Proton transfer in the intramolecular NHN$^+$ bonds in proton sponges with different hydrogen bridge flexibility.

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Rok wydania

2009

Czasopismo

Physical Chemistry Chemical Physics

Numer woluminu

11

Strony

1297-1302

DOI

10.1039/B814798A

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

The proton transfer in the intramolecular NHN$^+$ hydrogen bonds of selected proton sponges has been studied using theoretical calculations of the potential energy surfaces (PES). The proton-transfer trajectory follows very closely the lowest energy path, derived as the quantum-mechanical reaction coordinates (QMRC). The bond order is not conserved in the transfer process. Even in the most flexible proton sponges there are considerable constraints on the N⋯N distance and the hydrogen bonds do not behave as intermolecular bonds. The curvature of QMRC is not a suitable criterion to distinguish between inter- and intramolecular NHN$^+$ bonds. It appears that the determining factor for linearity is the degree of constraint, which is most likely the strongest in the benzene proton sponges. In the naphthalene proton sponges with relatively short N⋯N distances QMRC is more bent than in the benzene complexes with somewhat longer distances, opposite to what might be expected. It is important to note that in intramolecular complexes the PES is characterized by a single minimum, in contrast to a double minimum in intermolecular complexes. The experimentally determined NH bond lengths have been plotted on the potential energy surface and these points are all located on the QMRC curve, very close to the energy minimum of the PES. However, it is vital that the experimental X-ray hydrogen positions are then corrected to give the true internuclear NH distances.

Adres publiczny

https://doi.org/10.1039/B814798A

Strona internetowa wydawcy

https://www.rsc.org/