

Combination of "Buttressing" and "Clothespin" effects for reaching the shortest NHN hydrogen bond in proton sponge cations.

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Streszczenie

A series of previously unknown 2,4,5-tri- and 2,4,5,7-tetrasubstituted 1,8-bis(dimethylamino)naphthalenes and their salts with HBF_4 containing bulky spherically shaped substituents (Me, Br, and SiMe_3) in the naphthalene ring has been synthesized. Using XRD analysis of 11 samples, the influence of the so-called "buttressing" and "clothespin" effects on their molecular structure and the NHN hydrogen bond geometry in the solid cations were investigated. The combined action of both effects has been shown to significantly increase the compression of the hydrogen bond. As a result, the previous record of the hydrogen bond shortness ($\text{N}\cdots\text{N} = 2.524 \text{ \AA}$) has been surpassed in favor of $2.502 \text{ \AA}$ found for the tetrafluoroborate of 2,4,5,7-tetramethyl-1,8-bis(dimethylamino)naphthalene. The molecular structure of the latter differs by perfect symmetry and practically barrier-free proton transfer in the $[\text{NHN}]^+$ bond. On the basis of the results of quantum-chemical calculations, it is suggested that the value of $2.502 \text{ \AA}$ likely represents or lies very close to the theoretical limit for the short hydrogen bonds between the amine-type nitrogen atoms.

Słowa kluczowe

Salts, Reaction mechanisms, Nitrogen, Noncovalent interactions, Cations

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