

substitution induced stabilizing effects via more number of inter molecular hydrogen bonds. The strong intramolecular N-H...N bond locks the molecular conformation and eliminates conformational flexibility in all derivatives. The comparative study on detailed structural features, intermolecular interactions and modes of packing will be presented.

1. Thalladi, V.R., et al, (1998). J. Am. Chem. Soc. 120, 8702-8710.
2. Chandrakumar et al. Acta Cryst. (2005). E61, o2444-o2446.
3. Mohan, S. et al, (2003). Asian J. Chem. 15, 67-70.
4. Anilkumar G.N. et al, Acta Cryst. (2007). E63, o2077-o2079.

Keywords: organic crystal structures, chemical crystallography, hydrogen bonds

## P06.10.45

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### Crystal and molecular structure of biologically active thiophene 3 -furfuryl carboxamide derivative

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The synthesis and design of the compounds possessing important pharmacological and biological properties is an important area of research. In this respect, Schiff bases and their related thiophene derivatives containing amino and carboxyl functions have been synthesized. They have been found to exhibit broad spectrum of biological activities such as antiviral, antiinflammatory and antimicrobial activities<sup>1</sup>. Specifically, 2-aminothiophene-3-carboxylates and carboxamides were recognized as allosteric enhancers for A1 adenosine receptors<sup>2</sup>. In view of the above and in continuation of our work on structural studies of thiophene 3-carboxamide derivatives<sup>3</sup>, crystal structure of "2-[(1E)-(2-chlorophenyl)methylene]amino}-N-(2-furylmethyl)-4,5-dimethylthiophene-3-carboxamide" was determined. The compound C<sub>24</sub>H<sub>25</sub>N<sub>3</sub>O<sub>2</sub>S, crystallizes under Orthorhombic system, P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> space group, *a* = 6.1105(19), *b* = 15.977(5) and *c* = 18.575(6) Å, *V* = 1813.5(10) Å<sup>3</sup>, *Z* = 4, & *D* = 1.366 Mgm<sup>-3</sup>. The intensity data were collected using Bruker Smart CCD diffractometer using graphite monochromated MoK $\alpha$  radiation. The structure was solved using SIR92 program and refined using fullmatrix least squares on F<sup>2</sup> to an R value of 0.056 using SHELXL-97 for 2842 reflections with I > 2  $\sigma$ (I). In the non-planar molecule, the furan and chlorophenyl ring making dihedral angle of 89.1(2) and 15.8(7) $^\circ$  respectively with the thiophene ring. The crystal structure is stabilized by intramolecular N-H...N, C-H...Cl, C-H...S hydrogen bonds. The intermolecular C-H...O and C-H... $\pi$  interactions link the molecules in a zigzag manner inside the unit cell.

1. S. Mohan, et al, Asian J of Chem (2003).
2. George N. et al. / Bioorg. Med. Chem. 14 (2006) 2358-2365.
3. G. N. Anilkumar, et al, Acta Cryst. (2007). E63, o2077-o2079.

Keywords: small molecular crystallography, organic sulfur compounds, hydrogen bonds

## P06.10.47

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### Crystal structure of 2-amino-4,5,6,7-tetrahydro-1-benzothiophene -3-carboxamide

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Thiophene derivatives containing amino and carboxyl functions have been found to exhibit broad spectrum of biological activities like anti-viral, anti-inflammatory, antimicrobial activities. Specifically, the 2-amino-carboxylic acid esters were recognized as allosteric enhancers for A1 adenosine receptors. Recent Structure activity relation studies have shown that the amides also exhibit similar properties. Our earlier investigations on the structures of biologically active thiophene 3-carboxamides, has shown that the chloro substitution in the aryl amide group had a significant effect<sup>1</sup>. The ortho -chloro group reversed the orientation of the amide linkage and favoured the formation of more intra molecular hydrogen bonds. The para- chloro substitution induced stabilizing effects via more number of inter molecular hydrogen bonds. The titled compound in the present study bears a close structural relationship with the reported allosteric enhancers for adenosine<sup>2</sup> and hence its structure has been investigated. The compound C<sub>9</sub>H<sub>12</sub>N<sub>2</sub>OS, crystallizes under Tetragonal system, I 4<sub>1</sub>/a space group, *a* = *b* = 20.5807(16) Å and *c* = 8.9233(13) Å, *V* = 3779.6(7) Å<sup>3</sup>, *Z* = 16,  $\mu$  = 0.303 mm<sup>-1</sup>, & *D* = 1.38 gm<sup>-3</sup>. The three dimensional intensity data were collected using Bruker Smart CCD diffractometer using graphite monochromated MoK $\alpha$  radiation. The structure was solved using SIR92 program and refined till R value converges to 0.0576. The crystal structure stabilized by both intra and intermolecular N-H...O hydrogen bonds. Reference:

- (1) Acta Cryst. (2005). E61, o304-o306.
- (2) George N. et al. / Bioorg. Med. Chem. 14 (2006) 2358-2365.

Keywords: hydrogen bonds, chemical crystallography, organic compounds

## P06.10.48

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### An experimental and theoretical approach to the 2-chloro-1-(3-methyl-3-phenylcyclobutyl) ethanone

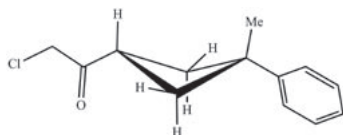
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The title compound, C<sub>13</sub>H<sub>15</sub>ClO, crystallize in orthorhombic space group *Pca*2<sub>1</sub>, and has a nonplanar conformation. The phenyl ring and chloroacetaldehyde group are in cis positions. The cyclobutane ring is puckered, with a dihedral angle of 26.81 (13) $^\circ$ . Molecules are linked to one another by intermolecular C-H...O interactions, forming a C(4) chain running parallel to the [001] direction [1]. The molecular structure of the title compound in the ground state (in vacuo) is optimized by HF and DFT(B3LYP) with the 6-31G(d) basis set and then compared with that of experimentally obtained.

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

## P06.10.49

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### Experimental versus theoretical electron density in the crystals of $\beta$ -aminophosphonic acids

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Investigated compounds are novel  $\alpha$ -substituted- $\beta$ -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  $C_\alpha$ - $C_\beta$  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  $n_\pi$  lone pairs of the phosphonic oxygen atoms to the  $\sigma^*$  orbital of the adjacent P- $C_\alpha$  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  $\sigma$ - $\sigma^*$  stereoelectronic interactions of the P- $C_\alpha$  and N- $C_\beta$  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

## P06.10.50

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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 <sup>1</sup>H and <sup>13</sup>C 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.

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

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

Keywords: thiazole, thiohydroxamic acid O-ester, thione

## P06.10.51

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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,