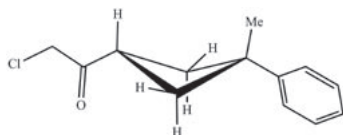


The optimized geometric bond lengths and bond angles obtained by using HF and DFT(B3LYP) show the best agreement with the experimental data.

[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

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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

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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.

[3] Arnone, M., Hartung, J., Engels, B. *J. Phys. Chem. A.*, 2005, 109, 5943.

[4] Hartung, J., Bachmann, J., Svoboda, I., Fuess, H., *Acta Cryst.* 2008, E64, m299.

Keywords: thiazole, thiohydroxamic acid O-ester, thione

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

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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.

[1] Oswald I.D.H., Motherwell W.D.S., Parsons S., *Acta Cryst.*, 2005,

B61, 46-57.

Keywords: hydrogen bonding, cocrystals, intermolecular packing

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Crystal structure of (4Z)-2-phenyl-4-(3,4,5-trimethoxybenzylidene)-1,3-oxazol-5(4H)-one

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1,3-oxazole is a very useful intermediate synthetic organic material for the synthesis of imidazole that possess a wide spectrum of biological activities such as herbicides, antibacterial, antifungal, etc. In addition, the oxazole itself is also found to possess antibacterial and antifungal activities. In view of this, the crystal structure of title compound has been determined. The yellow colored, block shaped crystals of size $0.3 \times 0.3 \times 0.2 \text{ mm}^3$ were grown by slow evaporation from the benzene solution. The compound crystallizes in triclinic system having space group $P\bar{1}$. The crystal data are: $a = 7.3732(8) \text{ \AA}$, $b = 15.7823(17) \text{ \AA}$, $c = 8.1325(8) \text{ \AA}$, $\alpha = 62.085(7)^\circ$, $\beta = 82.506(7)^\circ$, $\gamma = 91.954(6)^\circ$, $Z = 2$, $\mu = 0.100 \text{ mm}^{-1}$, $D_x = 1.367 \text{ Mg-m}^{-3}$. Intensity data on BRUKER AXS KAPPA APEX2 CCD diffractometer are collected in ω and ϕ scan with θ ranging from 2.53 to 25.0° and 2885 unique reflections are recorded. The structure is solved by SIR92 program and refined by SHELXL-97 program to final R-value of 0.0597 for 2114 reflections with $I > 2\sigma(I)$. In the structure, all the three rings are planar within themselves, and the benzene ring and benzylidene moiety making a dihedral angle of $11.23(15)$ and $3.19(14)^\circ$ respectively. An intermolecular C-H...O interaction forms a dimer that exhibit $R^2_2(14)$ graph-set motif. In addition crystal structure is stabilized by C-H... π and π - π stacking interactions.

Keywords: single-crystal X-ray diffraction, organic crystals, hydrogen bonding

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Two proton transfer compounds from benzene-1,2,4,5-tetracarboxylic acid and 1,10-phenanthroline

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Recently, there has been considerable interest in proton transfer systems and their structures. Two proton transfer compounds (phenH)(btcH₃) · H₂O, **1**, and (phenH)₂(btcH₂) · btcH₄, **2**, were obtained by the reaction of benzene-1,2,4,5-tetracarboxylic acid (btcH₄) with 1,10-phenanthroline (phen) in 1:1 and 1:2 molar ratio, respectively. The characterizations were performed using IR, ¹H and ¹³C NMR spectroscopy and single-crystal X-ray diffraction. The compound **1** is crystallized in triclinic system and $P1\bar{1}$ space group with following

cell parameters: $a = 7.8529(5) \text{ \AA}$, $b = 9.8333(6) \text{ \AA}$, $c = 12.2847(7) \text{ \AA}$, $\alpha = 94.5910(10)^\circ$, $\beta = 91.3670(10)^\circ$, $\gamma = 94.7300(10)^\circ$, $Z = 2$. The final R value of **1** is 0.0354 for 3627 total reflection. The compound **2** is crystallized in the space group $P2_1/c$ of the monoclinic system, and contains two molecules per unit cell. The structure has been refined to a final value for the crystallographic R factor of 0.0364 based on 4881 reflections. The unit cell parameters are: $a = 11.9154(6) \text{ \AA}$, $b = 13.5560(6) \text{ \AA}$, $c = 12.2030(6) \text{ \AA}$ and $\beta = 110.4880(10)^\circ$. The ranges of the D-H...A angles and the H...A and D...A distances indicate the presence of strong hydrogen bonding in both compounds. Hydrogen bonds with D...A distances ranging from 2.4331(15) to 3.4766(19) Å, are observed in the crystal structure of **1** whereas, the range of D...A distances in **2** is between 2.4472(13) to 3.4287(18) Å. In both structures, **1** and **2**, anionic and cationic units have been arranged in the lattice in a parallel manner connect the various components into self-associated supramolecular structures and providing considerable π - π stacking between (phenH)⁺ rings. The centroid distances between the planes are 3.4779(9) and 3.8707(8) Å, respectively.

Keywords: crystal structures, hydrogen bonding, supramolecular assemblies

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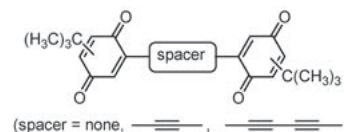
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X-ray structures of quinone dimers linked either directly or through acetylene spacers

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X-ray structures of two directly-linked quinone dimers have been investigated. Although the positions of tert-butyl substituents differed, their X-ray structures were significantly close. The carbonyl oxygen atoms underwent van der Waals contact in an intramolecular manner, and quinone moieties were distorted into the boat shape in common. As MO calculations indicated the quinone moiety became flexible when quinones were directly linked, the origins of the boat forms should be attributed to the intrinsic flexibility of the molecular skeleton as well as the packing demand. In contrast, quinone moieties of quinone dimers bearing acetylene and diacetylene spacers have been found to be planar. This may be arisen from no intramolecular contact of oxygen atoms by introduction of the acetylene spacers. Flexibility of the molecular skeleton of these molecules will also be discussed.



Keywords: inter- and intramolecular interactions, packing, isomers

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Homogeneous and heterogeneous mixed crystals composed of phenoxy radical and phenol

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