

Publication

Sulfone "Geländer" Helices: Revealing Unexpected Parameters Controlling the Enantiomerization Process

JournalArticle (Originalarbeit in einer wissenschaftlichen Zeitschrift)**ID** 4634304**Author(s)** Mannancherry, Rajesh; Solomek, Tomas; Cavalli, Diana; Malincik, Juraj; Häussinger, Daniel; Prescimone, Alessandro; Mayor, Marcel**Author(s) at UniBasel** [Mayor, Marcel](#) ; [Mannancherry, Rajesh](#) ; [Solomek, Tomas](#) ; [Cavalli, Diana](#) ; [Malincik, Juraj](#) ; [Prescimone, Alessandro](#) ; [Häussinger, Daniel](#) ;**Year** 2021**Title** Sulfone "Geländer" Helices: Revealing Unexpected Parameters Controlling the Enantiomerization Process**Journal** Journal of Organic Chemistry**Volume** 86**Number** 8**Pages / Article-Number** 5431-5442**Mesh terms** Circular Dichroism; Magnetic Resonance Spectroscopy; Stereoisomerism; Sulfones; X-Ray Diffraction

The two sulfonyl-bridged Geländer helices 1a and 2a are obtained by oxidation of the corresponding sulfide bridged precursors 1b and 2b. Both Geländer structures are fully characterized by NMR, high-resolution mass spectrometry, and optical spectroscopies. X-ray diffraction with a single crystal of 2a provides its solid-state structure. Both Geländer helices 1a and 2a are separated into enantiomers, and their racemizations are monitored by circular dichroism. For 1a, consisting of two equally sized macrocycles, a substantial increase in the enantiomerization barrier is observed upon going from the sulfide to the sulfone, and only a subtle rise is detected for the constitutional isomer 2a with two macrocycles of different size during the same transformation. This results not only in 1a with the highest configurational stability in the series of hitherto investigated Geländer structures but also challenges the so far hypothesized correlations between bridging structures and the Gibbs free energy of enantiomerization. The simulation of the enantiomerization process in the macrocyclic subunits suggests the proximity of the endotopic hydrogens as parameter responsible for the heights of the enantiomerization barrier.

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