Keywords: weak interactions, hydrogen bonds, high-pressure crystallography

FA4-MS26-P17

Hydrogen bonding and π-π stacking interactions in some important triheterocycles. Mukesh M. Jotani[a], Rina D. Shah[b], Jerry P. Jasinski[c], Edward. R. T. Tiekink[d], Ray J. Butcher[e] , [a]*Department of Physics, Bhavan's Sheth R. A. College of Science, Ahmedabad, Gujarat, India, 380 001.* [b]*Department of Chemistry, M. G. Science Institute, Ahmedabad, Gujarat, India, 380 009.*[c]*Department of Chemistry, Keene State College, 229 Main Street, Keene, NH 03435-2001, USA.* [d]*Department of Chemistry University of Malaya, 50603 Kuala Lumpur, Malaysia.* [e]*Department of Chemistry, Howard University, 525 College Street NW, Washington DC 20059, USA.*
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The synthesis of triheterocycles, *e.g.* tetrazolopyrrolopyrimidine derivatives, involves various nucleophilic displacement reactions, such as chlorination, azidolysis and amination, on fused pyrimidines. Phase Transfer Catalysis (PTC), an environmentally benign technique, offers many advantages over conventional methodologies: *viz*. use of non-polar solvents, reduced reaction time and temperature, suppression of side-products, high-yields, replacement of hard bases, facile work-up, *etc*. Generally, the amination of 4-chloroazines requires harsh reaction conditions while fused tetrazolopyrimidine possess latent amino functionality giving facile amination, making these synthetic routes non-viable. However, the reductive ring cleavage of tetrazolo [1,5-c] pyrrolo [3,2-e] pyrimidines results in the formation of 4-aminopyrrolo[2,3-a] pyrimidines, which are of direct relevance to the pharmaceutical industry as synthetic precursors for more complicated molecules. Moreover, such compounds are found to possess a wide spectrum of biological activity. In view of the above, crystallographic studies of four such methoxy- and halogen-substituted 4-aminopyrrolo[2,3-a] pyrimidine derivatives were performed using single crystal X-ray diffraction techniques. The presence of various crystal packing interactions, and their influence on molecular structure, are supported by semi-empirical Quantum Chemical Calculations, using MOPAC2009 programme. Key results from the combined crystallographic and theoretical studies will be presented.

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Keywords: Hydrogen bonds, X-ray crystallography, Semi-empirical calculations

FA4-MS26-P18

The Influence of Substituent Variation and Packing Forces on the Conformation of Biphenyl Derivatives. Gert J. Kruger[a] and Cedric W. Holzapfel[a], [a]*Department of Chemistry, University of Johannesburg, P O Box 524, Auckland Park, Johannesburg, 2006, South Africa*
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The conformation of biphenyl derivatives has been the subject of a number of crystallographic investigations in the past [1 – 3]. In this contribution we report the crystal structures of two novel compounds, methyl 4 -methoxy-2-nitrobiphenyl carboxylate and 4′,4 -methoxy-2-nitrobiphenyl. The torsion angles about the central C-C bond are 50.5° and 57.4° respectively. These values are within the range observed in the Cambridge Structural Database (version 5.31, november 2009) [4] for similarly substituted biphenyl derivatives. An analysis of the packing in the crystals and molecular modeling will be used to discuss the difference in torsion angles.

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Keywords: conformations, biphenyl derivatives, single-crystal X-ray diffraction

FA4-MS26-P19

A modulated cocrystal: *N′*-(propan-2-ylidene)nicotinohydrazide and sebacic acid. H. Krüger[a], V. Kahlenberg[a], A. Lemmerer[b] and J. Bernstein[b], [a]*Institute of Mineralogy and Petrography, University of Innsbruck, Austria,*[b]*Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, Israel*
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Trying to cocrystallise nicotinic acid hydrazide (niazid) with sebacic acid from an acetone solution, resulted in a reaction of the niazid with the solvent. Cocrystals were formed, which contain molecules of *N′*-(propan-2-ylidene)nicotinohydrazide (*p*-niazid) and sebacic acid [1]. These cocrystals exhibit an incommensurately modulated structure. Structural analysis was performed using single-crystal X-ray diffraction data, collected at 173 K. After solution and refinement of the average structure (which includes disorder of the sebacic acid molecule) the modulated structure was refined using the (3+1)-dimensional superspace approach [2]. The structure belongs to the planar monoclinic crystal system (a=5.07, b=44.51, c=6.40Å, β=94.6°, **q**=(-0.08, 0, 0.26)) and the superspace group was determined to be $P2_1/n(\alpha 0 \gamma)00$. Harmonic modulation functions of first order were successively introduced for all atom positions, but refined for non-hydrogen atoms only. The positions and modulation functions of the hydrogen atoms were fixed due to geometrical constraints. The final refinement included harmonic modulation waves for coordinates and ADPs for all non-hydrogen atoms. The *p*-niazid molecule, as well as the carboxylic groups of the sebacic acid are not much affected by the modulation, whereas the atoms of the hydrocarbon chain of the acid show a strong coordinated displacive modulation. The plane of the C-C bonds exhibits a rotation of up to 45° about the centre line of the ribbon. The crystal structure shows slabs packed with sebacic acid. These layers are oriented perpendicular to *b* and the sebacic acid molecules are tilted about 54° against *b*. We assume that weak intermolecular interactions within the sebacic acid layers cause the aperiodic

arrangement.

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Keywords: cocrystal, incommensurate modulated structure

FA4-MS26-P20

Fluconazole and its cocrystals with maleic and glutaric acids. Ivan Leban[a], Nina Lah[a], Žiga Hodnik[b], Danijel Kikelj[b], Jože Kastelic[c] ,[a]*Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, SI-1000 Ljubljana, Slovenia,* [b]*Faculty of Pharmacy, University of Ljubljana, Aškerčeva 7, SI-1000 Ljubljana, Slovenia,* [c]*Krka, d. d., Novo mesto, Šmarješka c. 6, SI-8501 Novo mesto, Slovenia.*
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Fluconazole (2-(2,4-difluorophenyl)-1,3-bis(1H-1,2,4-triazol-1-yl)-propan-2-ol), is a bis-triazole antifungal drug used to treat invasive infections caused by *Candida*. The drug is available in both oral and intravenous formulations. The crystal structures of three unsolvated forms, designated as polymorph I, II and III, as well as the structures of a monohydrate and the solvates containing ethyl acetate, acetone and benzene have already been reported [1],[2]. Here, the single-crystal X-ray structures of fluconazole (form III) and its cocrystals containing maleic and glutaric acids will be presented.
Fluconazole (III): triclinic, P-1, a=7.4907(10), b=7.7640(10), c=11.9547(10) Å, α=85.012(8), β=84.507(8), γ=75.553(8) °.
Fluconazole with maleic acid: $[(FluH_2)(Hmal)_2(H_2mal)]$, triclinic, P-1, a=5.4983(5), b=13.8723(16), c=18.433(3) Å, α=98.062(8), β=91.748(8), γ=95.479(8) °.
Fluconazole with glutaric acid: $[(Flu)(H_2glu)]$, triclinic, P -1, a=5.6897(10), b=10.6593(15), c=17.063(3)Åα=72.909(8), β=84.453 (8), γ=80.863(8) °.

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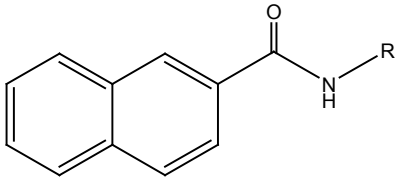
Keywords: fluconazole, maleic acid, glutaric acid

FA4-MS26-P21

Crystal packing in a series of N-phenyl-2-naphthamide derivatives. Jim Simpson[a], Aamer Saeed[b], Rasheed Ahmad Khera[b], [a]*Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, 9054 , New Zealand,* [b]*Department of Chemistry, Quaid-I-Azam University, Islamabad 45320, Pakistan*

Structures of seven N-phenyl-2-naphthamide derivatives



R = C_6H_5—, *p*—Cl—C_6H_4, *p*—CH_3—C_6H_4, *m* and *p*—CH_3O—C_6H_4, *o*—NO_2—C_6H_4 and C_6H_{10} have been determined and their crystal packing investigated. The pervasive intramolecular contact in all but one of the compounds involves classical N—H...O hydrogen bonding leading to the formation of C(4) chains [1]. The exception is the nitro derivative where a strong intramolecular N—H…O contact to an O atom of the *o*-NO_2 substituent takes precedence. Additional $C_{aromatic}$—H…O contacts support the formation of chains in some molecules with additional C_{methyl}—H…O interactions in the methoxy derivatives. C—H…π interactions occur in the majority of compounds but surprisingly, despite the presence of the planar naphthyl synthon, significant π…π stacking interactions are observed only for the nitro-derivative.

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Keywords: N-phenyl-naphthamides, structure, packing

FA4-MS26-P22

Highly Interpenetrated Organic Networks formed by Halogen Bonding Giancarlo Terraneo[a,b], Gabriella Cavallo[a], Pierangelo Metrangolo[a,b], Tullio Pilati[c], Giuseppe Resnati[a,b,c] , [a]*NFMLab - D.C.M.I.C. "Giulio Natta", Politecnico di Milano, Via L. Mancinelli 7, 20131 Milan, Italy,* [b]*CNST - IIT@POLIMI, Politecnico di Milano, Via G, Pascoli 70/3, 20133 Milan, Italy,* [c]*C.N.R. - I.S.T.M., University of Milan, Via C. Golgi 19, 20133 Milan, Italy*
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Halogen bonding (XB) [1], namely the noncovalent interactions wherein halogen atoms function as electrophilic species, can be described by the general scheme D···X-Y where X is the electrophilic halogen atom (Lewis acid, XB-donor), D is a neutral or anionic donor of electron density (Lewis base, XB-acceptor), and Y is carbon, nitrogen, halogen, etc. Recently, XB has proven its efficiency and reliability in the design and construction of self-assembled systems with quite different architectures and properties [2]. New aggregation processes can be realised, the novelty coming from either the molecular identity of assembled modules or from the way the modules are arranged in the supramolecular architecture. In this communication we describe the deliberate construction of highly interpenetrated organic networks. The focus will be on tetradentate tectons. In particular, we will show that DAB-*dendr*-$(NHC_6F_4I)_2$ self-assembles with (*E*)-1,2-bis-(4-pyridyl)-ethylene thanks to multiple N···I interactions that drive the formation of a supramolecular architecture composed of 2D square networks with a mode of interpenetration of class Ia. We will show that not only tetradentate XB-donor tectons, but also tetradentate XB-acceptors (*e.g.* tetrapyridyl pentaerythritol or cyclobutane derivatives) give rise to highly interpenetrated organic networks (Figure) [3].