The most twisted acyclic amides: structures and reactivity.

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The synthesis, crystal structures, and reactivity of the most twisted acyclic amides described to date are reported. Substitution at the nitrogen atom in simple benzamides with Ts and acyl or carbamate groups provides a unique way to achieve almost perpendicular twist in N-acyclic amides (τ = 77°, N = Ac; τ = 87°, N = Boc). The overlap between the Nlp and CO π* orbital is disrupted due to geometrical constraints around the N-substituents. The perpendicular acyclic twisted amides represent a transition state mimic of cis–trans peptide isomerization thus far only accessible by excessively twisted bridged lactams.

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