

MS06.P06

Acta Cryst. (2011) A67, C253**NMR, X-RAY and DFT studies on antioxidant triazolyl-benzimidazole derivatives**

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It is well known that benzimidazoles have a variety of biological activities such as antimicrobial, antitubercular, antioxidant, antiallergic and anticancer. In addition triazoles display anti-inflammatory, antiviral and antioxidant activities. In our previous study we described synthesis and antioxidant properties of compounds 5-(2-(p-chlorophenylbenzimidazol-1-yl-methyl)-4-(2-methylphenyl)-2,4-dihydro-[1,2,4]-triazole-3 thione (**A**) and 5-(2-(p-chlorophenylbenzimidazol-1-yl-methyl)-4-(2-bromophenyl)-2,4-dihydro-[1,2,4]-triazole-3 thione (**B**)).

The aim of this study was to clarify the restricted rotation around the –CH₂-N bond of the compounds **A** and **B** determined the structures by X-ray diffraction method. In NMR spectra of the compounds **A** and **B**, because of the restricted rotation around the –CH₂-N bond, methylene protons appear as an AB quartet in DMSO-d₆. The high temperature NMR spectra (296.1 K, 308.1 K, 323.1 K and 332.1 K) for the compound **A** show same behavior in DMSO-d₆. The NMR spectra in different solvents point out the same behavior.

The single crystal X-ray structures of these compounds show the presence of the intramolecular H-bond which were in good agreement with the results of the NMR spectra. Furthermore, DFT computations of the current compounds were all in agreement with the NMR results.

[1] G. Ayhan-Kılıçgil, C. Kus, T. Coban, B. Can-Eke, M. Iscan, *Journal of Enzyme Inhibition and Medicinal Chemistry* **2004**, 19(2), 129-135.

Keywords: NMR, X-ray, calculation

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Acta Cryst. (2011) A67, C253**Experimental and *ab initio* computational studies on N-(4-nitrobenzoyl)-N'-(1,5-dimethyl-3-oxo-2-phenyl-1H-3(2H)-pyrazolyl)-thiourea**

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The title molecule, N-(4-nitrobenzoyl)-N'-(1,5-dimethyl-3-oxo-2-phenyl-1H-3(2H)-pyrazolyl)-thiourea (C₁₉H₁₇N₅O₄S), was prepared and characterized by ¹H-NMR, ¹³C-NMR, IR and single-crystal X-ray diffraction. The molecular geometry, vibrational frequencies and gauge including atomic orbital (GIAO) ¹H- and ¹³C-NMR chemical shift values of the title compound in the ground state have been calculated by using the Hartree-Fock (HF) and density functional theory (DFT) methods with 6-31G(d) basis sets, and compared with the experimental data. The calculated results show that the optimized geometries can well reproduce the crystal structural parameters and the theoretical vibrational frequencies and ¹H- and ¹³C-NMR chemical shift values show good agreement with experimental data. To determine conformational flexibility, molecular energy profile of the title compound was obtained by semi-empirical (PM3)

calculations with respect to the selected torsion angle, which were varied from –180° to +180° in steps of 5°. The energetic behavior of the title compound in solvent media has been examined using B3LYP method with the 6-31G(d) basis set by applying the Onsager and the Polarizable Continuum Model (PCM). Besides, molecular electrostatic potential (MEP), frontier molecular orbitals (FMO) analysis and thermodynamic properties of the title compound were investigated by theoretical calculations.

Keywords: X-ray diffraction, IR, NMR, computation.

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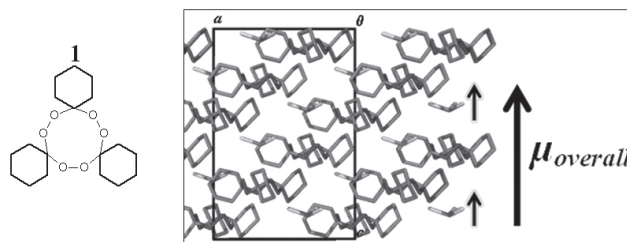
Acta Cryst. (2011) A67, C253**Guest polar ordering in 1,4,7-cyclohexane-1,2,4,5,7,8-hexaoxonane**

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Polar ordering is the alignment of molecules within a crystal such that it results in a net dipole that, in turn, leads to a polar axis that coincides with the net-dipole vector. Polar materials are used in non-linear optical, piezoelectric, pyroelectric and many other applications.[1] Inclusion complexes where both the host and guest molecules are polar-ordered, are rare. 1,4,7-cyclohexane-1,2,4,5,7,8-hexaoxonane (**1**) inclusion complexes are examples thereof.

Compound **1** forms isostructural polar-ordered inclusion complexes with CHCl₃, CHBr₃ and SiHCl₃ and crystallises in the polar space group *R3c* with the polar axis along [001]. The guest molecules reside within cavities formed by the arrangement of the host molecules. The cavities exhibit asymmetric features along the polar *c* axis, which induces the alignment of the guest molecules (along *c*). This was confirmed by computational methods. The asymmetric potential energy profile favored the guest molecule orientation observed in the crystal structure (0° conformation). The relative energies of the two orientations, 0° and 180°, calculated using density functional theory (DFT) revealed a 99.3% probability of obtaining the 0° conformation at 298.0 K, according to the Boltzmann distribution. The molecular quench dynamics simulations carried out suggest that the alignment of the guest molecules only occurs during the crystallization process.

This work presents a polar-ordered material where the polarity can be engineered by changing the included guest. The reason for the polar-ordering of the encapsulated guests can be explained by computational methods and the analysis of the polar-ordering of the host.



[1] K.T. Holman, A.M. Pivovar, M.D. Ward, *Science* **2001**, 294, 1907-1911.

Keywords: polar-ordering, inclusion