

Empirical energy-density relationships applied to the analysis of the basicity of strong organic superbases

Chamorro, E.

Escobar, C. A.

Sienra, R.

Pérez, P.

Site selectivity and reactivity in some strong organic super bases $RN=C(NR_2)R$, containing several possible sites for protonation, have been analyzed qualitatively in terms of global and local chemical reactivity descriptors defined in the context of conceptual density functional theory. On the basis of the condensed-to-site Fukui function values, the protonation site is predicted to be located at the imino nitrogen. Linear relationships between global energy-dependent quantities and the variation of the Fukui function (or the local softness) at the protonation site have been also found. These linear relationships can be interpreted within a local HSAB rule framework, as observed for instance for the gas-phase basicity of alkylamines and gas-phase acidity of alcohols and thioalcohols. This work extends the range of applicability of reactivity models developed for the treatment of substituent effects based on empirical energy-density Hammett-like relationships (J. Am. Chem. Soc. 2000, 12