Abstract: A redox-mediated molecular brake based on the sulfide-sulfoxide redox cycle is illustrated by modulation of the rotation rate of an N-Ar ‘shaft’ by varying the oxidation state of sulfur in 2-[2-(sulfur-substituted)phenyl]isoindolin-1-ones. N-Ar rotational barriers in methylsulfinyl (2) and methylsulfonyl (3) derivatives (13.6 kcal mol⁻¹) are ~5 kcal mol⁻¹ higher than sulfide 1. Rate reduction for N-Ar rotation is ~10⁴ s⁻¹ (280 K) upon oxidation. Correlated N-pyramidalization/N-Ar rotation reduces the effectiveness of the brake by decreasing the energy barrier to N-Ar bond rotation.

2-[2-(sulfur-substituted)phenyl]isoindolin-1-ones \{1 X = : , 2 X = O, 3 X = O₂\}

Line shape analysis of variable temperature \(^1\text{H}\) NMR spectra of the methylene region of 1 near the coalescence temperature.