The role of hydrogen bonding in conformational stabilization of 3,5,6- and 3,5-substituted (pyridin-2-yl)aminomethane-1,1-diphosphonic acids and related (pyrimidin-2-yl) derivative.

Autorzy

Ewa Matczak-Jon

Katarzyna Ślepokura

Wiktor Zierkiewicz

Paweł Kafarski

E. Dąbrowska

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Streszczenie

The crystal structures of three new members of the (pyridin-2-yl)aminomethane-1,1-diphosphonic acid (1-a) family are determined by X-ray diffraction and discussed with respect to molecular geometry and solid state organization.

The striking structural feature of (3,5-dibromo-6-methylpyridin-2-yl)aminomethane-1,1-diphosphonic acid (2) and (3-chloro-5-trifluoromethylpyridin-2-yl)aminomethane-1,1-diphosphonic acid (3) is that regardless of a multiple substitution on the pyridyl ring the key factor for their conformational stabilization is the intramolecular N–H···X (X = Cl, Br) hydrogen bond involving substituent at 3-ring position.

In contrast, the solid state conformation of (pyrimidin-2-yl)aminomethane-1,1-diphosphonic acid (4) is stabilized through intermolecular, bifurcated N–H···O hydrogen bonds, which is similar to that observed previously in 4- and 5-substituted Z-zwitterionic derivatives of (pyridin-2-yl)aminomethane-1,1-diphosphonic acid. Moreover, the 31P NMR spectra of 4 suggest similar dynamic process in solution, attributable to the rotation around the Cring–Namino bond. However, the rotational barrier in 4 is markedly lower as compared to 4- and 5-substituted (pyridin-2-yl)aminomethane-1,1-diphosphonic acids. This is attributed to low basicity of the nitrogen atom of the 1,3-diazinyl ring, which results in loss of conformational stabilization provided by intermolecular N–H···O hydrogen bonds in solution at low pH.

Słowa kluczowe

Bisphosphonates, hydrogen bonds, X-ray diffraction, NMR spectroscopy, DFT calculations