

SYNTHESIS, NMR-, IR-SPECTRAL AND STRUCTURAL STUDY OF A NEW 2-THIONE- AND 2-CYANOIMINEPYRIMIDINE DERIVATIVES

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Our interest in synthesis and structural studies of 2-thione- and 2-cyanoiminepyrimidine derivatives is accounted by biological activity these compounds. We synthesized several compounds belonging to this family of substances with the radioprotector properties for applications in prophylactic and medical treatments of different type of radiation damages of human organisms. By NMR-, IR-spectroscopy, neutron powder and single crystal X-ray diffraction methods we solved more than 10 crystal structures. The method of the synthesis, correlation between molecular structures of these compounds and their radioprotective properties tested on biological objects will be reported.

Keywords: PYRIMIDINE, RADIOPROTECTOR, BIOACTIVITY

REDETERMINATION OF THE ROOM TEMPERATURE STRUCTURE OF BaCuSi₂O₆

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The barium copper cyclosilicate BaCuSi₂O₆ was described in the tetragonal space group *I*-4*m*2 (No 119) at room temperature, with cell parameters *a*=7.042(3) Å and *c*=11.133(3) Å [1]. The structure consists of alternating Sr₂- and Cu₂Si₄O₁₂-layers normal to the *c* axis. The latter layers are in fact bilayers, containing four-membered rings of SiO₄ tetrahedra and Cu atoms. Four adjacent Si₄O₁₂ rings are connected within the bilayers by two Cu atoms coinciding in the (*a*,*b*) plane with a distance of 2.76 Å in the *c* direction. Thus, the Cu²⁺ ions (*S*=1/2) form quasi-isolated dimers parallel to the *c* axis, arranged in a square lattice within the Cu₂Si₄O₁₂-bilayers. These dimers have a very weak antiferromagnetic interlayer coupling. This arrangement leads to a disordered magnetic ground state at low temperatures, with a spin gap δ=4.1 meV between the singlet ground state *S*=0 and the first excited triplet state *S*=1 [2]. The Si₄O₁₂ rings are isolated from each other in the structure. Their study by means of Raman spectroscopy has been used to better understand the structure of amorphous SiO₂ [3]. By means of single crystal X-ray diffraction on a Stoe IPDS diffractometer, we have observed at 295 K the presence of superstructure reflections, corresponding to a (*a**sqrt(2),*a**sqrt(2),2*c) cell. We propose the space group *I*4₁*cd* for the room temperature structure of BaCuSi₂O₆, with cell parameters *a*=10.009(2) Å and *c*=22.467(6) Å.

Reference

- [1] L. W. Finger, R. M. Hazen and R. J. Hemley, *Am. Mineral.* 74: 952-955, 1989.
 [2] Y. Sasago, K. Uchinokura, A. Zheludev and G. Shirane, *Phys. Rev. B* 55: 8357-8360, 1997.
 [3] D. A. McKeown and M. I. Bell, *Phys. Rev. B* 56: 3114-3121, 1997.

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HYDROGEN BONDING PATTERNS IN PHENOLIC PYRIDIN-2-YL-METHYLHYDRAZONES

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Crystal structures are compared for the parent compound 2-(pyridin-2-yl-hydrazonomethyl)-phenol (1) and its derivatives with methoxyl (2) and hydroxyl (3) groups at positions 5 and 6 respectively, along with the hydrochloride of (2). Two kinds of hydrogen bonding occur in (1). The phenolic OH group forms an intramolecular hydrogen bond to the unprotonated N8 atom in the hydrazone chain, while the adjacent NH group interacts with N1 of the pyridine ring in a centrosymmetric base-pair dimer. This pattern persists in (2). However, the extra OH group in (3) attracts a water molecule of crystallisation, which from a special position donates its protons to the pyridine N1 of two separate molecules. The dimer is thereby abolished, but the intramolecular O-H···N8 hydrogen bond remains intact. Finally, protonation of (2) occurs on N1. This newly created proton donor group and the existing donors all form hydrogen bonds to the chloride ion, and both the dimer and the O-H···N8 hydrogen bonds are lost. *Ab initio* (6-31G*) molecular orbital calculations comparing (1) with a 2-fold rotamer about the phenolic C-O bond indicate that the O-H···N8 interaction releases 34 kJ/mol. Analogous calculations (3-21G) for (1), (2) and their stable centrosymmetric dimers show dimer energy lowered by a similar amount per N-H···N. The near equality of H bond energies can be ascribed to higher positive charge on H(O) than H(N) offset by greater negative charge on N1 than N8 and straighter N-H···N geometry.

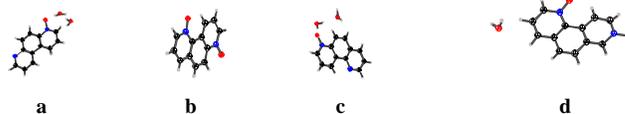
Keywords: PYRIDYLHYDRAZONES, HYDROGEN BONDING, AB INITIO CALCULATIONS

STRUCTURAL STUDIES OF PHENANTHROLINE N-OXIDES. THE PROBLEM OF AROMATICITY AND STABILITY

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There exist a considerable interest in phenanthroline derivatives because of their biological activity, complexation properties, inclusion in novel macrocycles and other possible applications [1]. In the case of mono- and di-N-oxides the η-electron structure of phenanthroline is strongly modified leading to significant changes in aromatic character and stability. The purpose of this communication is to present and discuss the crystal and molecular structure of (a) 4,7-phenanthroline 4-oxide, (b) 1,7-phenanthroline 1,7-dioxide, (c) 1,7-phenanthroline 7-oxide (d) 1,8-phenanthroline 1,8-dioxide. The systems were measured in 295 K and in 100 K. Application of the geometry-based HOMA model [2] and magnetic index NICS [3] to molecular geometries of the systems in question enriched by the structures of phenanthroline derivatives retrieved from Cambridge Structural Database (CSD) and from *ab-initio* B3LYP/6-311+G** calculations gives an insight on the extent of changes of electronic structure caused by replacing CH by N and N-O groups. The discussion of aromaticity and stability is additionally supported by the aromatic stabilization energies (ASE) values based on model homodesmotic reactions. The crystal structures of the title compounds are stabilized by a strong H-bond pattern involving interactions with water molecules. This aspect is also presented and discussed.



- [1] Newkome G. R. et al. *J. Org. Chem.*, **1989**, 54, 1766-1769.
 [2] Krygowski, T. M. *J. Chem. Inf. Comput. Sci.*, **1993**, 33, 70-78; Krygowski, T. M., Cyrański, M. K. *Tetrahedron*, **1996**, 52, 10255-10264.
 [3] Schleyer, P. v. R. et. Al., *J. Am. Chem. Soc.*, **1996**, 118, 6317-6318.

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