



# Structure, vibrational analysis, electronic properties and chemical reactivity of two benzoxazole derivatives: Functional density theory study



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## ABSTRACT

In the present work we calculate structural parameters, vibrational spectra (IR, <sup>1</sup>H NMR and UV–Visible Absorption) and corresponding mode of vibrational assignments of two ligands derived from benzoxazole; L<sup>1</sup>: 2-(5-(trifluoromethylpyridin-2-yl)-benzoxazole and L<sup>2</sup>: 2-(5-methylpyridin-2-yl)-benzoxazole at B3LYP/6-311++G\*\* level, in the gas phase. The HOMO and LUMO study is used to determine the charge transfer within the molecules. Reactivity descriptors such as ionization energy, electronic affinity, global hardness, global softness, electrophilicity, nucleophilicity and condensed Fukui functions using NBO population analysis are also determined to predict the reactivity of L<sup>1</sup> and L<sup>2</sup>. The calculated geometrical parameters are in good agreement with those of similar benzoxazole derivatives. Theoretical frequencies assignments confirmed the experimental ones of these benzoxazole derivatives.

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## 1. Introduction

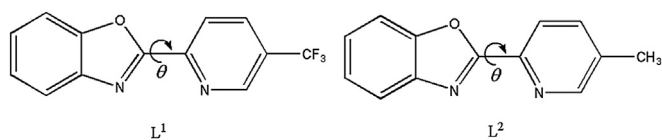
Benzoxazole is a five-membered ring compound containing both nitrogen and oxygen fused to a benzene ring. The benzoxazole nucleus and its derivatives are known to play extremely crucial roles in medicinal chemistry. Various benzoxazole derivatives were extensively studied for their biological and pharmacological activities concerning antibiotic [1,2], antimicrobial [3–5] antifungal [6–8] and antitumor activities [9–11]. These heterocyclic compounds are known to be effective complexing agents with various transition metal ions via nitrogen donor atoms [12–17]. Therefore, better antimicrobial and antitumor activities have been reported for a few metal-benzoxazole complexes [18–20] in comparison with isolated benzoxazole ligands. Unfortunately, the significant and rapid development of drug resistance by bacteria and viruses is an important motivation to synthesize new antimicrobial and

antiviral molecules [21–24]. For this reason Bouchoucha et al. [21,22] synthesized and characterized two ligands derived from benzoxazole; L<sup>1</sup>: 2-(5-(trifluoromethylpyridin-2-yl)-benzoxazole [22] and L<sup>2</sup>: 2-(5-methylpyridin-2-yl)-benzoxazole [21,22] (Fig. 1). Their transition metal complexes with manganese (II), nickel (II) copper (II) and iron (II) have been also synthesized and characterized [21,22]. Both ligands and their complexes exhibit antibacterial and antifungal activities. The microbial strains investigated included 3 g-negative bacteria (*Escherichia coli* ATCC 4157, *Pseudomonas aeruginosa* ATCC 9027, *Klebsiella pneumoniae* ATCC 4352), two Gram-positive bacteria (*Staphylococcus aureus* ATCC 6538, *Bacillus subtilis* ATCC 9372), three yeast (*Candida albicans* ATCC 24433, *Candida tropicalis* ATCC 10233, *Saccharomyces cerevisiae* ATCC 2601) and two moulds (*Aspergillus fumigatus* CBS 11326 ATCC, *Aspergillus niger* 135550/99) [21,22]. The minimum inhibitory concentration (MIC) values of the ligands and their complexes indicate that the iron complex is the most active antimicrobial compound. For example, its MIC value is 12.5 µg/mL on *A. fumigatus*.

In the absence of crystal structures and previous theoretical studies for the two ligands L<sup>1</sup> and L<sup>2</sup> to obtain the most stable molecular conformation and the nonexistence of quantum

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**Fig. 1.** Structure of two ligands derived from benzoxazole;  $L^1$ : 2-(5-(trifluoromethyl)pyridin-2-yl)-benzoxazole and  $L^2$ : 2-(5-methylpyridin-2-yl)-benzoxazole.  $\theta$  is the torsional dihedral angle formed by the planes of pyridine and benzoxazole rings.

mechanical studies to evaluate global and local reactivity descriptors, we report in this paper detailed geometrical studies of  $L^1$  and  $L^2$  and an evaluation of the reactivity exhibited by those two benzoxazole-pyridyl ligands at Density Functional Theory (DFT) level. Also, spectral studies, vibrational modes and assignments, NBO atomic charges and HOMO–LUMO analysis of these compounds are reported here. Results of theoretical calculations are compared with corresponding experimental data.

## 2. Theoretical aspects

DFT methods have been successfully exploited to define site selectivity and chemical reactivity such as the electronic chemical potential ( $\mu$ ), the absolute hardness ( $\eta$ ), the global softness ( $S$ ) and the global electrophilicity ( $\omega$ ) [25,26]. Parr and Pearson [27] defined the electronic chemical potential  $\mu$  by:

$$\mu = -\frac{1}{2}(I + A) = -\chi \quad (1)$$

where  $I$  and  $A$  are the ionization potential and electron affinity of the molecule, respectively and  $\chi$  is the electronegativity defined by Mulliken.

The global hardness is given by Refs. [27–30]:

$$\eta = \frac{1}{2}(I - A) \quad (2)$$

The global softness  $S$  is defined as:

$$S = \frac{1}{2\eta} \quad (3)$$

and the global electrophilicity index introduced by Parr [31] can be calculated from:

$$\omega = \frac{\mu^2}{2\eta} \quad (4)$$

$\omega$  measures the affinity of molecules to attract electrons. Nucleophilicity cannot be derived from the same model leading to the definition of the electrophilicity index [32–34]. This problem occurs because, for the right-hand side of the parabola model used by Parr et al., the electronic chemical potential becomes positive semi definite. This drawback of the philicity model is related to an empirical rule stating that big electrophilicity/nucleophilicity differences can be correlated to stepwise reaction mechanisms with a significant polar transition state, while small differences are related to nonpolar concerted mechanisms [35]. However, the nucleophilicity index can be simply represented as the negative of the ionization potential:

$$Nu = -I \quad (5)$$

Thus, a good nucleophile is characterized by high value of  $Nu$  and a good electrophile is characterized by low value of  $\mu$  and high value of  $\omega$ .

The hard and soft acids and bases (HSAB) principle has been very useful to predict the reactivity of chemical systems [36–38]. The HSAB principle has been used in a local sense in terms of DFT concepts such as the Fukui function  $f(r)$  [36]. Generally it is showed that the larger the value of the Fukui function  $f(r)$  the greater the reactivity.

The Fukui function is defined [36] as the first derivative of the electronic density  $\rho(r)$  with respect to the number of electrons  $N$  at constant external potential  $v$ :

$$f(r) = \left( \frac{\partial \rho(r)}{\partial N} \right)_v \quad (6)$$

The Fukui function is a local reactivity descriptor that indicates the preferred regions where a chemical species will change its density when the number of electrons is modified. Therefore, it indicates the propensity of the electronic density to deform at a given position upon accepting or donating electrons [36–38].

In addition, it is possible to define the corresponding atomic Fukui functions on the  $j$ th atom site as,

$$f_j^- = q_j(N) - q_j(N - 1) \quad (7)$$

for electrophilic attack;

$$f_j^+ = q_j(N + 1) - q_j(N) \quad (8)$$

for nucleophilic attack;

$$f_j^0 = \frac{1}{2} [q_j(N + 1) - q_j(N - 1)] \quad (9)$$

for radical attack on the reference molecule.  $q_j$  is the electronic population at the  $j$ th atomic site in the neutral ( $N$ ), anionic ( $N + 1$ ) or cationic ( $N - 1$ ) chemical species.

## 3. Computational methods

Calculations have been performed using Kohn–Sham's Density Functional Theory subjected to the gradient-corrected hybrid density functional B3LYP [39–41]. This functional is a combination of the Beck's three parameters non-local exchange potential with the non-local correlation functional of Lee et al. [42,43]. Energy scan studies have been carried out to localize minima and transition state for each molecule at B3LYP/6-311 + G\* level of theory. For each minima and transition state, a full geometry optimization was performed using this functional and the 6-311++G\*\* [44,45] basis set as implemented by Gaussian 03 W package [46], in gas phase. The vibrational frequencies were computed to make sure that the stationary points were minima. The population analysis has also been performed by the natural bond orbital (NBO) program [47], at the same level of theory, using Natural Bond Orbital (NBO) program [48] under Gaussian 03 program package.  $^1\text{H}$  NMR data were obtained from the DFT method using basis set 6-311++G\*\*. The characterization of excited states and electronic transitions were performed using the time-dependent DFT method (TD-DFT) on their correspondingly optimized ground state geometry. We used TD-DFT which is found to be an accurate method for evaluating the low-lying excited states of molecules and has been thoroughly applied to solve physical and chemical problems. Vertical excitation energies were computed for the first 10 singlet excited states, in order to reproduce the experimental electronic spectra.

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