

Structural and Electronic Properties of [Co(benzimidazole)₂I₂]

Rumyana Yankova^{1,*}, Lachezar Radev²

¹Department of Inorganic and Analytical Chemistry, Assen Zlatarov University, Bourgas, Bulgaria

²Department of Fundamental Chemical Technology, University of Chemical Technology and Metallurgy, Sofia, Bulgaria

Abstract The diiodobis(benzimidazole)Co(II) complex was obtained. The equilibrium geometry, harmonic vibrational frequencies and infrared intensities were calculated by density functional B3LYP method with the 6-31G(d,p) basis set and LANL2DZ for iodine. The experimental infrared spectrum was compared with calculated and complete vibrational assignment was provided. The scaled theoretical wavenumbers showed good agreement with the experimental values. The natural bond orbital analysis (NBO) was performed in order to study the intramolecular bonding interactions among bonds and delocalization of unpaired electrons. The calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) with frontier orbital gap were presented. The thermodynamic properties of the studied compound at different temperatures were calculated.

Keywords Diiodobis (benzimidazole)Co(II), Quantum chemical calculations, Geometry optimization, Electronic properties

1. Introduction

Benzimidazole possess wide spectrum of biological activities like including antibacterial, antifungal, antiviral, antiinflammatory, anticonvulsant, antidepressant, antihypertensive, analgesic, and hypoglycemic properties. Benzimidazole derivatives exhibit a wide variety of pharmacological properties including antitumor activity [1] and inhibition of nucleic acid synthesis [2]. The complexes of transition metal salts with benzimidazole derivatives were studied as models of some important biological molecules [3]. Metal complexes of biologically important ligands are more effective than free ones [4]. The complex of [Co(benzimidazole)₂I₂] was reported [5].

The aims of this study is to calculate optimal molecular geometry, vibrational wavenumbers and various normal modes associated with of [Co(benzimidazole)₂I₂] complex and provide complete vibrational assignment for the IR spectra. The objective of the present work is to investigate the nature of bonding in an diiodobis(benzimidazole)Co(II) complex, by using natural bond orbital (NBO) analysis. It was shown that the results from NBO calculations can provide the detailed insight into the electronic structure of molecule.

Density functional theory calculations are reported to

provide excellent vibrational frequencies of organic compounds if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for the anharmonicity [6-11].

2. Experimental

The [Co(benzimidazole)₂I₂] complex was prepared according to the method outlined by Goodgame [12]. The infrared spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer in the 4000 – 400 cm⁻¹ range, with the samples embedded in KBr matrixes. The thermogravimetric analysis was performed on an apparatus STA 449 F3 JUPITER (Netzsch) for TG-DTG/DSC at heating rate 10°C min⁻¹ from room temperature to 1000°C under flowing air (20 cm³ min⁻¹).

3. Computational Methods

The full optimization of [Co(benzimidazole)₂I₂] was carried out by Density Functional Theories (DFT) method using Gaussian 03 software [13]. It was used Becke's three parameter hybrid exchange functional with Lee–Yang–Parr correlation functional (B3LYP) [14-16] with added polarization functions – 6-31G(d,p) and LANL2DZ [17-19] for iodine. All calculations were converged to 10⁻⁸ a.u. The absence of imaginary frequencies in the calculated vibrational spectrum confirms that the structure corresponds

* Corresponding author:

r_yankova@yahoo.com (Rumyana Yankova)

Published online at <http://journal.sapub.org/ijmc>

Copyright © 2016 Scientific & Academic Publishing. All Rights Reserved

to minimum energy. The population analysis was performed by the natural bond orbital method [20] at B3LYP/6-31G(d,p) and LANL2DZ for iodine using NBO program [21] under Gaussian 2003 program package. Natural bond orbital analysis stresses the role of intermolecular orbital interaction in the complex, particularly charge transfer. This is carried out by considering all possible interactions between filled donor and empty acceptor orbitals and estimating their energetic importance by second-order perturbation theory. For each filled orbital of the donor (Φ_i) and the empty orbital of the acceptor (Φ_j), the stabilization energy ($\Delta E_{ij}^{(2)}$) associated with electron delocalization between donor and acceptor and it is calculated by equation (1) [22],

$$\Delta E_{ij}^{(2)} = q_i \frac{\langle \phi_i | F_{ij} | \phi_j \rangle^2}{\epsilon_j - \epsilon_i}, \quad (1)$$

where q_i is the donor orbital occupancy, ϵ_i and ϵ_j are NBO energies, F_{ij} is Fock matrix element between the i and j NBO orbitals. NBO analysis reveals the intra- and intermolecular interactions; it is one of the appropriate methods for investigating hyperconjugative interactions.

Table 1. Some optimized geometrical parameters of [Co(benzimidazole)₂I₂]

Parameters		Parameters	
Bond length (Å)		Bond angle (degree)	
Co–N ²⁽¹¹⁾	1.922	N ²⁽¹¹⁾ –C ³⁽¹²⁾ –N ⁴⁽¹³⁾	112.1
Co–I ³²⁽³³⁾	2.670	C ³⁽¹²⁾ –N ⁴⁽¹³⁾ –C ⁵⁽¹⁴⁾	107.9
N ²⁽¹¹⁾ –C ³⁽¹²⁾	1.319	N ⁴⁽¹³⁾ –C ⁵⁽¹⁴⁾ –C ⁶⁽¹⁵⁾	105.0
C ³⁽¹²⁾ –N ⁴⁽¹³⁾	1.358	C ⁵⁽¹⁴⁾ –C ⁶⁽¹⁵⁾ –N ²⁽¹¹⁾	108.8
N ⁴⁽¹³⁾ –C ⁵⁽¹⁴⁾	1.388	C ⁶⁽¹⁵⁾ –N ²⁽¹¹⁾ –C ³⁽¹²⁾	106.1
N ²⁽¹¹⁾ –C ⁶⁽¹⁵⁾	1.397	C ⁵⁽¹⁴⁾ –C ⁷⁽¹⁶⁾ –C ⁸⁽¹⁷⁾	116.6
C ⁵⁽¹⁴⁾ –C ⁶⁽¹⁵⁾	1.409	C ⁷⁽¹⁶⁾ –C ⁸⁽¹⁷⁾ –C ⁹⁽¹⁸⁾	121.5
C ⁵⁽¹⁴⁾ –C ⁷⁽¹⁶⁾	1.396	C ⁸⁽¹⁷⁾ –C ⁹⁽¹⁸⁾ –C ¹⁰⁽¹⁹⁾	121.6
C ⁷⁽¹⁶⁾ –C ⁸⁽¹⁷⁾	1.391	C ⁹⁽¹⁸⁾ –C ¹⁰⁽¹⁹⁾ –C ⁶⁽¹⁵⁾	117.5
C ⁸⁽¹⁷⁾ –C ⁹⁽¹⁸⁾	1.410	C ¹⁰⁽¹⁹⁾ –C ⁶⁽¹⁵⁾ –C ⁵⁽¹⁴⁾	120.3
C ⁹⁽¹⁸⁾ –C ¹⁰⁽¹⁹⁾	1.390	C ⁶⁽¹⁵⁾ –C ⁵⁽¹⁴⁾ –C ⁷⁽¹⁶⁾	122.5
C ¹⁰⁽¹⁹⁾ –C ⁶⁽¹⁵⁾	1.399	N ² –I ³² –N ¹¹ –I ³³	-17.3
Bond angle (degree)		C ³⁽¹²⁾ –N ²⁽¹¹⁾ –Co–N ¹¹⁽²⁾	-153.2
I ³² –Co–I ³³	163.5	C ¹⁰⁽¹⁹⁾ –C ⁶⁽¹⁵⁾ –N ²⁽¹¹⁾ –Co	1.4
N ² –Co–N ¹¹	174.4	C ⁶ –N ² –N ¹¹ –C ¹⁵	48.4
Co–N ²⁽¹¹⁾ –C ⁶⁽¹⁵⁾	127.1	C ⁶ –N ² –N ¹¹ –C ¹²	-128.0

4. Results and Discussion

1. Geometry Optimization

It is well known that DFT methods work better for systems containing transition metal atoms. For these reasons, it was decided to use the B3LYP level for analysis of [Co(benzimidazole)₂I₂] complex. The visualization of the optimized geometrical structure and atomic labeling of diiodobis(benzimidazole)Co(II) complex are presented in Figure 1. The optimized geometry is shown in Table 1.

Since the crystal structure of the title compound is not available till now, the optimized structure can only be compared with other similar systems for which the crystal structures have been solved. For example, the optimized bond lengths of C–C in phenyl ring fall in the range from 1.390 to 1.410 Å for B3LYP/6-31G(d,p) method which are in good agreement with those in crystal structure of aniline (1.380 – 1.403 Å) [23] and dibromobis(benzimidazole)Zn(II) (1.323 – 1.393 Å) [24].

As can be seen from Figure 1, the Co atom is coordinated square-planar by two I⁻ anions and two benzimidazole ligands. The optimized bond length of Co–I is 2.670 Å is in good agreement with this in crystal structure of similar complex (Hg–I – 2.767 Å) [25] and Co–N distance of 1.922 Å is in good agreement with this in crystal structure of dibromobis(benzimidazole)Zn(II) (Zn–N – 2.008 Å) [24]. Also the bond distances and angles within the benzimidazole molecules are comparable to those obtained earlier for the free benzimidazole [26].

2. Vibrational Spectral Analysis

The vibrational spectra of [Co(benzimidazole)₂I₂] was calculated by DFT with B3LYP functional having extended basis sets 6-31G (d,p) and LANL2DZ for iodine. Frequencies recorded experimentally for [Co(benzimidazole)₂I₂] are compared with the calculated obtained by DFT (Figure 2).

It is well known that the harmonic frequencies by DFT calculations are usually higher than the corresponding experimental quantities due to the facts of the electron correlation approximate treatment, the anharmonicity effect and basis set deficiency, etc. [27]. In order to improve the calculated values in agreement with the experimental values, it is necessary to scale down the calculated harmonic frequencies. The experimental assignments of IR for vibrations, IR theoretical and relative intensities were reported in Table 2.

These assignments are important to understand the molecular structure of the title molecule. Any discrepancies noted between the observed and the calculated wavenumbers due to the fact that the calculations were actually performed on single (isolated) molecules in the gaseous state contrary to the experimental values recorded in the solid state. Thus some reasonable deviations from the experimental values seem to be justified [28].

C–H vibrations: The frequency of the C–H stretching vibrations of the present case are observed at 3312 and 3116 cm⁻¹ and they are in good agreement with Augus *et al.* [29] and Bailey *et al.* [30] The theoretically computed values for C–H stretching vibrations assigned to aromatic C–H stretch (3302–3215 cm⁻¹) are in excellent agreement with experimental assignments. The frequencies 1238, 1188, 1139 and 974 cm⁻¹ are assigned to C–H in-plane bending vibrations. The theoretically calculated C–H in-plane bending vibrations are assigned in the region 1282–996 cm⁻¹ coincides exactly with literature data [31, 32]. Hence the bands at 765, 681 and 584 cm⁻¹ are assigned to give C–H

out-of-plane bending vibration. The calculated C–H out-of-plane bending vibrations are assigned in the region 756–587 cm^{-1} also coincides exactly with literature data.

N–H vibrations: Tsuboi [33] reported the N–H stretching frequency at 3481 cm^{-1} in aniline. In the present work (N–H) stretching is assigned to the band at 3543 cm^{-1} . The theoretically calculated value by B3LYP/6-31G(d,p) and LANL2DZ for iodine at 3682 cm^{-1} shows good agreement with experimentally. The N–H in-plane bending and N–H out-of-plane bending are assigned to the bands at 1492 and 491 cm^{-1} which agrees well with Venkateswaran and Pandya [34] and Evans [35]. The calculated values for N–H in-plane bending and N–H out-of-plane bending are 1501 and 495 cm^{-1} .

C=N, C–N vibrations: The identification of the C–N stretching frequency is a difficult task since there are problems in identifying these frequencies from other

vibrations. Pinchas et al. [36] assigned the C–N stretching band at 1368 cm^{-1} in benzamide. Kahovec and Kohlreusch [37] identified the stretching frequency of the C=N band in salicylic aldoxime at 1617 cm^{-1} . Referring to the above workers, the bands at 1299 cm^{-1} and 1503 cm^{-1} are assigned to C–N and C=N stretching, respectively. The theoretically computed values are 1302 and 1564 cm^{-1} .

Carbon vibrations: The vibrational frequencies at 1621 and 1597 cm^{-1} are assigned to C=C stretching. The theoretically computed values are 1679 and 1647 cm^{-1} , respectively. The vibrational frequencies at 1461, 1404, 433 and 428 cm^{-1} are assigned to C–C stretching. The theoretically computed values are 1447, 1404, 441 and 430 cm^{-1} .

Co–N and Co–I vibrations: The vibrational frequencies at 340 and 238 cm^{-1} are theoretically assigned to Co–N and Co–I stretching.

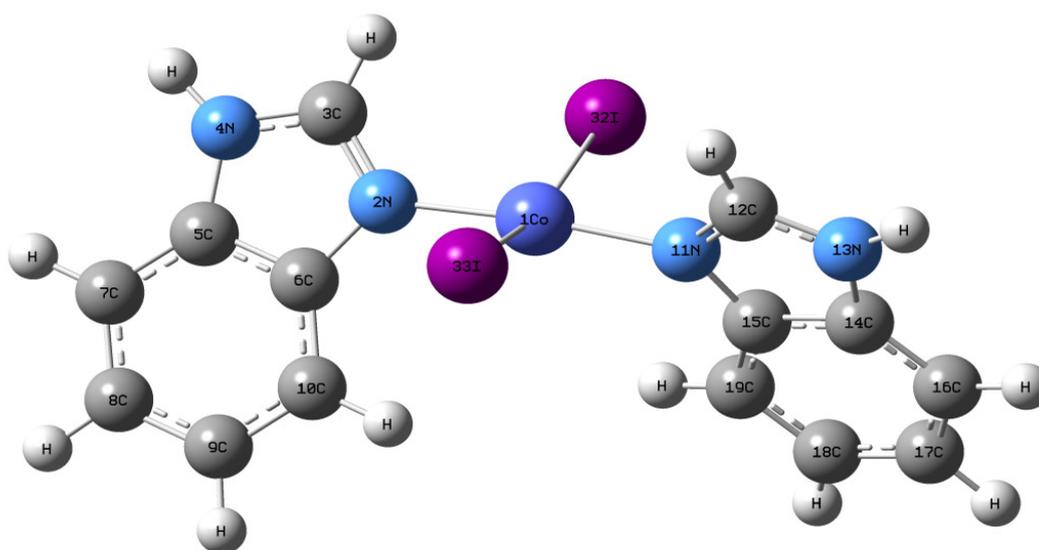


Figure 1. Optimized geometrical structure and atomic labeling of $[\text{Co}(\text{benzimidazole})_2]\text{I}_2$

Table 2. Some experimental and calculated characteristic frequencies (cm^{-1}), IR intensity and probable assignments of $[\text{Co}(\text{benzimidazole})_2]\text{I}_2$

Calculated frequencies	I_{Abs}	Experimental frequencies	Assignments	Calculated frequencies	I_{Abs}	Experimental frequencies	Assignments
3682	172	3543 <i>w</i>	$\nu_{(\text{N-H})}$ <i>ipb</i>	1156	25	1188 <i>m</i>	$\nu_{(\text{C-H})}$ <i>ipb</i>
3302	11	3312 <i>s</i>	$\nu_{(\text{C-H})}$ <i>ipb</i>	1136	19	1139 <i>s</i>	$\nu_{(\text{C-H})}$ <i>ipb</i>
3215	30	3116 <i>w</i>	$\nu_{(\text{C-H})}$ <i>ipb</i>	996	2	974 <i>m</i>	$\nu_{(\text{C-H})}$ <i>ipb</i> , <i>Rband</i>
1679	6	1621 <i>m</i>	$\nu_{(\text{C=C})}$, <i>Rband</i>	756	72	765 <i>s</i>	$\nu_{(\text{C-H})}$ <i>opb</i>
1647	10	1597 <i>m</i>	$\nu_{(\text{C=C})}$, <i>Rband</i>	642	3	681 <i>m</i>	$\nu_{(\text{C-H})}$ <i>opb</i> , <i>Rband</i>
1564	110	1503 <i>s</i>	$\nu_{(\text{C=N})}$, <i>Rband</i>	587	7	584 <i>s</i>	$\nu_{(\text{C-H})}$ <i>opb</i> , <i>Rband</i>
1501	20	1492 <i>m</i>	$\nu_{(\text{N-H})}$ <i>ipb</i>	495	135	491 <i>w</i>	$\nu_{(\text{N-H})}$ <i>opb</i>
1447	82	1461 <i>s</i>	<i>Rband</i>	441	18	433 <i>s</i>	<i>Rband ipb</i>
1404	11	1404 <i>s</i>	<i>Rband</i>	430	12	428 <i>s</i>	<i>Rband opb</i>
1302	13	1299 <i>s</i>	$\nu_{(\text{C-N})}$	340	6	–	$\nu_{(\text{Co-N})}$
1282	48	1265 <i>s</i>	$\nu_{(\text{C-H})}$ <i>ipb</i>	238	16	–	$\nu_{(\text{Co-I})}$

Scale factors of 0.9613 for calculated frequencies with B3LYP/6-31G(d,p)

s - strong; *m* - medium; *w* - weak; *vw* - very weak

ν - stretching; *Rband* - ring deformation; *ipb* - in-plane bending; *opb* - out-of-plane bending

I_{Abs} - Theoretical infrared intensities

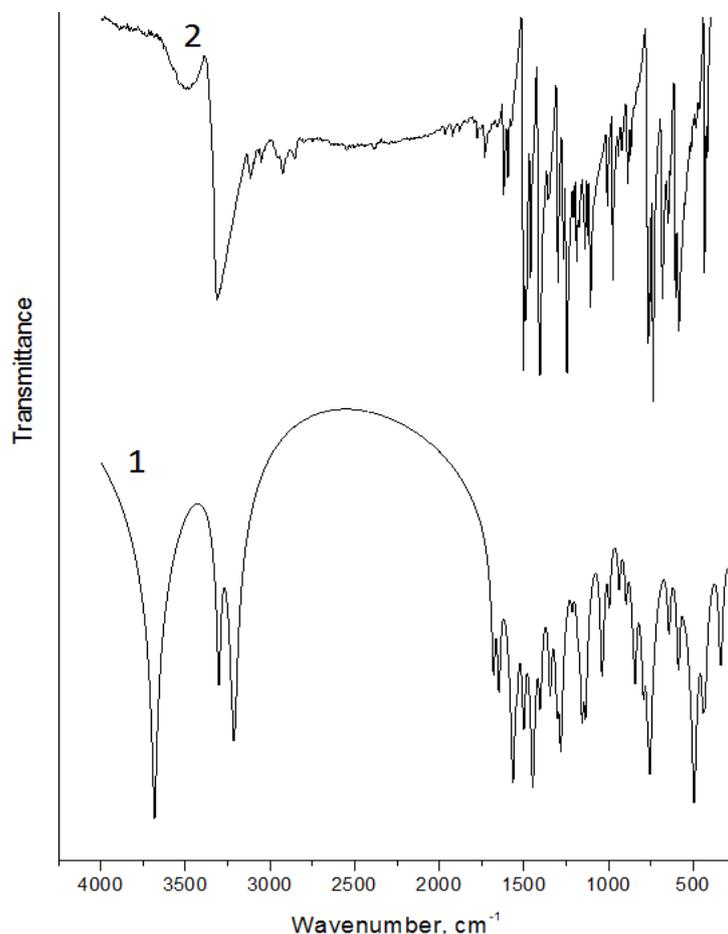


Figure 2. IR spectrum of $[\text{Co}(\text{benzimidazole})_2\text{I}_2]$, 1 – calculated, 2 – experimental

3. Natural Bond Orbital Analysis

The Natural Bond Orbital (NBO) analysis of $[\text{Co}(\text{benzimidazole})_2\text{I}_2]$, has provided the detailed insight into the nature of electronic conjugation between the bonds in this molecule. Table 3 collects the natural charges on atoms in the investigated compound. The largest negative charges (-0.583) are located on two nitrogen atoms, N^2 and N^{11} . The largest positive charge (0.681) is located on Co atom.

NBO analysis is an efficient method for study of the intra-molecular and inter-molecular bonding and interactions among bonds, and also provides a convenient basis for investigation charge transfer or conjugative interactions in molecular systems. This analysis also provides the study of filled NBOs (donors) and empty NBOs (acceptors) and their interactions with the stabilization energy $E^{(2)}$ resulting from the second-order perturbation theory. The larger $E^{(2)}$ value, the more intensive is the interaction between electron donors and acceptors, i.e. the more electron donating tendency from electron donors to acceptors and the greater the extent of conjugation of the whole system. This interaction results a loss of occupancy from the concentration of electron NBO of the idealized Lewis (bond or lone pair) structure into an empty (anti-bond or Rydberg) non-Lewis orbital.

Table 3. The NBO atomic charges of $[\text{Co}(\text{benzimidazole})_2\text{I}_2]$, calculated by the B3LYP method with 6-31G(d,p) basis set and LANL2DZ for iodine

Atom	Natural charges	Atom	Natural charges
Co ¹	0.681	C ⁵⁽¹⁴⁾	0.133
I ³²⁽³³⁾	-0.486	C ⁷⁽¹⁶⁾	-0.262
N ²⁽¹¹⁾	-0.583	C ⁸⁽¹⁷⁾	-0.230
N ⁴⁽¹³⁾	-0.559	C ⁹⁽¹⁸⁾	-0.240
C ³⁽¹²⁾	0.269	C ¹⁰⁽¹⁹⁾	-0.221
C ⁶⁽¹⁵⁾	0.131		

Table 4 lists the selected values of the calculated second order interaction energy ($E^{(2)}$) between donor-acceptor orbitals in $[\text{Co}(\text{benzimidazole})_2\text{I}_2]$. The strongest interactions are the electron donations from a lone pair orbital on the nitrogen atoms, $\text{LP}(1)\text{N}^{2(11)}$ to the antibonding acceptors $\text{LP}(6)^*\text{Co}$ and $\text{LP}(8)^*\text{Co}$ orbitals which result in stabilization of the system. These interactions increases $\text{ED}(0.164, 0.067\text{e})$ ($\text{LP}(6)^*\text{Co}$ and $\text{LP}(8)^*\text{Co}$) that weakens $\text{LP}(1)\text{N}^{2(11)}$ $\text{ED}(0.880)$ leading to stabilization of 31.10 kcal/mol and 9.62 kcal/mol. There occurs a strong intramolecular hyper-conjugative interaction of $\text{N}^{2(11)}-\text{C}^{3(12)}$ from $\text{N}^{4(13)}-\text{C}^{5(14)}$ of $\pi\text{N}^{4(13)}-\text{C}^{5(14)} \rightarrow \pi^*\text{N}^{2(11)}-\text{C}^{3(12)}$ which increases $\text{ED}(0.200\text{e})$ that weakens $\pi\text{N}^{4(13)}-\text{C}^{5(14)}$ $\text{ED}(0.914\text{e})$

leading to stabilization of 16.53 kcal/mol. Also there occurs a strong inter molecular hyper conjugative interaction of $N^{2(11)} - C^{3(12)}$ and $C^{7(16)} - C^{8(17)}$ from $N^{4(13)} - C^{5(14)}$ of $\pi^* N^{4(13)} - C^{5(14)} \rightarrow \pi^* N^{2(11)} - C^{3(12)}$ and $\pi^* N^{4(13)} - C^{5(14)} \rightarrow \pi^* C^{7(16)} - C^{8(17)}$ which increases ED(0.200e) and ED(0.159e) that weakens the respective bonds $N^{4(13)} - C^{5(14)}$ ED(0.405e) leading to stabilization of 52.43 and 39.54 kcal/mol respectively. The hyper conjugative interaction of $LP(4)I^{32(33)} \rightarrow LP(5,6,7)Co$ leading to stabilization of 31.57, 16.42 and 25.20 kcal/mol.

The frontier orbitals (highest occupied molecular orbital – HOMO and lowest unoccupied molecular orbital – LUMO) are very important in defining reactivity. The HOMO exhibits the ability to donate an electron and LUMO as an electron acceptor serves the ability to obtain an electron. The frontier orbitals (HOMO, LUMO) of $[Co(benzimidazole)_2]_2$ calculated by B3LYP/ 6-31G(d,p) and LANL2DZ for iodine are plotted in Figure 3.

Energy of frontier orbitals and energy of the gap are:

$$E_{HOMO} = -520.1378 \text{ kJ/mol}$$

$$E_{LUMO} = -155.7972 \text{ kJ/mol}$$

$$\Delta E_{LUMO-HOMO} = 364.3406 \text{ kJ/mol}$$

High values of E_{HOMO} have a tendency of the molecule to donate electrons to appropriate acceptor molecules with low energy, empty molecular orbitals. The energy of the lowest unoccupied molecular orbital indicates the ability of the molecule to accept electrons. The lower value of E_{LUMO} , the

more probable it is that the molecule would accept electrons. Consequently, concerning the value of the energy of the gap $\Delta E_{LUMO-HOMO}$, larger values of the energy difference will provide low reactivity to a chemical species. Lower values of the energy difference will render good inhibition efficiency, because the energy to remove an electron from the last occupied orbital will be low. The results for the calculations of the ionization potential (I) and the electron affinity (A) by application of the Koopman's theorem [38] are shown. According to the Hartree–Fock theorem, the frontier orbital energies are given by: $I = -E_{HOMO} = 520.1378 \text{ kJ/mol}$; $A = -E_{LUMO} = 155.7972 \text{ kJ/mol}$. This theorem establishes a relation between the energies of the HOMO and the LUMO and the ionization potential and the electron affinity, respectively. Although no formal proof of this theorem exists within DFT, its validity is generally accepted. Electronegativity (χ), chemical potential (μ) and global hardness (η), their operational and approximate definitions for $[Co(benzimidazole)_2]_2$ are: $\chi = -\mu = (I + A)/2 = 337.9675 \text{ kJ/mol}$; $\eta = (I - A)/2 = 182.1703 \text{ kJ/mol}$.

4. Thermodynamic Properties

The values of some thermodynamic parameters (such as zeropoint vibrational energy, thermal energy, molar capacity at constant volume, rotational constants, entropy and dipole moment) of title molecule by DFT/B3LYP/6-31G(d,p) method and LANL2DZ for iodine at 298.15 K in ground state are listed in Table 5.

Table 4. Second-order interaction energy ($E^{(2)}$, kcal/mol) between donor and acceptor orbitals in $[Co(benzimidazole)_2]_2$

Donor NBO (i)	ED (i)/e	Acceptor NBO (j)	ED (j)/e	$E^{(2)}$ kcal/mol	$E(j) - E(i)$ a.u.	$F(i,j)$ a.u.
n1 N ¹¹	0.880	n6* Co ¹	0.164	31.10	0.49	0.160
n1 N ¹¹	0.880	n8* Co ¹	0.067	9.62	0.61	0.100
$\pi N^{13} - C^{14}$	0.914	$\pi^* N^{11} - C^{12}$	0.200	16.53	0.33	0.098
$\pi^* N^4 - C^5$	0.405	$\pi^* N^2 - C^3$	0.200	52.43	0.02	0.053
$\pi^* N^4 - C^5$	0.405	$\pi^* C^7 - C^8$	0.159	39.54	0.08	0.094
$\pi^* N^{13} - C^{14}$	0.405	$\pi^* N^{11} - C^{12}$	0.200	52.43	0.02	0.053
$\pi^* N^{13} - C^{14}$	0.405	$\pi^* C^{16} - C^{17}$	0.159	39.54	0.08	0.094
n2 I ³²	0.974	n7* Co ¹	0.123	11.37	0.67	0.116
n4 I ³²	0.801	n5* Co ¹	0.343	31.57	0.13	0.086
n4 I ³²	0.801	n6* Co ¹	0.164	16.42	0.30	0.090
n4 I ³²	0.801	n7* Co ¹	0.123	25.20	0.53	0.152
n2 I ³³	0.974	n7* Co ¹	0.123	11.37	0.67	0.116
n4 I ³³	0.801	n5* Co ¹	0.343	31.57	0.13	0.086
n4 I ³³	0.801	n6* Co ¹	0.164	16.42	0.30	0.090
n4 I ³³	0.801	n7* Co ¹	0.123	25.20	0.53	0.152
n1 N ²	0.880	n6* Co ¹	0.164	31.10	0.49	0.160
n1 N ²	0.880	n8* Co ¹	0.067	9.62	0.61	0.100
$\pi N^4 - C^5$	0.914	$\pi^* N^2 - C^3$	0.200	16.53	0.33	0.098

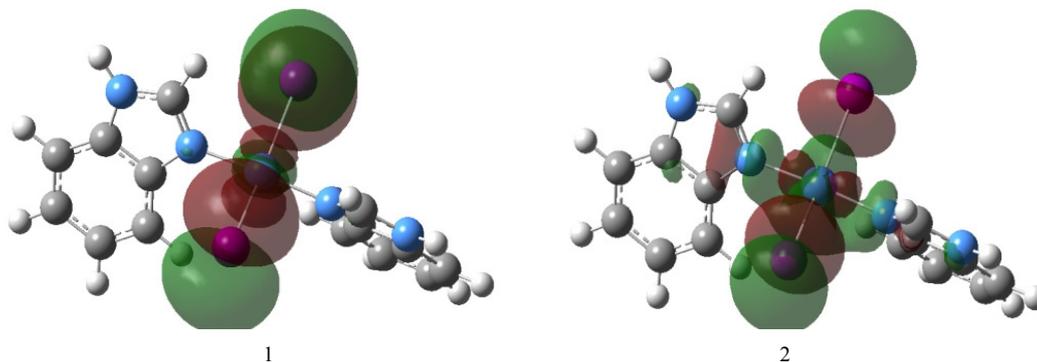


Figure 3. Electron distribution of HOMO – 1 and LUMO – 2 for $[\text{Co}(\text{benzimidazole})_2\text{I}_2]$

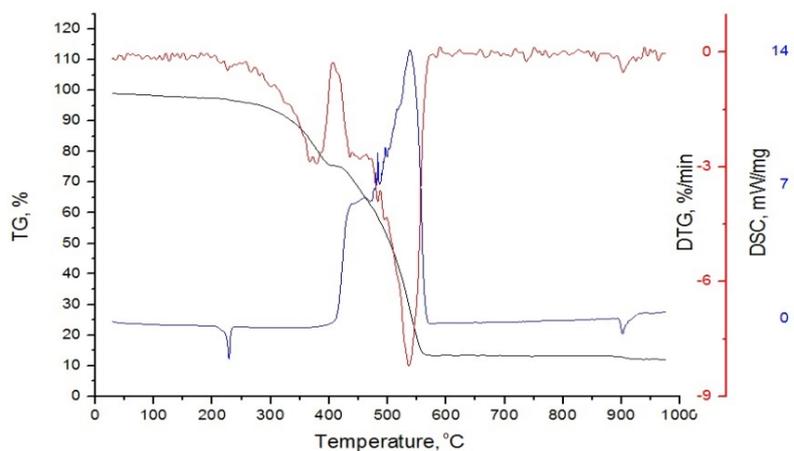


Figure 4. Thermo-gravimetric analysis of the $[\text{Co}(\text{benzimidazole})_2\text{I}_2]$

Table 5. The calculated thermodynamical parameters of $[\text{Co}(\text{benzimidazole})_2\text{I}_2]$ at 298.15 K in ground state

Parameters	Calculated
Zero point vibration energy (kcal mol⁻¹)	146.54812
Rotational constants (GHz)	
A	0.19547
B	0.12567
C	0.10028
Rotational temperature (K)	
A	0.00938
B	0.00603
C	0.00481
Thermal energy (kcal mol⁻¹)	
Total	159.287
Translational	0.889
Rotational	0.889
Vibrational	157.509
Molar capacity at constant volume (cal mol⁻¹ K⁻¹)	
Total	74.305
Translational	2.981
Rotational	2.981
Vibrational	68.343
Entropy (cal mol⁻¹ K⁻¹)	
Total	161.760
Translational	44.793
Rotational	36.121
Vibrational	79.467

The global minimum energy obtained for structure optimization is -2165.2787052 a.u. The standard thermodynamic functions enthalpy (ΔH_m°), entropy (S_m°) and heat capacity ($C_{p,m}^\circ$) for the title compound were obtained using DFT/B3LYP method with 6-31G(d,p) and LANL2DZ for iodine on the basis of vibrational analysis and statistical thermodynamics [39]. The vibrational frequencies are scaled by 0.9613 [40].

The stoichiometric composition of the phase synthesized was confirmed by the thermo-gravimetric analysis carried out. Figure 4 shows TG/DTG/DSC curves of decomposition of the titled compound synthesized.

It was determined from the TG curve that $[\text{Co}(\text{benzimidazole})_2\text{I}_2]$ is stable up to about 473 K (200°C), after that temperature begin decomposition of the molecule. That's why the enthalpies, entropies and heat capacities observed at different temperatures going from 100K to 450 K and listed in Table 6.

It can be observed that these thermodynamic functions are increasing with corresponding temperature ranging from 100 to 450 K due to the fact that the molecular vibrational intensities increase with temperature [41]. The correlation equations between entropy, heat capacity, enthalpy changes and temperatures were fitted by quadratic formulas and the corresponding fitting factors (R^2) for these thermodynamic properties are 0.9998, 0.9996 and 1 respectively. The corresponding fitting equations are as follows and the

correlation graphics are shown in Figures 5–7.

$$S_m^\circ = 308.78 + 1.3463.T - 0.0005.T^2 \quad (R^2 = 0.9998)$$

$$C_{p,m}^\circ = 52.635 + 0.9078.T - 0.0002.T^2 \quad (R^2 = 0.9996)$$

$$\Delta H_m^\circ = -0.5553 + 0.0606.T - 0.0004.T^2 \quad (R^2 = 1)$$

All thermodynamic datas supply helpful information for the further study on the $[\text{Co}(\text{benzimidazole})_2\text{I}_2]$. They can be used to compute the other thermodynamic energies according to relationships of thermodynamic functions and estimate directions of chemical reactions according to the second law of thermodynamics in thermochemical field. All thermodynamic calculations were done in gas phase and they could not be used in solution.

Table 6. Thermodynamic properties at different temperatures at the B3LYP/6-3G(d,p) level and LANL2DZ for iodine, for $[\text{Co}(\text{benzimidazole})_2\text{I}_2]$

T [K]	S_m° [J mol ⁻¹ K ⁻¹]	$C_{p,m}^\circ$ [J mol ⁻¹ K ⁻¹]	ΔH_m° [kJ mol ⁻¹]
100	436.14	144.08	9.67
150	501.97	183.45	17.85
200	560.35	224.80	28.05
250	615.11	267.78	40.36
298.15	665.83	309.10	54.25
300	666.74	310.67	54.82
350	718.75	351.79	71.40
400	768.26	390.00	89.95
450	816.23	424.74	110.34

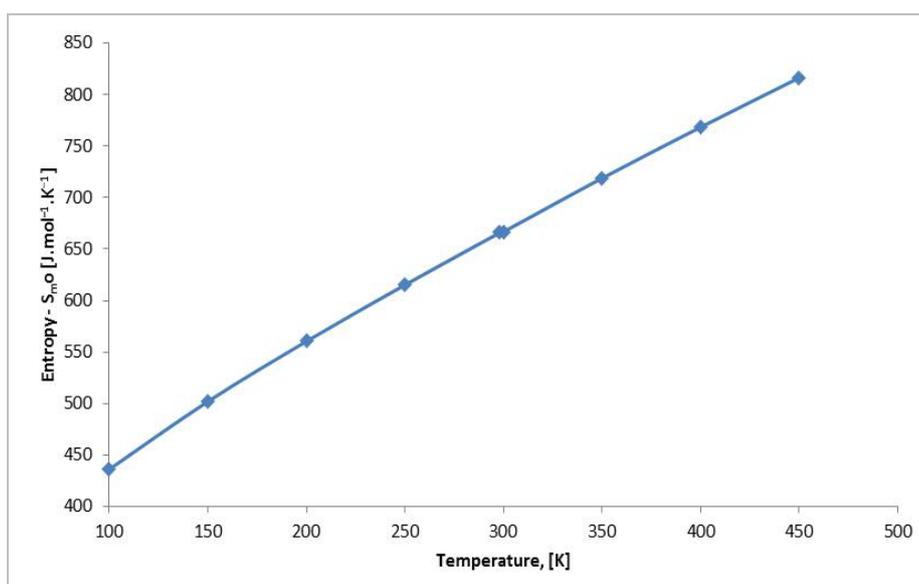


Figure 5. Correlation graphic of entropy and temperature for $[\text{Co}(\text{benzimidazole})_2\text{I}_2]$

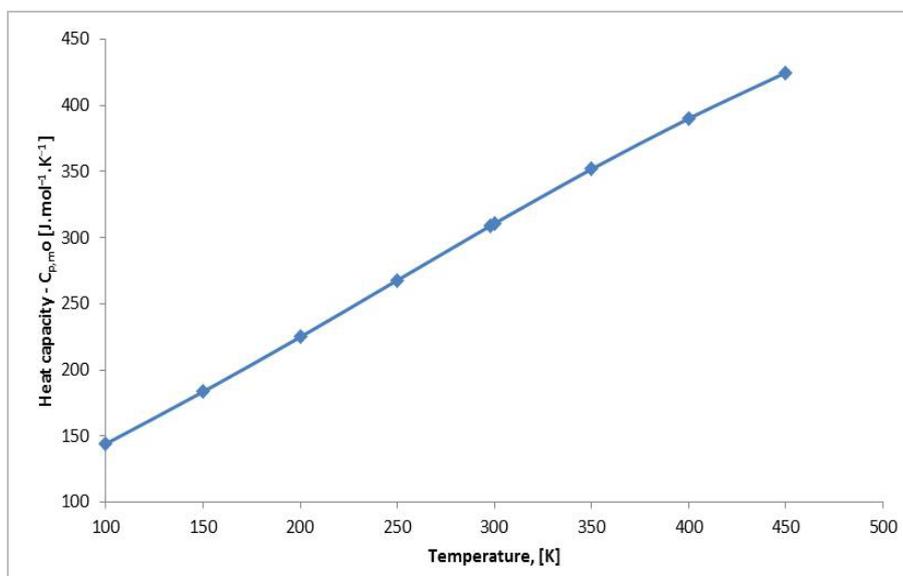


Figure 6. Correlation graphic of heat capacity and temperature for $[\text{Co}(\text{benzimidazole})_2\text{I}_2]$

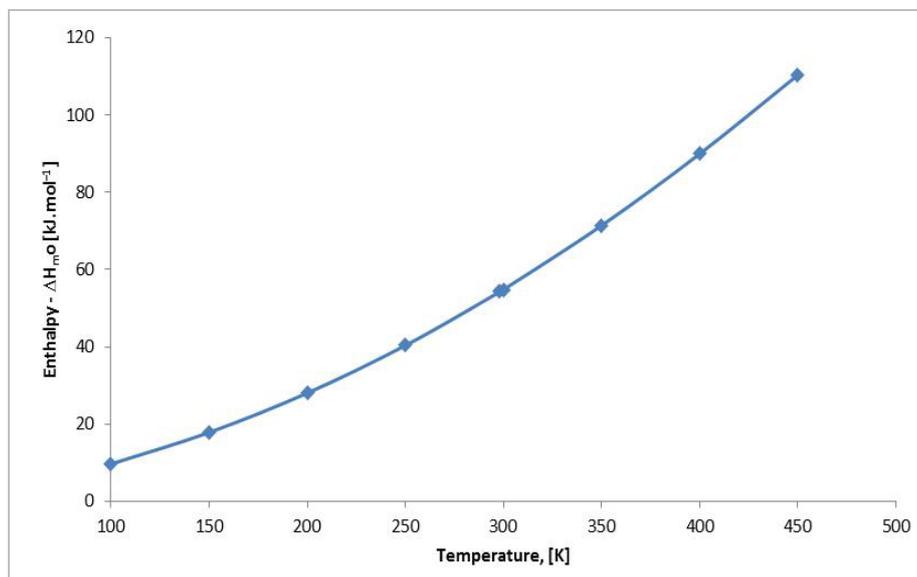


Figure 7. Correlation graphic of enthalpy and temperature for $[\text{Co}(\text{benzimidazole})_2\text{I}_2]$

5. Conclusions

The equilibrium geometries and harmonic frequencies of diiodobis(benzimidazole)Co(II) complex were determined and analysed at DFT level of theory utilizing 6-31G(d,p) basis set and LANL2DZ for iodine. The difference between the observed and scaled wavenumber values of most of the fundamentals is good. Any discrepancy noted between the observed and the calculated frequencies may be due to the fact that the calculations were done on a single molecule in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions. Therefore, the assignments made at higher levels of theory with only reasonable deviations from the experimental values, seem to be correct. The Natural orbital charges calculated by B3LYP/6-31G(d,p) and LANL2DZ for iodine were presented. The transactions give stabilization to the structure were identified by second order perturbation energy calculations. Using NBO analysis the stability of the molecule arising from hyper-conjugative interaction and charge delocalization was analyzed. The strongest electron donation occurs from a lone pair orbital on the nitrogen atoms, $\text{LP}(1)\text{N}^{2(11)}$ to the antibonding acceptor $\text{LP}^*(6;8)\text{Co}$ orbitals and from a lone pair orbital on the iodine atoms, $\text{LP}(2;4)\text{I}^{32(33)}$ to the antibonding acceptor $\text{LP}^*(5;6;7)\text{Co}$ orbitals. The correlations between the statistical thermodynamics and temperature are also obtained. It is seen that the heat capacities, entropies and enthalpies increase with the increasing temperature owing to the intensities of the molecular vibrations increase with increasing temperature. The present quantum chemical study may lead to the understanding of properties and activity of $[\text{Co}(\text{benzimidazole})_2\text{I}_2]$.

REFERENCES

- [1] A.A. Spasov, I.N. Yozhitsa, L.I. Bugaeva, V.A. Anisimova, Benzimidazole derivatives: Spectrum of pharmacological activity and toxicological properties, *Pharmaceutical chemistry Journal*, 33 (1999) 232–243.
- [2] R.A. Bucknall, S.B. Carter, A reversible inhibitor of nucleic acid synthesis, *Nature*, 213 (1967) 1099–1101.
- [3] S.O. Podunavac-Kuzmanovic, V.M. Leovac, N.U. Perisic-Janjic, J. Rogan, J. Balaz, Complexes cobalt (II), zinc (II) and copper (II) with some newly synthesized benzimidazole derivatives and their antibacterial activity, *Journal of the Serbian Chemical Society*, 64 (1999) 381–388.
- [4] I.S. Ahuja, I. Prasad, Isonicotinamide complexes with some metal (II) halides and pseudohalides, *Inorganic and Nuclear Chemistry Letters*, 12 (1976) 777–784.
- [5] Ş. Yurdakul, M. Kurt, Vibrational spectroscopic studies of metal (II) halide benzimidazole, *Journal of molecular structure*, 650 (2003) 181–190.
- [6] Lee, Sang Yeon, Bong Hyun Boo, Molecular structure and vibrational spectra of 9-fluorenone density functional theory study. *Bull. Korean Chem. Soc*, 17(1996) 760–764.
- [7] Lee, Sang Yeon, Bong Hyun Boo, Density functional theory study of vibrational spectra of anthracene neutral and radical cation, *Bull. Korean Chem. Soc*, 17.8 (1996) 755.
- [8] F.J. Devlin, J.W. Finley, P.J. Stephens, M.J. Frisch, Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields: a comparison of local, nonlocal, and hybrid density functionals, *The Journal of Physical Chemistry*, 99 (1995) 16883–16902.
- [9] N.C. Handy, C.W. Murray, R.D. Amos, Study of methane, acetylene, ethene, and benzene using Kohn-Sham theory, *The Journal of Physical Chemistry*, 97 (1993) 4392–4396.
- [10] N.C. Handy, P.E. Maslen, R.D. Amos, J.S. Andrews, C.W. Murray, G.J. Laming, The harmonic frequencies of benzene, *Chemical physics letters*, 197 (1992) 506–515.

- [11] N. Sundaraganesan, S. Ilakiamani, H. Saleem, P.M. Wojciechowski, D. Michalska, FT-Raman and FT-IR spectra, vibration-al assignments and density functional studies of 5-bromo-2-nitropyridine, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 61 (2005) 2995–3001.
- [12] M. Goodgame, F.A. Cotton, Preparation and Magnetic and Spectral Studies of Some Cobalt (II) Complexes of Benzimidazole, *Journal of the American Chemical Society*, 84 (1962) 1543–1548.
- [13] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision B.04, Gaussian, Inc., Wallingford CT, 2004.
- [14] C.T. Lee, W.T. Yang, R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev.*, B 37 (1988) 785–789.
- [15] A.D. Becke, Densityfunctional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.*, 98 (1993) 5648–5652.
- [16] R.G. Parr, W. Yang, Density-functional theory of atoms and molecules (Vol. 16), Oxford university press, 1989.
- [17] P.J. Hay, W.R. Wadt, Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg, *J. Chem. Phys.*, 82 (1985) 270–283.
- [18] W.R. Wadt, P.J. Hay, Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi, *J. Chem. Phys.*, 82 (1985) 284–298.
- [19] P.J. Hay, W.R. Wadt, Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals, *J. Chem. Phys.*, 82 (1985) 299–310.
- [20] A.E. Reed, L.A. Curtiss, F. Weinhold, Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint, *Chemical Reviews*, 88 (1988) 899–926.
- [21] E.D. Gledening, A.E. Reed, J.A. Carpenter, F. Weinhold, NBO. version 3.1.
- [22] F. Weinhold, C.R. Landis, Natural bond orbitals and extensions of localized bonding concepts, *Chem. Educ. Res. Pract.*, 2 (2001) 91–104.
- [23] M.A. Palafox, J.L. Nunez, M. Gil, Accurate scaling of the vibrational spectra of aniline and several derivatives, *Journal of Molecular Structure: THEOCHEM*, 593.1 (2002) 101–131.
- [24] E. Şahin, S. Ide, M. Kurt, Ş. Yurdakul, Structural investigation of dibromobis (benzimidazole) Zn (II) complex, *Journal of molecular structure*, 616 (2002) 259–264.
- [25] Z.Y. Wu, D.J. Xu, C.H. Hung, Synthesis and crystal structure of diiodobis (thiourea) mercury (ii)-bis (diazfluoren-9-one), *Journal of Coordination Chemistry*, 57 (2004) 791–796.
- [26] C.J. Dik-Edixhoven, H. Schenk, H. Van der Meer, *Cryst. Struct. Commun.* 2 (1973) 23.
- [27] M. Karabacak, M. Çınar, M. Kurt, An experimental and theoretical study of molecular structure and vibrational spectra of 2-chloronicotinic acid by density functional theory and ab initio Hartree–Fock calculations, *Journal of Molecular Structure*, 885 (2008) 28–35.
- [28] Halls, Mathew D., Julia Velkovski, and H. Bernhard Schlegel, Harmonic frequency scaling factors for Hartree-Fock, S-VWN, B-LYP, B3-LYP, B3-PW91 and MP2 with the Sadlej pVTZ electric property basis set, *Theoretical Chemistry Accounts*, 105.6 (2001) 413–421.
- [29] W.R. Augus, C.K. Ingold, A.H. Leekie, *J. Chem. Soc.*, (1936) 925.
- [30] C.R. Bailey, S.C. Carson, R.R. Gordon, C.K. Ingold, Structure of benzene. Part XIX. The infrared spectra of 1:4-dideuterobenzene and 1:2:4:5-tetradeuterobenzene: description and analysis, *Journal of the Chemical Society*, 63 (1946) 288–299.
- [31] E.F. Mooney, The infrared spectra of chlorobenzene and bromobenzene derivatives—III. Toluenes, *Spectrochimica Acta* 20.9 (1964)1343–1348.
- [32] G. Joshi, N.L. Singh, Infrared absorption spectrum of orthofluorotoluene, *Spectrochimica Acta Part A: Molecular Spectroscopy*, 23.5 (1967) 1341–1344.
- [33] M. Tsuboi, 15 N isotope effects on the vibrational frequencies of aniline and assignments of the frequencies of its nh 2 group, *Spectrochimica Acta*, 16.4 (1960) 505–512.
- [34] C.S. Venkateswaran, N.S. Pandya, The Raman spectra of organic compounds: aniline. *Proceedings of the Indian Academy of Sciences-Section A.*, Springer India, 15(5) (1942) 390–395.
- [35] J.C. Evans, The vibrational assignments and configuration of aniline, aniline-NHD and aniline-ND 2, *Spectrochimica Acta*, 16.4 (1960) 428–442.
- [36] S. Pinchas, David Samuel, Marta Weiss-Brodav, The infrared absorption of 18 O-labelled benzamide, *Journal of the Chemical Society*, (1961) 1688–1692.
- [37] L. Kahovec, K.F. Kohlrausch, *Studien zum Raman-Effekt. Monatshefte für Chemie/Chemical Monthly*, 74.1 (1941) 104–117.
- [38] V.S. Sastri, J.R. Perumareddi, Molecular orbital theoretical studies of some organic corrosion inhibitors, *Corros. Sci.*, 53 (1997) 617–622.
- [39] K.K. Irikura, THERMO.PL, National Institute of Standards and Technology, Gaithersburg, MD, 2002.
- [40] J.P. Merrick, D. Moran, L. Radom, An evaluation of harmonic vibrational frequency scale factors, *J. Phys. Chem. A*, 111 (2007) 11683–11700.
- [41] J. Ott, J. Bevan, J. Boerio-Goates, *Calculations from Statistical Thermodynamics*, Academic Press., 2000.