

Reversible twisting of primary amides via ground state N—C(O) destabilization: highly twisted rotationally inverted acyclic amides.

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Rok wydania

2018

Czasopismo

Journal of the American
Chemical Society

Numer woluminu

140

Strony

727-734

DOI

10.1021/jacs.7b11309

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

Since the seminal studies by Pauling in 1930s, planarity has become the defining characteristic of the amide bond. Planarity of amides has central implications for the reactivity and chemical properties of amides of relevance to a range of chemical disciplines. While the vast majority of amides are planar, nonplanarity has a profound effect on the properties of the amide bond, with the most common method to restrict the amide bond relying on the incorporation of the amide function into a rigid cyclic ring system. In a major departure from this concept, here, we report the first class of acyclic twisted amides that can be prepared, reversibly, from common primary amides in a single, operationally trivial step. Di-*tert*-butoxycarbonylation of the amide nitrogen atom yields twisted amides in which the amide bond exhibits nearly perpendicular twist. Full structural characterization of a range of electronically diverse compounds from this new class of twisted amides is reported. Through reactivity studies we demonstrate unusual properties of the amide bond, wherein selective cleavage of the amide bond can be achieved by a judicious choice of the reaction conditions. Through computational studies we evaluate structural and energetic details pertaining to the amide bond deformation. The ability to selectively twist common primary amides, in a reversible manner, has important implications for the design and application of the amide bond nonplanarity in structural chemistry, biochemistry and organic synthesis.

Adres publiczny

<http://dx.doi.org/10.1021/jacs.7b11309>

Strona internetowa wydawcy

<https://www.acs.org/content/acs/en.html>