

Out-basicity of 1,8-bis(dimethylamino)-naphthalene : the experimental and theoretical challenge.

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Streszczenie

A possibility of non-conventional two-step protonation of 1,8-bis(dimethylamino)naphthalene (proton sponge) is discussed. Unlike the generally accepted mechanism, involving relatively slow direct penetration of a proton into the cleft between the peri-NMe₂ groups, it consists of the rapid addition of a proton to the out-inverted NMe₂ group with the subsequent slower rotational transfer of the proton into the inter-nitrogen space to produce a stable chelated cation. The following approaches were employed during the work: (1) competitive hydrogen bond formation in a specially designed alcohol in which the OH group might chelate either the proton sponge 1-NMe₂ group or another basic center (N,N-dimethylaniline) of known basicity; (2) measuring the basicity of naphtho[1,8-b,c]diazabicyclo[3.3.3]undecane considered to be a close analogue of the proton sponge capable exclusively of out-protonation; (3) X-ray, spectral and DFT studies of structure, energy and stereodynamics of compounds obtained, including their conformers. For the first time, the pK_a value of an organic base with a perfectly flat nitrogen atom is reported. The final conclusion is made that both pathways of proton sponge protonation, traditional and non-conventional, contribute in parallel with a still undefined ratio. The estimated out-basicity of the proton sponge is at least 5.5 orders of magnitude lower than the directly measured in-basicity.

Adres publiczny

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