

Structural Investigation of a Configurationally Stable Seven-Membered Bridged Biaryl of Relevance for Atroposelective Biaryl Syntheses*

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The atroposelective ring opening of lactone-bridged biaryl systems is the key step in the total synthesis of a series of axially chiral biaryl natural products and useful reagents or catalysts for asymmetric synthesis. For a more in-depth understanding of the mechanism and stereochemical course of this remarkable cleavage reaction, a seven-membered ether analog of such useful biaryl lactones has been investigated structurally, both experimentally, by X-ray diffraction analysis, and by *ab initio* calculations (B3LYP/6-31G*). In a nearly perfect agreement, both methods show that these seven-membered bridged biaryls do not constitute helicene-like distorted molecules, but ‘true’ biaryls, whose sufficiently long lactone or ether bridge allows the two aromatic systems to adopt a large dihedral angle to each other, without any noticeable deviation from planarity for the two aromatic systems – in contrast to related six-membered analogs, which can rather be considered as helicene-like twisted polycyclic systems.

Key words: Bridged Biaryls, Crystal Structure, Density Functional Theory Calculations