# Intermolecular interactions in the solid state of ionic secondary Mannich bases.

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## Streszczenie

Two new secondary Mannich bases, 4-bromo-2-[(aminopropyl)methyl]-phenol (**1**) and 4-nitro-2-[(aminopropyl)methyl]-phenol (**2**), were synthesized. Crystal structures were determined at liquid nitrogen temperature. It was found that in both compounds the proton transfer forms exist in the solid state. In the case of **1**, this was unexpected, because of the weak acidity of *p*-bromophenol being the parent component of this Mannich base. The reason for that was found to be the formation of the $O^{-}\cdots H–N^{+}$ hydrogen bonded tetramer in the solid state. Two cyclic aggregates $R_4^2(8)$ and $R_2^2(12)$ describe the pattern of hydrogen bonded interactions in the crystals of both compounds. Additionally, C–H···π interactions stabilize the crystal structures. The hydrogen bonds in **1** are slightly stronger (N···O distances 2.708 and 2.733 Å) than in **2** (2.721 and 2.765 Å, respectively) despite the fact that *p*-nitrophenol participating in **2** is a stronger acid. The influence of permittivity of surroundings and the hydrogen bonding pattern on the properties of intermolecular hydrogen bonds are discussed on the basis of B3LYP and MP2 calculations with basis sets 6-31+G(d,p) and 6-31++G(2d,2p). The coupling between hydrogen bonds in crystals was studied with the application of the IR spectra of isotopically diluted species. It was found that such a coupling is stronger for **2**, forming weaker hydrogen bonds. Both the theory of IR spectra and quantum chemical calculations demonstrate that the source of the observed behavior is electronic participation in vibronic absorption.

Adres publiczny

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Strona internetowa wydawcy

https://www.acs.org/content/acs/en.html