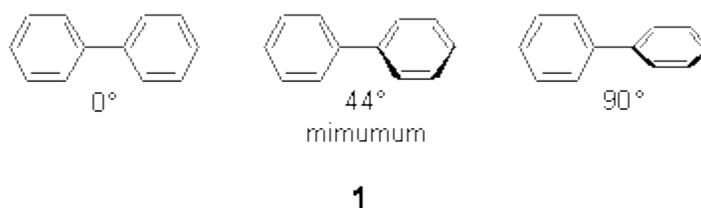


# ROTATIONAL BARRIER OF BIPHENYL

Just how difficult can it be to compute rotational barriers? Well, it turns out that for biphenyl **1**, the answer is “very”!



The experimental barriers for rotation about the C<sub>1</sub>-C<sub>1'</sub> bond of biphenyl are 6.0 ± 2.1 kcal mol<sup>-1</sup> at 0° and 6.5 ± 2.0 kJ mol<sup>-1</sup> at 90°.<sup>1</sup> CCSD(T) with extrapolated basis set approximation computations by Sancho-García and Cornil overestimate both barriers by more than 4 kJ mol<sup>-1</sup> and, more critically in error, predict that the 0° barrier is higher in energy than the 90° barrier.<sup>2</sup>

Now Johansson and Olsen have reported a comprehensive study of the rotational barrier of biphenyl.<sup>3</sup> They tackled a number of different effects:

1. Basis sets: The cc-pVDZ basis set is simply too small to give any reasonable estimate (See Table 1).

2. Correlation effects: HF, MP2, SCS-MP2 and CCSD overestimate the barriers and get the relative energies of the two barriers wrong, regardless of the basis set. While CCSD(T) does properly predict the barrier at  $0^\circ$  is lower than that at  $90^\circ$ , even this level overestimates the barrier heights (Table 1).

**Table 1.** Computed torsional barriers in  $\text{kJ mol}^{-1}$ .

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	<u>MP2</u>		<u>CCSD(T)</u>	
	<u><math>0^\circ</math></u>	<u><math>90^\circ</math></u>	<u><math>0^\circ</math></u>	<u><math>90^\circ</math></u>
cc-pVDZ	12.23	7.68	10.89	7.23
aug-cc-pVDZ	9.68	7.45	9.23	6.67
cc-pVTZ	9.86	9.13	8.85	8.50
aug-cc-pVTZ	9.78	9.43	8.83	8.86
cc-pVQZ	9.65	9.33	8.68	8.74
aug-cc-pVQZ	9.35	9.31	8.39	8.76

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3. Their best CCSD(T) energy using a procedure to extrapolate to infinite basis set still gives barriers that are too high, though in the right relative order:  $E(0^\circ)=7.97$  and  $E(90^\circ) = 8.79 \text{ kJ mol}^{-1}$ .

4. Inclusion of Core-Core and Core-Valence correlation energy reduces the  $0^\circ$  barrier and raises the  $90^\circ$  barrier a small amount. With an extrapolation for completeness in the coupled clusters expansion, their best estimates for the two barriers are 7.88 and 8.94 for the  $0^\circ$  and  $90^\circ$  barriers, respectively.
5. Relativity has no effect on the barrier heights. (This is a great result – it suggests that we don't have to worry about relativistic corrections for normal organics!)
6. Intramolecular basis set superposition error might be responsible for as much a 0.4 kJ difference in the energies of the two barriers.
7. Inclusion of vibrational energies along with all of the other corrections listed above leads to their best estimate of the two barriers:  $E(0^\circ)=8.0$  and  $E(90^\circ) = 8.3 \text{ kJ mol}^{-1}$ , which are at least in the correct order and within the experimental error bars.

Source: <http://comporgchem.com/blog/?p=93>