

**NATURAL BOND POPULATION ANALYSIS OF
DIBROMOBIS(BENZIMIDAZOLE)Cu (II) COMPLEX**

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ABSTRACT

The heterocycles are good ligands due to the presence of possible coordination sites. The complexes of transition metal salts with benzimidazole derivatives are important biological molecules. The structure of dibromobis(benzimidazole)Cu (II) complex was calculated by Density Functional Theory (DFT) method, with Becke's three parameter exchange-functional of Lee, Yang and Paar and 6-31G(d,p) basis set. The electronic properties and the bond orders of the molecule were calculated. The natural bond orbitals calculations were performed in order to understand second-order interactions between the filled and vacant orbitals, which is a measure of the intramolecular delocalization or hyper conjugation. The strongest electron donation become from the lone pair orbitals on the nitrogen atoms, LP(1) N to the antibonding acceptor orbitals LP*(6;8;9) Cu and from the lone pair orbitals on the bromine atoms, LP(1;4) Br to the antibonding acceptor orbitals LP*(6;7) Cu.

Key words: dibromobis(benzimidazole)Cu (II) complex, Density functional theory, NBO analysis

INTRODUCTION

The pharmacological properties and biological activity of the benzimidazole derivatives [1-4], have led researchers to investigate the coordination behavior of benzimidazole derivatives with transition metal ions.

To predict properties of metal complexes with benzimidazole and choose their application, theoretical study seems to be necessary. The use of density functional theory makes an important contribution to promotion of theoretical calculations. A great number of metal complexes with benzimidazole are investigated with DFT method and are determined their geometry, electronic structure and chemical reactivity [5-9].

The molecular structural parameters of dibromobis(benzimidazole)Cu (II) complex and its chemical reactivity are calculated with DFT-B3LYP method using 6-31G(d,p) basis set [10]. Quantum chemical descriptors such as global hardness and softness, chemical potential, electronegativity and electrophilicity index, HOMO–LUMO energy gap and HOMO/LUMO energy are studied. Molecular electrostatic potential analysis is shown that the most negative charge is localized around bromine atoms, while a large electropositive potential is observed in the area of the benzimidazole ligands. The vibrational frequencies of the fundamental modes of the compound are precisely assigned, analyzed and the theoretical results are compared with the experimental ones.

The objective of the present work is to investigate the nature of bonding in the dibromobis(benzimidazole)Cu (II) complex, by using natural bond orbital (NBO) analysis. The results from NBO calculations can provide the detailed insight into the electronic structure of molecule.

EXPERIMENTAL

The dibromobis(benzimidazole)Cu (II) complex was synthesized according to the method outlined by M. Bukowska-Strzyzewska and A. Tosik [11]. Identification of [Cu(benzimidazole)₂Br₂] was carried out by means of FT-IR spectroscopy. The infrared spectra were recorded on a Nicolet iS 50 Thermo Scientific FT-IR spectrophotometer in the frequency region of 4000 – 400 cm⁻¹ using nujol. 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).

COMPUTATIONAL METHODS

The full optimization of dibromobis(benzimidazole)Cu (II) complex was carried out by Density Functional Theories (DFT) method using Gaussian 03 software [12]. It was used Becke's three parameter hybrid exchange functional with Lee–Yang–Parr correlation functional (B3LYP) [13-15] with added polarization functions – 6-31G(d,p). All calculations were converged to 10^{-8} a.u. Vibrational analysis was performed at each stationary point found, that confirm its identity as an energy minimum. The population analysis was performed by the natural bond orbital method [16] at B3LYP/6-31G(d,p) level of theory using NBO program [17] under Gaussian 2003 program package. The software package GaussView, Version 6 [18] was used for the data preparation and visualization of the results.

Natural bond orbital analysis stresses the role of intermolecular orbital interaction in the complex, particularly charge transfer. It is easy to connect traditional bonding concepts (local bonding, orbital hybridization) with the results of the NBO analysis. 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 [19],

$$\Delta E_{ij}^{(2)} = q_i \frac{\langle \phi_i | F_{ij} | \phi_j \rangle^2}{\varepsilon_j - \varepsilon_i}$$

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.

RESULTS AND DISCUSSION

The equilibrium geometry was determined by the energy minimization. The ground state optimized geometrical structure with bond lengths (Å) and atomic labelling of dibromobis(benzimidazole)Cu (II) complex are shown in Figure 1.

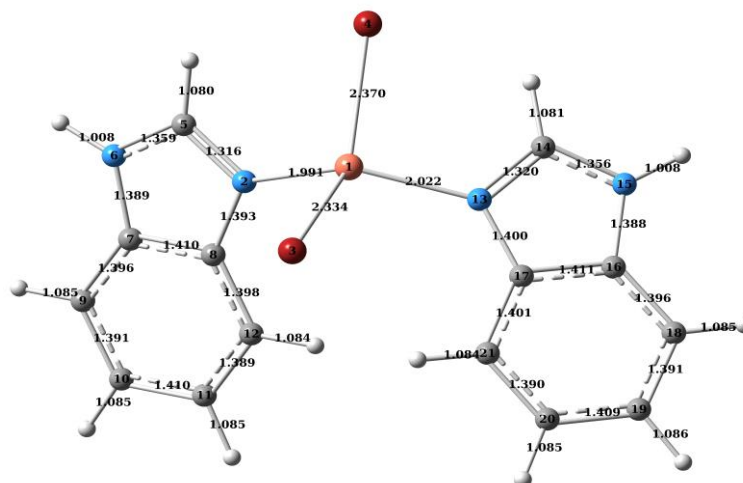


Figure 1. The optimized structure of $[\text{Cu}(\text{benzimidazole})_2\text{Br}_2]$ (C-atoms are in grey, Br-atoms are in dark red, N-atoms are in blue, Cu-atom is in light red, H-atoms are in white)

The Natural Bond Orbital (NBO) analysis of $[\text{Co}(\text{benzimidazole})_2\text{Br}_2]$, is provided the detailed insight into the nature of electronic conjugation between the bonds in the molecule. Table 1

collects the natural charges on atoms and the order of the bonds in the investigated compound. The largest negative charges (−0.570, −0.580) are located on two nitrogen atoms, N² and N¹³. The largest positive charge (0.770) is located on Cu atom.

Table 1. The NBO atomic charges and bond orders of [Cu(benzimidazole)₂Br₂], calculated by the B3LYP method with 6-31G(d,p) basis set

Atom	Natural charges	Bond	Bond order
Cu ¹	0.770	Cu ¹ -N ²	0.492
N ²	-0.570	Cu ¹ -N ¹³	0.479
Br ³	-0.504	Cu ¹ -Br ³	0.882
Br ⁴	-0.553	Cu ¹ -Br ⁴	0.781
C ⁵	0.274	N ² -C ⁵	1.473
N ⁶	-0.564	N ¹³ -C ¹⁴	1.460
C ⁷	0.127	C ⁵ -N ⁶	1.174
C ⁸	0.133	C ¹⁴ -N ¹⁵	1.180
C ⁹	-0.263	N ⁶ -C ⁷	0.971
C ¹⁰	-0.232	N ¹⁵ -C ¹⁶	0.973
C ¹¹	-0.244	C ⁷ -C ⁸	1.331
C ¹²	-0.219	C ¹⁶ -C ¹⁷	1.329
N ¹³	-0.580	C ⁸ -N ²	1.064
C ¹⁴	0.269	C ¹⁷ -N ¹³	1.072
N ¹⁵	-0.564	C ⁷ -C ⁹	1.376
C ¹⁶	0.124	C ¹⁶ -C ¹⁸	1.377
C ¹⁷	0.128	C ⁹ -C ¹⁰	1.474
C ¹⁸	-0.267	C ¹⁸ -C ¹⁹	1.472
C ¹⁹	-0.231	C ¹⁰ -C ¹¹	1.386
C ²⁰	-0.246	C ¹⁹ -C ²⁰	1.386
C ²¹	-0.227	C ¹¹ -C ¹²	1.480
		C ²⁰ -C ²¹	1.474
		C ¹² -C ⁸	1.374
		C ²¹ -C ¹⁷	1.378

In the NBO method, delocalization of electron density (ED) between occupied Lewis-type orbitals and formally unoccupied (antibonding or Rydberg) non-Lewis NBOs corresponds to a stabilizing donor–acceptor interaction. The strength of this interaction can be estimated by the second order perturbation theory. Thus, the results obtained from NBO analysis provide convenient basis for investigating conjugative interactions in molecular systems. The larger stabilization energy $E^{(2)}$ 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. The second-order perturbation theory analysis of Fock matrix in NBO basis of [Cu(benzimidazole)₂Br₂] display strong intra-molecular conjugative and hyperconjugative interactions and delocalization of electron density within the molecule.

In NBO analysis large $E^{(2)}$ value shows the intensive interaction between electron-donors and electron-acceptors, and greater the extent of conjugation of the whole system. Some important interactions between Lewis and non-Lewis orbitals along with their interacting stabilization energies are shown in Table 2. This table lists the selected values of the calculated second order interaction energy ($E^{(2)}$) between donor–acceptor orbitals in [Cu(benzimidazole)₂Br₂]. The strongest interactions are the electron donations from a lone pair (LP) orbital on the nitrogen atom, LP(1) N² to the antibonding acceptors LP(6)* Cu and LP(8)* Cu orbitals, which result in stabilization of the system. These interactions increases ED(0.204, 0.081e) – (LP(6)* Cu, LP(8)* Cu) that weakens LP(1) N² – ED(0.916e) leading to stabilization of 19.85 kcal/mol and 18.80 kcal/mol, respectively.

Table 2. Second-order interaction energy ($E^{(2)}$, kcal/mol) between donor and acceptor orbitals in[Cu(benzimidazole)₂Br₂]

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 ²	0.916	n6* Cu ¹	0.204	19.85	0.46	0.129
n1 N ²	0.916	n8* Cu ¹	0.081	18.80	0.60	0.135
n1 N ⁶	0.800	π^* N ² -C ⁵	0.188	29.52	0.26	0.112
n1 N ⁶	0.800	π^* C ⁷ -C ⁸	0.232	15.80	0.31	0.089
n1 Br ³	0.992	n7* Cu ¹	0.113	13.74	0.90	0.148
n4 Br ³	0.873	n6* Cu ¹	0.204	39.44	0.57	0.197
n4 Br ³	0.873	n7* Cu ¹	0.113	40.32	0.67	0.209
n1 Br ⁴	0.993	n7* Cu ¹	0.113	14.07	0.90	0.150
n4 Br ⁴	0.878	n6* Cu ¹	0.204	30.79	0.58	0.176
n4 Br ⁴	0.878	n7* Cu ¹	0.113	43.22	0.68	0.217
n1 N ¹³	0.913	n6* Cu ¹	0.204	19.61	0.46	0.127
n1 N ¹³	0.913	n9* Cu ¹	0.079	12.91	0.53	0.105
π N ¹⁵ -C ¹⁶	0.912	π^* N ¹³ -C ¹⁴	0.188	16.76	0.33	0.099
n1 C ¹⁷	0.517	π^* N ¹³ -C ¹⁴	0.188	26.38	0.09	0.073
π^* N ¹⁵ -C ¹⁶	0.407	π^* N ¹³ -C ¹⁴	0.188	41.36	0.03	0.054

$E^{(2)}$ – means energy of hyper-conjugative interactions (stabilization energy) in kcal/mol.

$E(j) - E(i)$ – Energy difference between donor and acceptor i and j NBO orbitals in a.u.

$F(i, j)$ – is the Fock matrix elements between i and j NBO orbitals in a.u.

The strongest interactions are the electron donations from a lone pair orbital on the nitrogen atom, LP(1)N¹³ to the antibonding acceptors LP(6)* Cu and LP(9)* Cu orbitals, which result in stabilization of the system. These interactions increases ED(0.204, 0.079e) – (LP(6)* Cu, LP(9)* Cu) that weakens LP(1) N¹³ – ED(0.913e) leading to stabilization of 19.61 kcal/mol and 12.91 kcal/mol, respectively. There occurs a strong intramolecular hyper-conjugative interaction of N²-C⁵ from N⁶ of LP(1) N⁶ → π^* N²-C⁵, which increases ED(0.188e) that weakens LP(1) N⁶ – ED(0.800e) leading to stabilization of 29.52 kcal/mol. Also there occurs a strong inter molecular hyper conjugative interaction of N¹³ – C¹⁴ from N¹⁵-C¹⁶ of π N¹⁵-C¹⁶ → π^* N¹³ – C¹⁴ and π^* N¹⁵-C¹⁶ → π^* N¹³ – C¹⁴, which increases ED(0.188e) that weakens the respective bond N¹⁵-C¹⁶ ED(0.912, 0.407e) leading to stabilization of 16.71 and 41.36 kcal/mol, respectively. Also the hyper conjugative interaction of LP(1) C¹⁷ → π^* N¹³-C¹⁴ leading to stabilization of 26.38 kcal/mol. The hyper conjugative interaction of LP(4) Br³ → LP(6,7)* Cu leading to stabilization of 39.44 and 40.32 kcal/mol, respectively; LP(4) Br⁴ → LP(6,7)* Cu leading to stabilization of 30.79 and 43.22 kcal/mol, respectively.

CONCLUSION

The geometry of [Cu(benzimidazole)₂Br₂] was optimized with DFT/B3LYP methods using 6-31G(d,p) basis set. The Natural orbital charges calculated by B3LYP/6-31G(d,p) method 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 the lone pair orbitals on the nitrogen atoms, LP(1) N²⁽¹³⁾ to the antibonding acceptor orbitals LP*(6;8;9) Cu and from the lone pair orbitals on the bromine atoms, LP(1;4) Br³⁽⁴⁾ to the antibonding acceptor orbitals LP*(6;7) Cu. The present quantum chemical study may lead to the understanding of properties and activity of [Cu(benzimidazole)₂Br₂].

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