FA4-MS36-P01

Experimental and DFT studies of (E)-1-((3-bromophenylimino)methyl)naphthalene 2-ol. Tufan Akbal[a], Ahmet Erdönmez[a] and Erbil Ağar [b],
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The title compound, $C_{17}H_{12}BrNO$, crystallizes in a enol imine tautomeric form.
The structure is stabilized by O-H…N intramolecular hydrogen bonds. Molecular geometry from X-ray experiment of the title compound in the ground state have been compared using the density functional method (B3LYP) with 6-31G(d,p) basis set. To determine conformational flexibility, molecular energy profile of the title compound was obtained by DFT calculations with respect to two selected degrees of torsional freedom, which were varied from−180º to +180º in steps of 10º. The two rings are not coplanar and dihedral angle them is $16.73(0.17)^0$. The C9-O1 and C7-N1 bond lengths verify the enol-imine tautomeric form. These distances agree with the literature [1]. The C6-Br1 bond length in is also in a good agreement with the corresponding distances in the literature [2].

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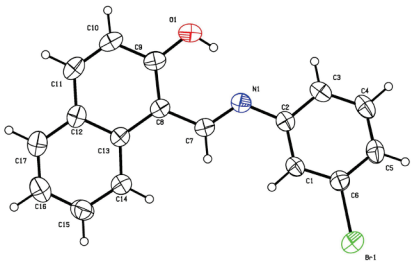
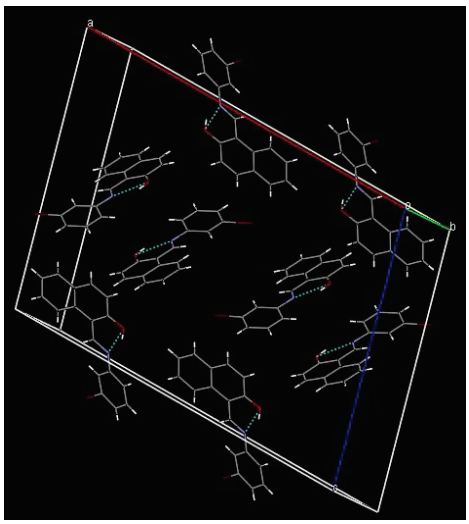
Keywords: tautomerism, crystal and molecular structure, density functional theory(DFT) studies





FA4-MS36-P02

Structural Analysis and DFT calculations of (E)-1-((4-chlorophenylimino)methyl)-napthalen-2-ol. Ahmet Erdönmez[a], Gökhan Alpaslan[a], Mustafa Macit[b], Orhan Büyükgüngör[a], [a]*Ondokuz Mayıs Univ., Department of Physics, Samsun-Turkey,* [b]*Ondokuz Mayıs Univ., Department of Chemistry, Samsun-Turkey.*
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The molecular and crystal structure of the title compound, $C_{21}H_{12}ClN_3O$, has been determined by X-ray single crystal diffraction technique. The compound crystallizes in the monoclinic, space group $P2_1/c$ with unit cell dimensions a= 4.7596(2), b= 20.3483(7), c= 14.3293(6), β=82.857(6)°, V= 1330.45(9)Å^3, Z=4, R_1=0.038 and wR_2=0.093.
Crystallographic analysis reveals that the title compound, $C_{17}H_{12}NOCl$, possesses both OH and NH tautomeric character in its molecular structure. The occupancies of the enol and keto tautomers are 0.51(5) and 0.49(5) respectively. In order to explain the tautomerizm process and its effects on the molecular geometry in the solid state, the geometry optimization in gas phase for enol and keto tautomers of the title compound were calculated using density functional method (B3LYP) with the 6-31G(d,p) basis set. To be able to describe the potential barrier height for the intramolecular proton transfer, Potential Energy Surface (PES) scan was performed based on the optimized geometry of enol tautomeric form at the B3LYP/6-31G(d,p) level by varying the redundant internal coordinate O-H bond distance. The calculated results show that the enol form is also predicted to be 1.21 kcal/mol more stable than the keto form in the gas phase by the DFT method.

Keywords: crystal structure analysis, density functional theory, tautomerism

FA4-MS36-P03

Asp214→Ala Mutation Reorganizes the Active Site of *Citrobacter freundii* Tyrosine Phenol-lyase. Dalibor Milić[a], Tatyana V. Demidkina[b], Dubravka Matković-Čalogović[a], Alfred A. Antson[c], [a]*Department of Chemistry, Faculty of Science, University of Zagreb, Croatia,* [b]*Engelhardt Institute of Molecular Biology, Russian Academy of Sciences, Moscow, Russia,* [c]*York Structural Biology Laboratory, Department of Chemistry, University of York, UK*
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Tyrosine phenol-lyase (TPL) from *Citrobacter freundii* and other bacteria is a homotetrameric protein. This pyridoxal-5'-phosphate (PLP)-dependent enzyme catalyzes the reversible hydrolytic cleavage (β-elimination reaction) of L-tyrosine to give phenol and ammonium pyruvate [1]. The active site (one per each subunit) is situated at an interface between the small and large domain of one subunit, and the large domain of the adjacent subunit [2]. It can assume either the open or closed conformation [3]. We suggest that the active site closure is fundamental to the cleavage of L-tyrosine Cβ–Cγ bond [4]. D214A and D214N TPL mutants from *C. freundii* were shown to be inactive for the β-elimination of L-tyrosine and its derivatives [5]. We present the structure of D214A TPL mutant solved at 1.9 Å resolution. This structure indicates that

the mutation prevents the protonated N1 nitrogen atom of the PLP pyridine ring from creating a hydrogen-bond with the side chain of residue 214. Instead, new hydrogen bonds are formed between the PLP O3' atom and the side chains of Asn185 and Thr216, and between the deprotonated PLP N1 atom and a nearby water molecule that is hydrogen bonded with Glu103 and Thr126. These new interactions cause a significant conformational change in the active site, including reorientation of PLP and the side chains of Asn185 and Thr103, and translocation of the helix α4', together with the catalytically important Thr124, by ~1.5 Å from the active site cleft. The open active site cleft as a whole is slightly more closed than in the wild type holoenzyme. These results explain the observed inactivity of D214A mutant [5].

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Keywords: vitamin B6, enzymatic structure-activity relationships, mutations

FA4-MS36-P04

Experimental charge density studies, electrostatic and topological analysis of 1-(2'-Aminophenyl)-2-methyl-4-nitro-1H-imidazole crystals.

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High resolution diffraction data of crystals of small organic molecules, such as 4-nitro-1H-imidazole derivatives, are achievable within a period of days, thanks to the development of the measurement devices.
Processing these data in the standard manner to solve and refine the structures and to obtain the information about the geometry and interactions is usually performed applying the Independent Atom Model (IAM). Within this approximation all atoms are treated as 'spherical balls' with the electron density concentrated around the nuclei. However, this assumption neglects transfer of the charge density into the bonding regions – especially for the covalent bonds – and the transfer associated with the intermolecular interactions.
To improve the electron density distribution model and to allow for the detailed analysis of the intra- and interactions in the molecules and in the supramolecular assemblies, such as the 1-(2'-Aminophenyl)-2-methyl-4-nitro-1H-imidazole, the Hansen-Coppens formalism [1] and Atoms-in-Molecule approach [2] for topological analysis are used. The multipole model has been implemented in the MoPro program suite [3] and allows electrostatic and topological calculations for both small molecules and biological macromolecules at subatomic resolution.
Within this poster the experimental charge density distribution of the title compound will be presented. The crystal structure of this 4-nitroimidazole derivative was published recently, using standard resolution data [4], however no detailed analysis of the influence of the substituents on the electron distribution was performed. The main observed interactions are the strong and weak hydrogen bonds (N-H···N, N-H···O and C-H···O, C-H···Cg (centroid of the aromatic ring), respectively). These regions, with a special attention paid to the nitro group (as hydrogen bond acceptor), will be analysed.
This is a part of our project to investigate the weak interactions in the series of 4-nitro-1H-imidazole derivatives, to examine the influence of the different substituent groups on the charge density distribution within the aromatic ring.

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Keywords: 4-nitro-1H-imidazole derivatives, multipole refinement, high resolution diffractiondichalcogenides compound, Trigonal prism

FA4-MS36-P05

Supramolecular π-π and Hydrogen Bond Interactions in Arylsulfonate Complexes.

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Six novel compounds were synthesized under hydrothermal conditions by reaction of divalent cations (M^{2+} = Co^{2+}, Ni^{2+}, Mn^{2+}, Cu^{2+} and Zn^{2+}) with two different arylsulfonates and phenanthroline. $Co_2(2,6\text{-AQDS})_2(phen)_4$ (**1**) (2,6-AQDS = anthraquinone-2,6-disulfonate, phen = 1,10-phenantroline) crystallizes in a space group P-1, is a dimeric molecular complex and exhibits 2D supramolecular arragement via π-π aromatic slipped and T-shaped stacking interactions [1]. The compounds $Co(1,5\text{-AQDS})(Phen)_2(H_2O)$ (**2**), $Ni(1,5\text{-AQDS})(Phen)_2(H_2O)$ (**3**), $Mn(1,5\text{-AQDS})(Phen)_2(H_2O)$ (**4**), $Cu(1,5\text{-AQDS})(Phen)_2(H_2O)$ (**5**) and $Zn(1,5\text{-AQDS})(Phen)_2(H_2O)$ (**6**) (1,5-AQDS = anthraquinone-1,5-disulfonate) are a series of isostructural molecular compounds of space group P-1. Their structures are formed by one arylsulfonate and two phenanthroline molecules in octahedral arrangement around the metal cation. These molecular complexes have 2D supramolecular structure by combination of π-π aromatic slipped interaction, T-shaped stacking interactions, as well as C-H…O and O-H…O interactions. Catalytic activity of **1-5** for oxidation of organic sulfides [2] was studied.

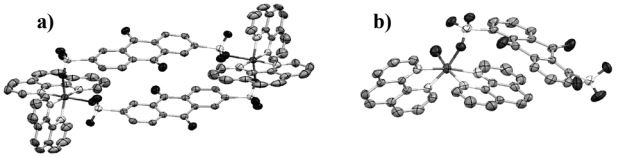

Figure 1. a) Dimeric structure of compound **1** and b) monomeric structure of compound **2.**

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Keywords: Arylsulfonates, stacking interaction, hydrothermal