



# Theoretical studies and spectroscopic characterization of novel 4-methyl-5-((5-phenyl-1,3,4-oxadiazol-2-yl)thio)benzene-1,2-diol

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## ABSTRACT

The structural, electronic, and spectroscopic properties of 4-methyl-5-((5-phenyl-1,3,4-oxadiazol-2-yl)thio)benzene-1,2-diol (MPOTB) have been carried out at *ab initio* and DFT levels. A detailed study of geometrical parameters, Infrared spectrum, chemical shifts (<sup>13</sup>C NMR, <sup>1</sup>H NMR), and electronic properties of the title compound is presented. The correlation between the theoretical and the experimental <sup>13</sup>C, and <sup>1</sup>H chemical shifts of MPOTB were about 1.02–1.03 and 0.98–1.00, respectively. The electronic properties, such as molecular electrostatic potential, NBO atomic charges, HOMO and LUMO energies were performed at above levels. Rather high hardness of MPOTB introduces it as a stable molecule. As a result, the calculated findings were compared with the observed values and generally found to be in good agreement.

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## 1. Introduction

1,3,4-Oxadiazole derivatives are important heterocyclic compounds with a broad range of biological, medicinal, and pharmacological properties [1–3]. Some of them have antibacterial, antifungal, anti-inflammatory, and hypoglycemic activity. These also lie in the field of photosensitizer, liquid crystals, and electron-conducting and hole-blocking materials in organic light-emitting diodes [1,2]. In view of these useful properties, a number of preparative methods have been reported for the synthesis of these molecules [1,4–8].

Recently, highly improved computers have a good ability to correctly describe the physicochemical properties of small molecules with nearly chemical accuracy. So, regarding the importance of 1,3,4-oxadiazole derivatives, computational chemistry could be valuable to discover physicochemical properties of relatively small molecules [9]. *Ab initio* and density functional theory (DFT) calculations could provide excellent vibrational frequencies, NMR data, and single-crystal X-ray analyses of the organic compounds. The

geometric parameters and single-crystal X-ray structure of the molecule determine both experimentally and theoretically via X-ray crystallography and the computational methods in the ground state, respectively [10]. Hence, it can play an important role in the modern drug discovery. The computational prediction of molecular properties for the selected medium-sized organic is more essential than modeling interactions with macromolecules in the drug development. Conformational modeling and simulation of the spectroscopic parameters can help in the interpretation of the NMR data from pharmaceuticals, synthetic intermediates, metabolites, degradation products and undesired impurities.

In this work, 4-methyl-5-((5-phenyl-1,3,4-oxadiazol-2-yl)thio)benzene-1,2-diol molecule (MPOTB) optimized at the HF/6-31G(d), B3LYP/6-31G(d), and M063X/6-311++G(d,p) levels of theory, while other calculation were performed at two first levels [11–14]. The calculated IR and NMR spectra were compared with the experimental data. The optimized geometrical parameters and the X-ray crystallography data were exposed parallel results.

## 2. Computational methods

The theoretical computations were performed at Hartree Fock, B3LYP and M062X levels using the Gaussian 09W program package

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[15]. The optimized structure characterized as a global minima on the potential energy surface (PES) [16]. In DFT calculations the Becke's three parameter exchange–functional (B3) combined with gradient-corrected correlation functional of Lee, Yang and Parr (LYP) [11–13], and the M06-2X functional is a high nonlocality functional with double the amount of nonlocal exchange (2X) [14] by implementing the split-valance polarized 6-31G(d) and/or the split-valance polarized diffused 6-311++G(d,p) basis sets has been utilized for the computation of molecular structure optimization and vibrational frequencies [17–20]. To obtain natural charge data of atoms NBO calculations were performed at the both levels [21,22].

Optimized structural parameters were used in the isotropic chemical shift, vibrational frequency, HOMO-LUMO gap, and electronic property calculations. The nuclear magnetic resonance (NMR) chemical shift calculations were performed using Gauge-Invariant Atomic Orbital (GIAO) method at HF and B3LYP level using 6-31G(d) basis set in DMSO as a solvent.

In a typical procedure, 100 mL mixture of water/acetonitrile (95/5) containing phosphates ( $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$ ) as the buffer and supporting electrolyte was preelectrolyzed at the potential of 0.15 V versus the Ag|AgCl|KCl (3 M) as a reference electrode in an undivided cell. Subsequently, 4-methylbenzene-1,2-diol (2 mmol) and 4-methyl-5-((5-phenyl-1,3,4-oxadiazol-2-yl)thio)benzene-1,2-diol (2 mmol) were added to the cell. Finally, the electrolysis was performed at the same potential. The electrolysis was terminated when the decay of the current became more than 95%. The process was interrupted several times during the electrolysis and the carbon anode was washed in acetone to reactivate it. At the end of electrolysis, the cell was placed in a refrigerator overnight. The precipitated solid was collected by filtration and then was washed several times with distilled water. After purification, products were characterized using IR,  $^1\text{H}$ NMR,  $^{13}\text{C}$  NMR, X-ray spectral data. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum was recorded on a Bruker DRX-300 Avance Instruments. The FT-IR spectrum was recorded on a Bruker IFS-66 FTIR Spectrophotometer, in the solid state (KBr), the equipment details are described before [4].

### 3. Results and discussion

#### 3.1. Geometry

The theoretical NMR and IR spectra are depending on the optimized geometrical parameters. The optimized bond lengths and bond angles at HF/6-31G(d), B3LYP/6-31G(d) (with its related PES), and M062X/6-311++G\*\* levels of theory, and the atoms

numbering of MPOTB are presented (Figs. 1 and 2, Table 1). The solid state structure was determined by X-ray crystal structure analysis (Fig. 3, Table 1) [4]. A very good agreement is shown in experimental and the theoretical data (Figs. 1–3, Table 1), which shows the reliability of the proposed levels of theory [23–26]. As the experimental values of MPOTB are known, the theoretically calculated values may supply an idea about the geometry of the molecule and also an idea of how the geometry of the molecule changes from one level to another. According to the both theoretical calculations, MPOTB with  $C_1$  symmetry has a non-planar structure. The correlation coefficients for bond lengths computed from the HF, B3LYP, M062X methods with the experimental values were found to be 0.9969, 0.9982, and 0.9979, respectively. Similarly, the correlation coefficients for bond angles computed from the HF, B3LYP, and M062X methods with the experimental values were found to be 0.9834, 0.9817, and 0.9806, respectively. The agreement for bond angles is not as good as that for the bond length. The slight variation with the experimental value is due to the fact that optimization is performed in an isolated condition, whereas the crystal environment affected the experimental X-ray structure.

Both theoretical and X-ray data show bond length between single and double bond for C–C in the benzene cycles. The calculation determined C–C bond length in benzene in the range of 1.365–1.393 Å using HF, 1.390–1.407 Å using B3LYP, and 1.384–1.397 Å using M062X, similarly X-ray structure shows 1.377–1.401 Å for their corresponding C–C bond, while both of experimental and theoretical show, C–C single bond for  $\text{C}_4\text{--}\text{C}_7$  (about 1.46 Å) and  $\text{C}_{14}\text{--}\text{C}_{26}$  (1.51 Å). That means there is no conjugation between benzene cycle and oxadiazole cycle. Moreover, a good agreement is found on bond angles in theoretical level and experiment (Figs. 1 and 3, Table 1). All of  $\angle\text{CCC}$  in its benzene cycles are about  $120^\circ$ , which admit the  $\text{sp}^2$  hybrid for corresponding carbons. The smallest one is shown  $\angle\text{C}_{13}\text{C}_{14}\text{C}_{15}$ ,  $116.8^\circ$  in X-ray and  $117.2^\circ$ ,  $117.4^\circ$ , and  $117.3^\circ$  in HF, B3LYP, and M062X in turn. The small  $\angle\text{NCO}$  in oxadiazole cycle,  $112.3\text{--}112.4^\circ$  in X-ray and  $111.8\text{--}112.3^\circ$  at HF,  $111.9\text{--}113^\circ$  at B3LYP, and  $112.0\text{--}112.8^\circ$  at M062X, display that C have higher p character than usual  $\text{sp}^2$  in  $\text{C}=\text{N}$  and  $\text{C}\text{--}\text{O}$  bonds. So, the bond length of  $\text{N}=\text{C}$  and  $\text{C}\text{--}\text{O}$  should be larger than their corresponding in common.

In fact, our theoretical geometry, in particular using the 6-31G(d) and 6-311++G(d,p) basis sets, closely resembled the experimental data. The standard deviation for the bond lengths using HF, B3LYP, and M062X levels were 0.012, 0.007, and 0.008 Å, respectively. While, it was found 1.1 and  $1.2^\circ$  in turn of *ab initio* and DFT for the bond angles.

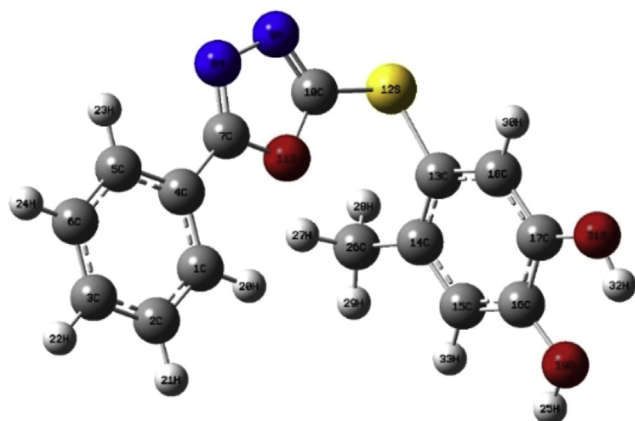


Fig. 1. The optimized structure of MPOTB molecule.

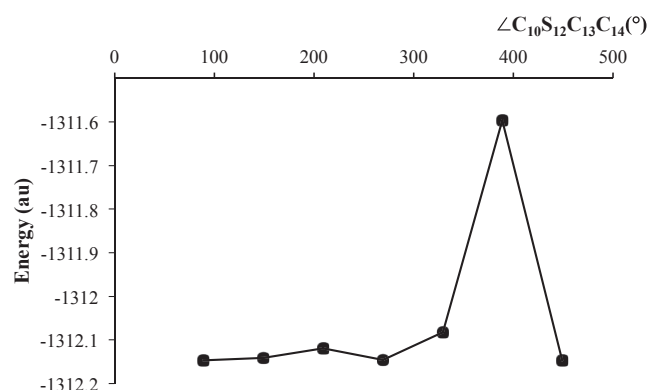


Fig. 2. The Potential Energy Surface (PES) of MPOTB molecule using B3LYP/6-31G(d).

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