

COMPUTATIONAL DESIGN OF NOVEL BICYCLO[2.2.2]OCTANE BASED PROTON SPONGES

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Proton sponges are subclass of superbases possessing two or more basic subunits placed at rigid backbone in such way to efficiently chelate the captured proton [1]. Backbone is usually constructed from aromatic subunits due to their stability, availability and inertness toward many reaction conditions. However, aromatic subunit is known to decrease basicity of some basic groups like amines or guanidines with respect to their alkylated analogues [2]. A number of proton sponges based on the polycycloalkyl backbones were modeled assessing the gas-phase basicity above 1250 kJmol^{-1} [3,4].

Herein, we present the results on the computational design of novel bicyclo[2.2.2]octane based proton sponges (Figure 1) in which the basic groups (guanidines) are positioned at either secondary or tertiary carbon atoms in a way to allow intramolecular hydrogen bonding upon protonation. Basicities of these novel proton sponges in the gas-phase (GB) and in acetonitrile (pK_a) were calculated. Additionally, guanidine group extrusion energy (E_{diss}), hydrogen bond stabilization energy (HBSE) and the barrier for the guanidine group rotation (E_{rot}) were estimated.

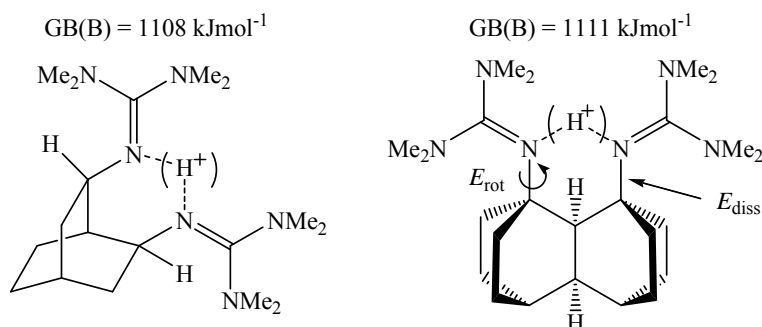


Figure 1. Representative examples of the bicyclo[2.2.2]octane-based proton sponges.

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