

BASIS SETS FOR OR

What is the appropriate basis set to use for computing optical rotations? Hedgård, Jensen, and Kongsted examined the optical rotation of **1-6** using B3LYP and CAM-B3LYP at two different wavelengths.¹ They examined a series of different basis sets, including the aug-pCS sets²(developed for NMR computations), the aug-cc-pVXZ series and 6-311++G(3df,3pd). They compared the computed optical rotation with the different basis sets with the value obtained from an extrapolated basis set computation. The mean absolute deviation using either B3LYP or CAM-B3LYP at the two different basis sets are listed in Table 1. The bottom line is that aug-pcS-2 is the preferred method, but this basis set is rather large and computations of big molecules will be difficult. The aug-pcS-1 set is the best choice for large molecules. Errors with the extensive Pople basis set and the aug-cc-pVXZ sets are quite sizable and of concern (especially at the shorter wavelength). It should also be mentioned that even with the largest aug-pcS basis sets extrapolated to the CBS limit, the computed value of the optical rotation of **3** has the wrong sign! Clearly, basis set choice is not the only issue of concern. We remain in need of a robust methodology for computing optical activity.

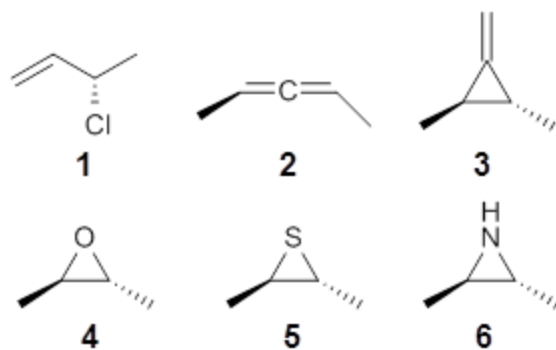


Table 1. Mean absolute deviation of the optical activities of **1-6** evaluated at two wavelengths.

Basis set	589.3 nm		355.0 nm	
	B3LYP	CAM-B3LYP	B3LYP	CAM-B3LYP
aug-pcS-1	4.5	2.2	20.8	15.3
aug-pcS-2	1.4	1.1	4.0	1.5
aug-cc-pVDZ	15.6	13.6	62.2	144.1
aug-cc-pVTZ	3.9	6.3	9.2	37.0
6-311++G(3df,3pd)	6.4	10.3	20.5	40.7

Source: <http://comporgchem.com/blog/?p=2465>