

°. There are numerous publications devoted to the synthesis of halogenobutadienes containing atom of chlorine. They possess a broad spectrum of useful properties: they are employed as monomers for the preparation of valuable polymers and copolymers resistant to heat, light, chemical corrosion, etc. and they show algicidal, bactericidal fungicidal activities[1]. A number of halogenobutadienes manifest high antitumour activity. However, there are a few reports on the crystal structures of nitrobutadiene compounds[2,3]. It is the first publication about single crystal structure of 1,1,3-tris(arylthio)nitrobutadiene derivative.

The title compound, (I), was synthesized from 2-nitropentachlorobutadiene and benzyl mercaptan[4]. It is noted that, our spectroscopic data are in accordance with reported by this article but apparently, title compound is not a 1,1,4-substituted, but a 1,1,3-substituted regioisomer instead. This indication was proven by X-Ray analysis newly. Crystallographic analysis was carried out and the results are presented in this paper.

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Keyword: single-crystal structure analysis; sulfur compounds; synthetic organic chemistry

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NBO Analysis – A Useful Tool on Interpretation of Results of Crystal Structure Determination.

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General picture of crystal structure of compounds, especially of molecular crystals, can be appropriately complemented by means of Natural Bond Orbital (NBO) analysis, which provides a detailed view on the electronic structure of compounds. NBO analysis is based on a method for optimal transformation of a given wavefunction into a localized form, corresponding to the one-center (“lone pair”) and two-center (“bond”) elements of the Lewis structure picture [1]. NBO analysis provides information on localization of the individual Natural Atomic Orbitals (NAOs), degree of delocalization of the electronic structure, resonance structures, charge balance, bond orders (Wiberg indices) and other useful information on electronic structure of a compound. This method has been successfully applied in our works on several crystal structures of push-pull olefins [2-4], where the charge balance, possible and preferred resonance structures and Wiberg indices have been analysed. The contribution of lone pairs of respective atoms to electronic density of a bifunctional monophenol

[5], pyrazoline chromophore [6], fluoroquinolone [7] and imidazol[2, 1/b]thiazoles [8] (Fig. 1) and deviations from the expected bond orders in those compounds have been analyzed. NBO analysis revealed the impact of electronic redistribution to geometrical parameters in these molecules. It was found that the electronic delocalization caused shortening of the respective single bonds and/or elongating of some double bonds, when compared to typical bond lengths in the crystal structures of similar compounds.

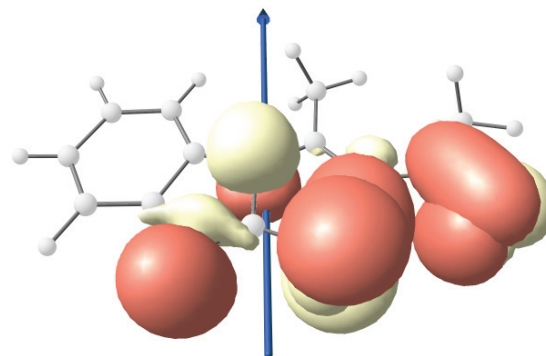


Fig. 1 The contributions of lone pairs of respective atoms to the electronic structure of 2-acetyl-3-methylbenzo[d]imidazol[2, 1/b] thiazole. The arrow represents the direction of total dipole moment.

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Keywords: DFT; electron density distribution in bonds; orbital calculations

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Hindered Rotation in N-(Acyloxy)-4-methylthiazole-2(3H)-thiones.

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Dynamic processes associated with a topological exchange of substituents in mixed anhydrides composed of carboxylic and cyclic thiohydroxamic acids were unexpectedly slow at ~298 K [1]. At ~320 K signal coalescence occurred for anhydrides derived from cyclic thiohydroxamic acid N-hydroxy-4-methylthiazole-2(3H)-thione and β-disubstituted carboxylic acids. At temperatures significantly above this point, fast exchange of diastereotopic substituents was evident from averaged

NMR signals. Eyring parameters for underlying dynamic processes were determined and compared to values modeled from a combined X-ray diffraction and computational study on selected *N*-(acyloxy)-4-methylthiazole-2(3*H*)-thiones [1,2,3]. The data suggest that the dynamic process occurs via N,O-rotation toward the less hindered face of the thiohydroxamate subunit. Topomerization toward the sterically more encumbered site, i.e. the thione sulfur, seems to require a stepwise two fold $\sim 90^\circ$ N,O-rotation with an inserted back and forth flip about the *N*-acyloxy C,O-bond. The proposed mechanism has implications for interpreting decomposition chemistry, which is of tremendous importance for this product class [1].

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Keywords: modelling; thiazolethione; variable temperature NMR

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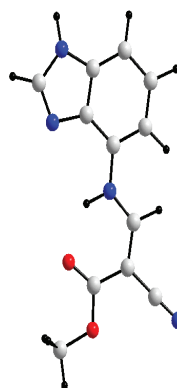
Methyl 3-((benzimidazol-4(7)-yl) amino)-2-cyano-prop-2-enoate-powder Diffraction and DFT Study. Lubomír Smrčok^a, Rosanna Rizzi^b, Pavel Mach^a, Michela Brunelli^c, Viktor Milata^d. ^a*Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, SK-845 36 Bratislava, Slovak Republic.* ^b*Istituto di Cristallografia - Sede di Bari Via Amendola, 122/o 70126 Bari, Italy.* ^c*European Synchrotron Radiation Facility, B.P. 220, F-38043 Grenoble CEDEX, France.* ^d*Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, SK-812 37 Bratislava, Slovak Republic.* *present address: ILL, Institut Laue-Langevin, B.P. 156, 38042 Grenoble cedex 9, France.
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Monoclinic ($P2_1/c$) crystal structure of the title compound was solved using RT synchrotron powder diffraction data (ID31/ESRF). The *ab initio* crystal structure determination was carried out by EXPO2009, the updated version of the EXPO2004 program [1]. A total of 879 extracted integrated intensities (450 independent observations because of the reflection overlapping) were used in the direct methods procedure to solve the crystal structure. The *E*-map corresponding to the best figure of merit (CFOM=0.999) was selected and optimized by applying cycles of least-squares to the molecular models derived from the electron density maps, followed by $2F_o - F_c$ electron density calculations. In each electron density map peaks were automatically located and their connectivity established by the standard EXPO2004 routines. The structure was refined by geometry optimization done by energy minimization in solid state using DFT/plane waves approach [2]. Molecules in the structure are assembled in ribbons running approximately parallel to (010). Each molecule (see figure below) in a

ribbon is connected to the adjacent with three hydrogen bonds: two moderate N-H...N1 and a weaker C-H...O. The ribbons are linked by three weak C-H...N bonds with the –CN groups playing the role of acceptor.

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Keywords: powder diffraction; DFT



FA4-MS05-P28

Synthesis, Characterization and Crystal Packing-Geometry of 1,5-dihydro-2H-cyclopenta [1,2-b:5,4-b']dipyridin-2-One. Leyla Tatar Yıldırım^a, Akın Baysal^b, Feyyaz Durap^b, Saim Ozkar^c. ^a*Hacettepe University, Department of Engineering Physics, Beytepe, TR-06800, Ankara, Turkey.* ^b*Dicle University, Department of Chemistry, TR-21280 Diyarbakir, Turkey.* ^c*Middle East Technical University, Department of Chemistry, TR-06531 Ankara, Turkey.* E-mail: tatar@hacettepe.edu.tr

Chemistry of diazafluorene has been rarely reported [1, 2]. Diazafluorene is a weaker ligand than bipy (in spectrochemical series), which translates into a significant energy change in the ligand-field (LF) states [3]. Consequently, diazafluorene complexes are expected to exhibit spectroscopic properties different from those with 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) ligands.

Using hydrazine as reducing agent, 1H-cyclopenta[1,2-b:5,4-b']dipyridine-2,5-dione [2,4] was selectively reduced to 1,5-dihydro-2H-cyclopenta[1,2-b:5,4-b']dipyridin-2-one. 1,5-dihydro-2H-cyclopenta[1,2-b:5,4-b']dipyridin-2-one was isolated as an analytically pure, colorless, solid and characterized by IR, ¹H-NMR and ¹³C-NMR spectroscopy, as well as elemental analysis. The crystal-packing have been structurally characterized by the single crystal X-ray crystallography. The crystal structure of the compound is involved intermolecular hydrogen bonds and, the short van der Waals interactions including helical and linear strand formation. The molecular packing in the solid state is square pyramidal porous structure along the c axis, as