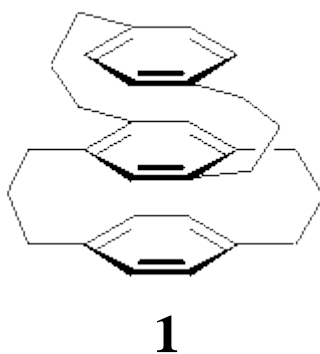


OPTICAL ACTIVITY OF A [3,3]PARACYCLOPHANE

Computed optical activity was utilized in establishing the absolute configuration of the [3, 3] paracyclophane **1**.¹ The helical twist of this molecule makes it chiral.



The specific rotation of (-)-**1** was measured to be -123° [$\text{dm (g/cm}^3)^{-1}$]. Seven different conformations of *R*-**1** were optimized, having either D_2 , C_2 , or C_1 symmetry, at B3LYP/TZVP. The two lowest energy conformers (at B3LYP/6-31G(d) – the authors did not supply coordinates in their supporting materials!) are shown in Figure 1.

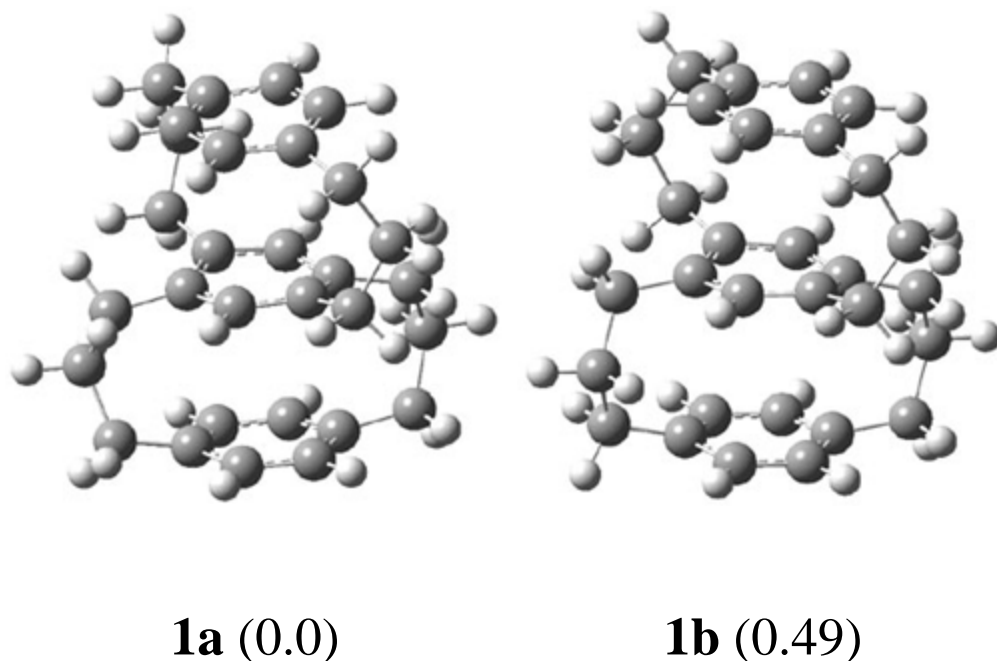


Figure 1. B3LYP/6-31G (d) optimized structures and relative energy (kcal mol⁻¹) of the two lowest energy conformers of **1**.

The TDDFT computed value for $[\alpha]_D$ for the lowest energy conformer is -171.7° [dm (g/cm³)⁻¹]. In fact, the range of $[\alpha]_D$ for seven conformers is -124.4 to -221.8 . These values are consistent with the experimental observation in both sign and magnitude. The computed CD spectrum of the seven *R*-**1** conformations are similar to the experimental spectra of (-)-**1**. Thus, one can conclude that the two enantiomers are *R*-(-)-**1** and *S*-(+)-**1**.

Source: <http://comporgchem.com/blog/?p=106>