

Synthesis, Molecular Structure, IR and Raman Spectra as well as DFT Quantum Chemical Calculations for N-thiocynoacetylpiperidine and its Methyl Derivatives

E. Kucharska¹, W. Szaśiadek¹, H. Ban-Oganowska¹, M. Mączka², J. Hanuza^{1,2}

¹Department of Bioorganic Chemistry, Institute of Chemistry and Food Technology, Faculty of Engineering and Economics, University of Economics, Komandorska 118/120, 53-345 Wrocław, Poland

²Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna 2, 50-950 Wrocław, Poland

The thiocyanate (rhodanide) compounds are used as biocides in the leather making industry. Commercial biocidal formulations form the blend of active ingredients that combine the rapid antimicrobial actions of thiocyanate components with the fungicidal properties of the second component, e.g. thiocyanomethylthiobenzothiazole derivatives [1 and references therein].

Syntheses of N-thiocynoacetylpiperidine and its 2-, 3- and 4-methyl derivatives are described. The following compounds have been studied:

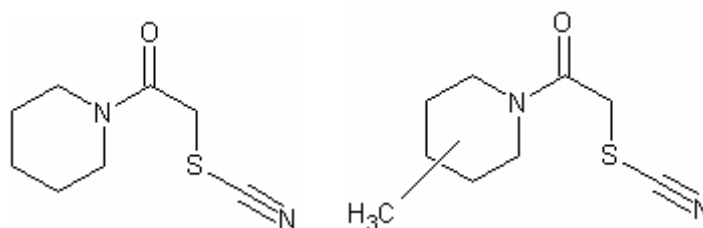


Fig. 1: Structures of N-thiocynoacetylpiperidine and its methyl derivatives

FT-IR and Raman spectra of these compounds have been measured and compared to the spectra of piperidine and alkylamides of thiocynoacetic acid. The 6-31G(d,p) basis set with the B3LYP functional has been used to discuss the structure and vibrational dynamics of the compounds studied. The calculated bond parameters of the optimized structures take the following average values, distances: C≡N 1.167, S-CN 1.700, S-CH₂ 1.856, H₂C-CO 1.534, OC-N 1.367, C=O 1.228 Å and angles: S-C≡N 177.9, H₂C-S-C 100.6, H₂C-CO-N 119.2, N-C=O 123.3°. These data fit well to the X-ray data of similar compounds [2]. The vibrational characteristics of the SCN, CO, CH₂ bridge groups and piperidine ring are reported with their relation to the molecular structures. The most characteristic vibrations have been observed in the following regions: ν(CN): 2156-2149, ν(CO): 1626-1616, ν_{as}(CH₂): 3015-2912, ν_s(CH₂): 2902-2850, ν(S-C): 648-615 and δ(SCN): 475-452 cm⁻¹. The energy of these modes depends on the substitution place of the methyl group. The other normal modes of the SCN, CO, CH₂ groups and piperidine ring with the PED values have been described. The role and influence of the substitution position of the methyl chromophore are discussed.

[1] L. Muthusubramanian, V.S. Sundara Rao, R.B. Mirta, J. Cleaner Production 11 (2003) 695-697.

[2] S. Thamocharan, V. Parthasarathi, R. Malik, D.P. Jindal, P. Piplani, A. Linden, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. 59 (2003) o422-o425.