

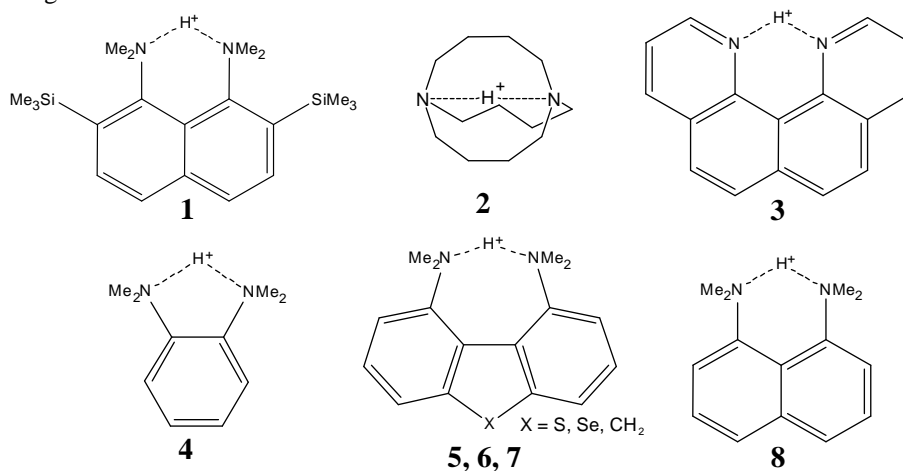
Proton behavior in proton sponges

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Hydrogen bonds are an essential concept in chemistry and have been studied extensively by both theoretical and experimental methods. An interesting special case is short strong hydrogen bonds present in proton sponges. In principle, three cases are possible. The potential energy surface (PES) of the hydrogen motion indeed has only one symmetric minimum. Alternatively, there can be two minima separated by a small barrier, such that the proton still moves freely between them even at 0 K. Finally, if the barrier is slightly larger, the proton motion can be frozen at low temperature, but still occurs easily at higher temperature.

We performed quantum-chemical calculations on selected molecules with short strong N...H...N hydrogen bridges:



A number of density functionals (PBEPBE, B3LYP, MPWB1K, and MPW1B95) were tested and the results were compared with those obtained by the second-order Møller–Plesset perturbation theory. All three possible shapes for the PES were found. Cations **1** and **2** exhibit a true single-well potential, while cations **3–7** have a barrier of 1.59, 2.31, 0.04, 0.02, and 0.17 kcal·mol⁻¹ at PBEPBE level correspondingly. The symmetric single-well or a very shallow potential with a lower barrier is facilitated by a short N...N distance and by antiparallel arrangement of the nitrogen lone pairs. Different density functionals yield very different barriers, with PBE results approaching the MP2 values most closely, while MPWB1K and MPW1B95 tremendously overestimate the barrier height.

The three-dimensional vibrational Schrödinger equation was solved numerically to describe the proton motion in cations **1** and **3–5**. For cations **1** and **5**, the ground-state vibrational wavefunction has a single maximum located at the PES middle point. Cation **4** has the wavefunction with two maxima located near the PES minima; the tunneling is substantial. Finally, the wavefunction of cation **3** has two weakly pronounced maxima, thus exhibiting a situation intermediate between those of cations **1** and **4**.