INTRA- AND INTERMOLECULAR DYNAMICS OF AZA-AROMATIC SYNTHONS: A CASE STUDY OF THE 4,4′-BIPYRIDINE

E.V. Raksha[1], D. Zagorac[2,3], E.A. Goremychkin[1], A.B. Eresko[1], S. Dabylova[4], J. Zagorac[2,3], M. Pejić[2,3], T. Škundrić[2,3], S. Butulija[2], B. Matović[2], D.M. Chudoba[1]

[1] *Joint Institute for Nuclear Research, Dubna, Russian Federation*
[2] *Institute of Nuclear Sciences "Vinča", University of Belgrade, Belgrade, Serbia*
[3] *Center for synthesis, processing and characterization of materials for application in extreme conditions "CextremeLab", Belgrade, Serbia*
[4] *Institute of nuclear physics, Almaty, Republic of Kazakhstan*

E-mail: elenaraksha@jinr.ru

This study systematically investigates the intra- and intermolecular dynamics of aza-aromatic synthons for MOFs, which have a wide range of potential applications, including the production and use of functional materials for spintronics and microelectronics, as well as the development of highly effective catalysts. The torsion energy profile in aza-aromatic molecules is primarily influenced by two opposing trends: π-conjugation between the aza-phenyl rings, which favors a coplanar conformer, and steric repulsion, which stabilizes a nonplanar structure. We use a multidisciplinary approach that has previously been shown to be effective in studying the molecular dynamics of the 4,4′-bipyridine synthon (Fig. 1) [1-4].

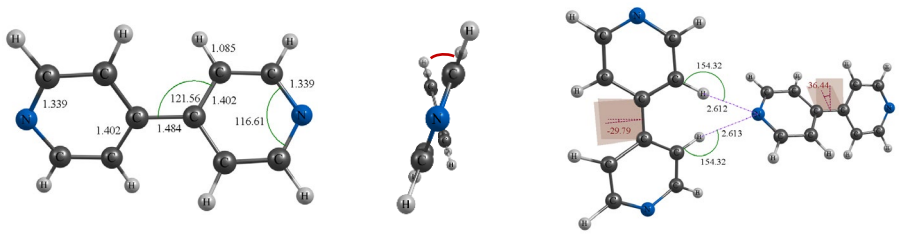

Fig. 1. Equilibrium geometries of the 4,4'-bipyridine (a) and its dimer (b) (B3LYP/6-31G(d,p) theory level)

Experimental studies of 4,4'-bipyridine using inelastic neutron scattering were performed in the energy transfer range of 0-160 meV at 5 K (NERA inverse geometry spectrometer at IBR-2, JINR, Dubna). DFT methods were used to study the molecular dynamics of 4,4'-bipyridine and its dimer, which are stabilized by non-valent C-H-N interactions (Fig. 1). The dimer's 4,4'-bipyridine molecules have varying torsion angles (φ), indicating the relative orientation of the pyridine fragments. This is consistent with the results of X-ray structural analysis [5]. The vibrational spectrum of 4,4'-bipyridine in the low-wavenumber region is characterized by non-valent C-H-N interactions. A comparison of experimental and DFT results contributes to our understanding of 4,4'-bipyridine dynamics and flexibility, as well as their potential applications in MOF design.

[1] D. Zagorac, M. Fonović, S. Butulija, et al. (2025) Journal of Alloys and Compounds, 1010, 178343.
[2] D.T.Teppala, M.Pejić, D. Zagorac, et al. (2026) International Journal of Applied Ceramic Technology, 23 (1), e70120.
[3] P. Gergelezhiu, E. Raksha, L. Savostina, et al. (2025) Phys. Part. Nuclei Lett., 22, 1102.
[4] Ł. Hetmańczyk, E.A. Goremychkin, J. Waliszewski, et al. (2021) Molecules. 26(16), 5043.
[5] N.M. Boag, K.M. Coward, A.C. Jones, M.E. Pemble, J.R. Thompson (1999) Acta Crystallographica, Section C: Crystal Structure Communications. 55, 672.