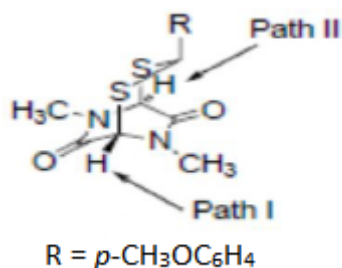


**BROKEN SYMMETRY AND RELATIVE PROTON ACIDITIES
WITHIN A BICYCLIC THIOACETAL.** Brice Lee, and Robert Q. Topper
Department of Chemistry, The Cooper Union, New York, NY 10010

For the known bicyclic thioacetal (structure below)¹, a large difference in the acidity of the seemingly similar two bridgehead hydrogens was observed. Based on the precedents of Kishi et al.,² deprotonation would follow the course suggested by Path I in preference to Path II. However, there is no apparent reason that could explain the different acidities of the two hydrogens. Assuming that the electronic states are somehow strongly asymmetric despite the apparently symmetric geometry, B3LYP calculations are used to investigate the acidity of both sites using SPARTAN to selectively deprotonate each site and compute the relative proton affinities of each carbon, using SM8, with water and tetrahydrofuran as the solvents. Current work extends the approach to varying the R group's identity such as -H, -CH₃, and -C₆H₅.



¹ D. Wu, L.J. Williams, S.J. Danishefsky, *Angew. Chem. Int. Ed.* 2000, 39 (3866).

² a) Y. Kishi, T. Fukuyama, S. Natatsuka, *J. Am. Chem. Soc.* 1973, 95, 6490; b) T. Fukuyama, S. Natatsuka, Y. Kishi, *Tetrahedron* 1981, 37, 2045.