Computational Thermochemistry of Superbases Derived from the Cyclopropene Imine Core

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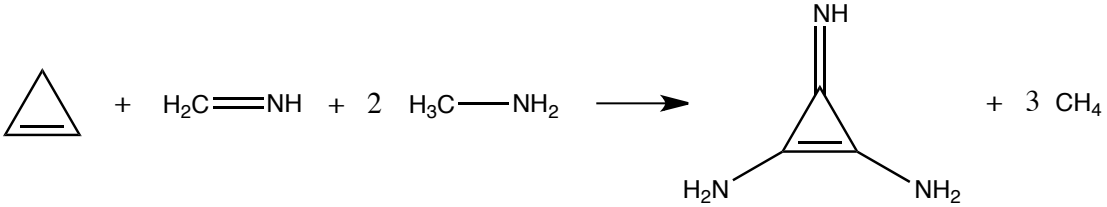
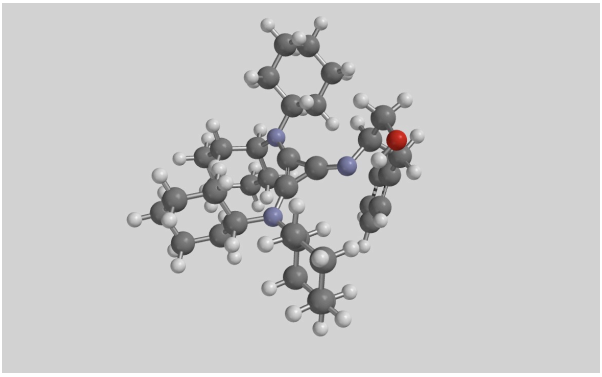
The thermochemical properties of superbase species derived from cyclopropene imine (CPI) [1] are estimated by computations on isodesmic reactions, e.g.:

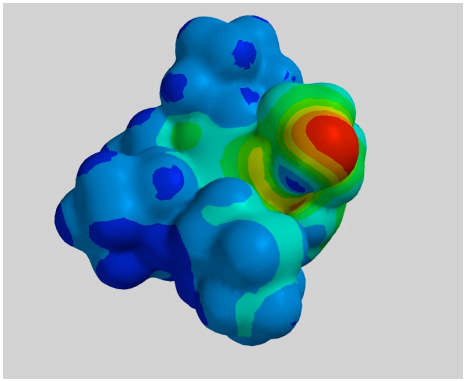


Gas phase proton affinities and basicities, as well as enthalpies of formation of gas phase superbases, guanidines and the parent 1, 2-diamino cyclopropene imine shown above are well represented by the thermochemical schemes W1BD, G4, and CBS-QB3. DFT calculations with modern functionals M06-2X and wB97DX in the cc-pVTZ Dunning basis allow characterization of larger systems.

We compute pKa values of the conjugate acid of N(imino)-*tert*-butyl-N, N, N, N(amino)-*tetra*-isopropyl CPI in acetonitrile, in fair agreement with the experimental value of 26.9 reported by Bandar and Lambeth [2]. More approximate calculations describe the Bandar-Lambert catalyst shown below.



Structure of the Bandar-Lambert Catalyst



Electrostatic field on an isodensity surface

[1] Maksić, Z. B., Kovačević, B. J., *J. Phys. Chem. A*, 103:6678-6684, 1999.
[2] Bandar, J. S., Lambert, T. H. *J. Am. Chem. Soc.*, 134:5552-5555, 2012.