137}) and rotational transition states.[1]

The lowest energy bowl inversion transition state (P_{49}) lies 9.6 kcal mole^{-1} above PP_{44}. It is shown in Figure 2.

The bowl inversion barrier is comparable to that found in other substituted corannulenes,[2] which are typically about 9-12 kcal mol^{-1}).



P_{49}
9.58

Figure 2. PBE0/6-31G* optimized geometry and relative free energy of the lowest energy bowl inversion transition state.[1]

Interestingly, it is easier to invert the bowl than to rotate about the C_1-$C_{1'}$ bond. And this offers an explanation for the experimental ^{1}H NMR behavior. At low temperature, crossing the low rotational barriers associated with loss of conjugation occurs. So, using the examples from Figure 1, PP_{44} andPP_{111} appear as a single time-averaged signal in the NMR. This leads to three pairs of enantiomers (*S.PP/R.PP, S.MM/R.PP, and S.PM/R.MP)*, giving rise to the three sets of NMR signals.

Source: http://comporgchem.com/blog/?p=90