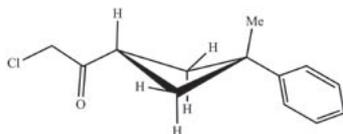


The optimized geometric bond lengths and bond angles obtained by using HF and DFT(B3LYP) show the best agreement with the experimental data.

[1] Dinçer, M., Özdemir, N., Yılmaz, İ. & Büyükgüngör, O. 2007. *Acta Cryst.* E63, o3489.



Keywords: crystallographic analysis, organic crystals, theoretical calculations

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Experimental versus theoretical electron density in the crystals of β -aminophosphonic acids

Jakub M. Wojciechowski^{1,2}, Henryk Krawczyk³, Lukasz Albrecht³, Wojciech M. Wolf²

¹Technical University of Lodz, Chemistry, Zeromskiego 116, Lodz, lodzkie, 90-924, Poland, ²Institute of General and Ecological Chemistry, Technical University of Lodz, Zeromskiego 116, 90-924 Lodz, Poland, ³Institute of Organic Chemistry, Technical University of Lodz, Zeromskiego 116, 90-924 Lodz, Poland, E-mail : j.m.wojciechowski@gmail.com

Investigated compounds are novel α -substituted- β -aminophosphonic acids which are similar to herbicides used in agriculture [1]. X-ray analysis accompanied by the *ab initio* B3LYP and MP2 calculations showed high level of electron density delocalizations in all investigated structures and antiperiplanar arrangement around the central C_α - C_β bond. The phosphorus atom is located within the center of distorted tetrahedron. The largest distortions follow from the Coulombic repulsion interactions between the oxygen atoms bearing the negative charge. This effect was further investigated with the natural bond orbital methodology. Wavefunctions were calculated at the B3LYP/6-31G++(d,p) level for the X-ray coordinates. In all compounds the main electron density delocalizations involve back-donation from the n_π lone pairs of the phosphonic oxygen atoms to the σ^* orbital of the adjacent P- C_α bond. Those interactions act against the depletion of electron density in the phosphorus originated by the neighboring electronegative oxygen atoms. The molecular conformation is stabilized by the mutual anti σ - σ^* stereoelectronic interactions of the P- C_α and N- C_β bonds. In all crystals N atom of the terminal amine group is protonated and adopts virtually tetrahedral geometry with all three hydrogen atoms involved in the intermolecular hydrogen bonding. The crystal structure of 1-(aminomethyl)vinylphosphonic was further examined using the high resolution low temperature X-ray data and the multipole atom model. Experimental electron density was carefully examined and compared with the densities calculated at the MP2 and B3LYP levels of theory. The Bader's theory Atoms in Molecules was applied.

[1] Krawczyk H., Albrecht L., Wojciechowski J., Wolf W.M. *Tetrahedron*, 2008, in press.

Keywords: multipole refinements, aminophosphonic and phosphonic acids, stereoelectronic effects

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Lessons from a decade of X-ray crystallographic work on N-(hydroxy)thiazole-2(3H)-thione derivatives

Ingrid Svoboda¹, Hartmut Fuess¹, Jens Hartung²

¹Darmstadt University of Technology, Materials Science, Petersenstr. 23, Darmstadt, Hessa, D-64287, Germany, ²TU Kaiserslautern, Department of Organic Chemistry, Germany, E-mail: svoboda@tu-darmstadt.de

N-(Hydroxy)thiazole-2-thiones are valuable reagents for generation of oxygen-centered radicals in photochemical or microwave-induced reactions. The compounds exhibit a number of unusual characteristics. The majority of peculiarities have been clarified over the past ten years in combined experimental and theoretical efforts [1,2]. X-ray crystallography has contributed significantly to this progress by providing a sound structural basis for (i) assessment of computational methods that are able to model thermal rearrangements and pathways of N,O homolysis following photochemical excitation [3], (ii) discussing alkylation selectivity of ambident thiohydroxamate nucleophiles on the basis of investigated salts [4], (iii) interpreting major thermally-induced decomposition pathways leading to heteroatom rich compounds that are difficult to characterize using ¹H and ¹³C NMR analysis alone, (iv) clarifying configuration of unexpected isomerization products [5]. Major guidelines of the pursuit of structural thiazole-2(3H)-thione chemistry will be presented in detail.

[1] Hartung, J., Schwarz, M., Synlett, 1997, p. 848.

[2] Hartung, J., Schwarz, M., Svoboda, I., Fuess, H., Duarte, M.-T. *Eur. J. Org. Chem.* 1999, p. 1275.

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Keywords: thiazole, thiohydroxamic acid O-ester, thione

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Hydrogen-bonded network structures of cocrystals of some naphthalenediol with pyrazine

Hideki Saitoh, Takayuki Nakatsuka

Saitama University, Graduate School of Science and Engineering, 255 Shimo-okubo, Sakura-ku, Saitama, Saitama, 338-8570, Japan, E-mail : saito@chem.saitama-u.ac.jp

Hydrogen bond plays an important role in the molecular packing patterns for some crystal structures by its directional interaction. It is often utilized for attempts to design the crystal structures in crystal engineering and supermolecular chemistry, etc. The systematic structural study for the cocrystals of hydroquinone with several hydrogen-bond acceptors was reported [1], and the hydrogen-bond motifs and the hydrogen-bonded network patterns were discussed. In molecular packing, weak hydrogen bond is regarded as important interaction too. In our study, the structures of the cocrystals of naphthalene-1,5-diol, -1,6-diol and -2,6-diol with pyrazine (Py) were determined at 250 K, though the cocrystals were unstable at room temperature. These cocrystals are formed with same composition of naphthalenediol-pyrazine ratio 1:1. The 1,5-diol-Py and 1,6-diol-Py are triclinic $P1\bar{1}$ while the 2,6-diol-Py is monoclinic $P2_1/c$. In these cocrystals, primary intermolecular interaction constructing the structures is O-H...N hydrogen bond forming the chain motifs of the -(naphthalenediol-pyrazine)- sequence. There is a motif of C-H...O weak hydrogen bond between the pyrazine and the naphthalenediol in the 2,6-diol-Py, and it forms the ring motif of graph-set $R_4^4(10)$, which founded in the cocrystal of hydroquinone-pyrazine [1], together with the O-H...N hydrogen bond. It is found that the structure of the cocrystal of naphthalene-2,6-diol with pyrazine is well similar as a whole to that of the hydroquinone-pyrazine.

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