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QTAIM, ELE, LOL and NBO investigations of the Cp2Sn=NHC complex

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Abstract: In this study, quantum chemical calculations using MPW1PW91 method was applied to analyze of electronic structure of a carbene complex of stannocene, Cp_2SnNHC. Natural population analysis (NPA) was used to calculate natural charges of atoms in the molecule. Natural Bond Orbital (NBO) analysis was illustrated electronic structure. Stabilization energies of several important donor-acceptor electron interactions were determined. Quantum theory of atoms in molecules analysis (QTAIM), Electron localization function (ELF) and Localized orbital locator (LOL) analyses were employed to illustrate the $Sn=C_{carbene}$ bond in this complex.

Keywords: Carbene complex, Natural Bond Orbital (NBO) analysis, Quantum theory of atoms in molecules analysis (QTAIM), Electron localization function (ELF), Localized orbital locator (LOL).

Introduction

Then the primal synthesis and separation of Wanzlick− Arduengo-type N-heterocyclic carbenes (NHCs) [1-3], they have become into the one of the most important ligands in transition-metal chemistry [4-6]. By applying the computational methods, the effects and structure of these complexes have been displayed [7-13]. Besides, various examples of main-group metal complexes with NHCs are realized [14]. Additionally, carbenes have played a notable role in the separation of low-valent main-group compounds [15-17]. several NHC complexes such as stannylene, plumbylene, and germylene, [18-22], along with regarded stannyleneisonitrile complexes [23], have been described. Even now, although NHC complexes of group 2 and 4 metallocenes are recognized [24, 25] and also Lewis acid−base adducts of plumbocene and stannocene with bipyridine and tetramethyl ethylene diamine have been reported [26, 27], the significance of the Lewis acidic character of these metallocenes and the reactivity of group 14 metallocenes (tetrelocenes) toward NHCs is unspecified. According to this, several attempts have been carried out to investigate the reactivity of stannocenes, one of the longest acknowledged group 14 metallocenes, toward NHCs. Preparation and spectroscopic effects of the various stannocenecarbene complexes have been announced[28]and their bonding characterization have been inspected [29]. I the present investigation, we reported Natural Bond Orbital (NBO) analysis, Quantum theory of atoms in molecules analysis (QTAIM), Electron localization function (ELF), Localized orbital locator (LOL) investigations on the electronic structure and properties of the Cp_2Sn=NHC complex**.**

Result and Discussion

Natural Bond Orbital (NBO) analysis

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NBO calculations were performed to obtain a more detailed comprehension of the effects that govern the most stable conformations in isolated phase. NBO is an essential tool for studying intra- and intermolecular bonding interactions, and also a convenient basis for investigating charge transfer or conjugative interaction in molecular systems. A number of orbitals are electron donor and a number of them are acceptors. The difference of energy between such bonding and anti-bonding orbitals causes the susceptibility of the molecule to interactions [45, 46]. The larger difference of energy [$E^{(2)}$], the more intensive is the interaction, suggesting a stronger donating tendency of an electron of one orbital and a higher accepting tendency of other orbitals, which cause a stronger interaction between them.

Electron configuration

Figure **1** presents the structure of Cp_2Sn=NHC complex. Natural Bond Orbital (NBO) analysis of studied carbene complex of stannocene has provided the detailed insight into the electronic structure in this molecule. According to the NBO results, the electron configuration of Sn is: [core]5s(1.87)5p(1.04)5d(0.01)6p(0.01). Thus

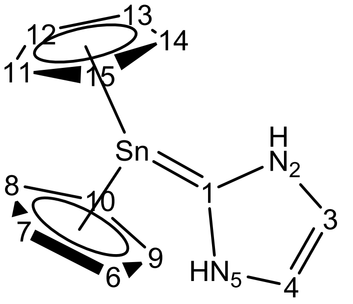

Figure 1: The structure of Cp_2Sn=NHC complex.

Natural population analysis

Natural charges on atoms are listed in Table **1**. 45.99532 core electrons, 2.90743 valence electrons (on 5s, 5p and 5d atomic orbitals) and 0.03579 Rydberg electrons (mainly on 6p orbital) give the total of 48.934electrons. This is consistent with the calculated natural charge +1.061 e on Sn atom in the carbene complex, which corresponds to the difference between 48.94e and the total number of electrons in the isolated Sn atom (50 e).

Table 1: Natural atomic charges in the Cp_2Sn=NHC complex.

Atom	Q
Sn	1.06146
C1	0.10976
N2	-0.54394
C3	-0.06351
C4	-0.06371
N5	-0.54422
C6	-0.28553
C7	-0.29323
C8	-0.30580
C9	-0.45970
C10	-0.34395
C11	-0.30955
C12	-0.29570
C13	-0.27957
C14	-0.34281
C15	-0.47628

The largest negative charges (-0.54394 and -0.54422 e) are located on two nitrogen atoms, N2 and N5. These partial charges distribution on the skeletal atoms reveals that the electrostatic repulsion or attraction between atoms can provide an important role to the intramolecular interaction. The C1 atom coordinated to Sn has larger positive charge (0.10976e). Figure 2 shows distribution of natural atomic charge in the Cp_2Sn=NHC complex.

Second order perturbation theory analysis of Fock matrix in NBO basis

The second order Fock matrix has been utilized for estimating of interactions corresponding to the donor-acceptor in the NBO analysis [47]. For every donor (i) and acceptor (j), the stabilization energy $E^{(2)}$ corresponding to the delocalizing i→ j is evaluated as:

$$E^{(2)}=-q_i \frac{(F_{i,j})^2}{E_j - E_i}$$

where q_i represents the *i*th donor orbital occupancy and E_i and E_j correspond to the donor and acceptor orbitals, respectively. $E_j - E_i$ represents the difference of energy between the donor orbital and acceptor orbital; i.e., the greater donating tendency of the electron donors toward electron acceptors the larger extent corresponding to conjugating the whole system. The stabilization energies of several important donor-acceptor electron interactions have remarkable influences on the stabilities of the studied molecule (Table **2**).

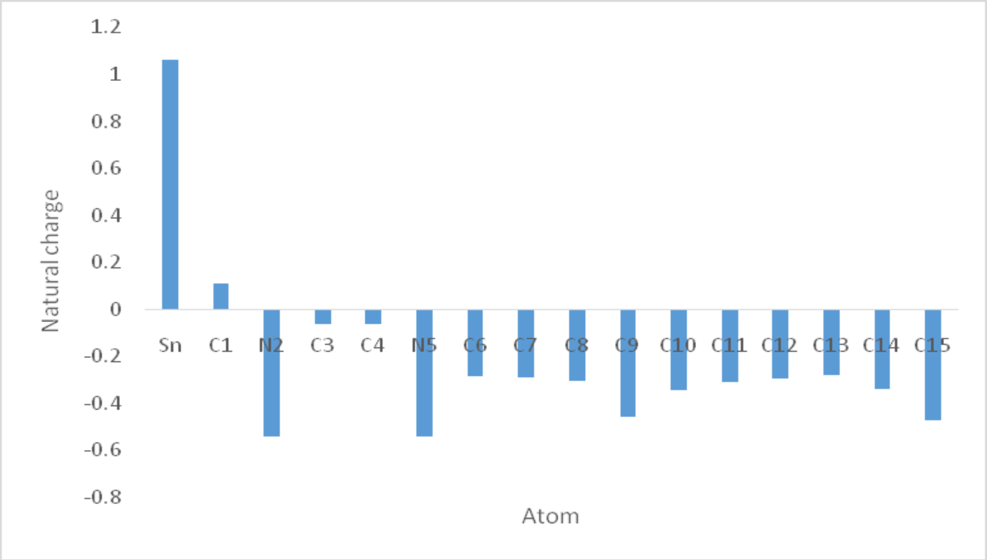

Figure 2: Distribution of natural atomic charge in the Cp_2Sn=NHC complex.

Table 2: Results of second order perturbation theory analysis of Fock Matrix in NBO Basisof several important donor-acceptor electron interactions in the Cp_2Sn=NHC complex.

Donor NBO (i) →Acceptor NBO (j)	E(2), kcal/mol	E(j)-E(i)	F(i,j), a.u.
LP (1) C1→ LP*(2)Sn	48.94	0.33	0.118
LP (1) C1 → LP*(3)Sn	50.07	0.32	0.115
LP (1) N2→BD*(2) C1 - N5	72.68	0.28	0.128
LP (1) N2→BD*(2) C3 - C4	33.85	0.30	0.095
LP (1) C15→LP*(2)Sn	74.13	0.14	0.101
BD(2)C13-C14→LP(1) C15	51.16	0.09	0.088
BD(2)C11-C12→LP(1) C15	50.57	0.09	0.086
LP(1)C15→BD*(2)C13-C14	48.27	0.19	0.095
LP(1)C15→BD*(2)C11-C12	48.68	0.20	0.096
LP (1) C10 →LP*(2)Sn	77.70	0.14	0.102
BD (2) C6 -C9 →LP (1) C10	47.96	0.10	0.088
BD (2) C8 - C7→LP(1) C 10	49.96	0.10	0.087
LP (1) C10→BD*(2)C6 -C9	50.06	0.19	0.095
LP (1) C10→BD*(2)C8 - C7	49.24	0.19	0.097

Quantum theory of atoms in molecules (QTAIM) analysis

The AIM-based analysis of electron density is used to determine the physical and chemical properties of molecular systems [48-56].

Electron density

The electron density is defined as:

$$\rho(r) = \eta_i\, |\varphi_i(r)|^2 = \sum_i \eta_i \left|\sum_l C_{l,i}\, \chi_i(r)\right|^2$$

Where χ is basis function, η_i is occupation number of orbital (i), φ is orbital wave function, and C is coefficient matrix.

In QTAIM theory a bond between two atoms is determined by a line of maximum electron density (bond path), that links the two nuclei and intersects a zeroflux surface in the gradient field at a (3,-1) saddle point (bond critical point). Electron density of in bond critical point (BCP) of Sn-$C_{carbene}$bond in the basis of the QTAIM calculations is 0.04728a.u. QTAIM analysis shows that density of alpha and beta electrons are 0.02364 and 0.02364 a.u, respectively. Figure **3** presents plot of electron density of in the studied complex in the Sn-$C_{carbene}$ line. It can be observed the highest electron density at 1.561 Bohr. Figure 4 presents plot of electron density of in the studied complex in the Sn-$C_{carbene}$–N2 plane. It can be observed the highest electron density at Sn atom.

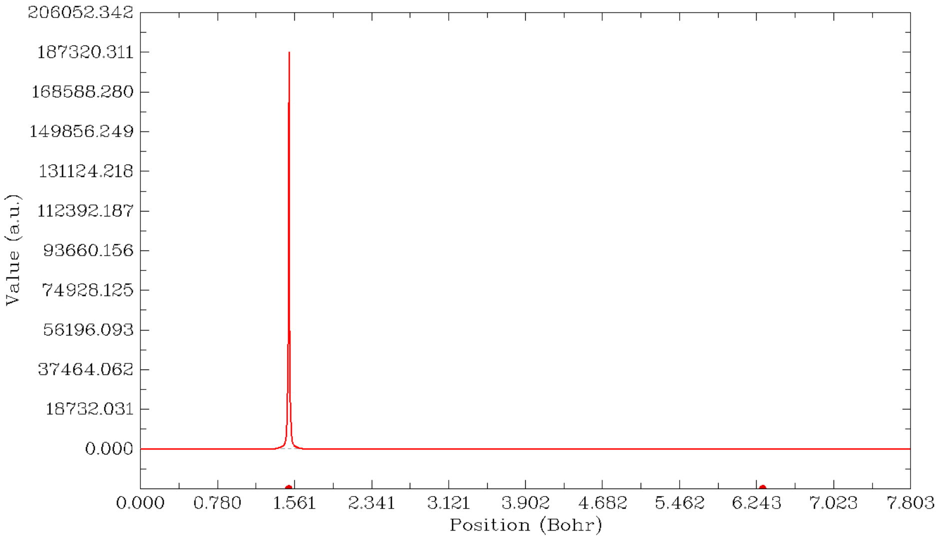

Figure 3: Plot of electron density of in the studied complex in the Sn-$C_{carbene}$ line in the Cp_2Sn=NHC complex.

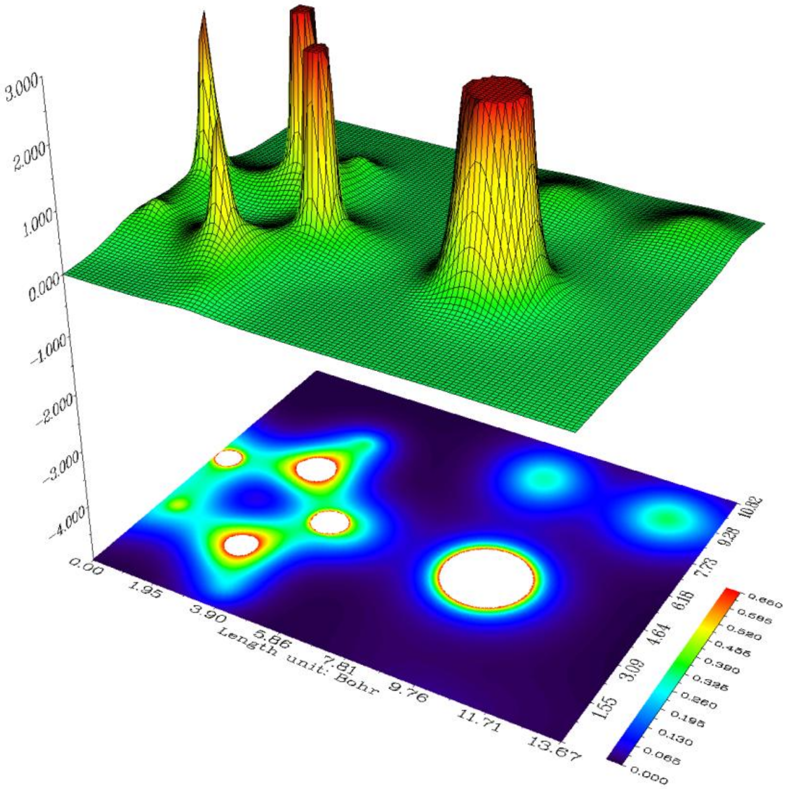

Figure 4: Plot of electron density of in the studied complex in the Sn-$C_{carbene}$–N2 plane in the Cp_2Sn=NHC complex

Laplacian of electron density

The Sn-$C_{carbene}$ bond is polar bond, as is the situation regularly in the coordinate bonds. Laplacian of electron density of in bond critical point (BCP) of Sn-$C_{carbene}$ bond in the basis of the QTAIM calculations is 0.80644 a.u. The positive Laplacian value reveals charge depletion in the bond critical points. This value is expected for closed-shell.

Figure **5** presents plot of Laplacianelectron density of in the studied complex in the Sn-$C_{carbene}$–N2 plane. It can be observed the highest electron density at Sn atom.

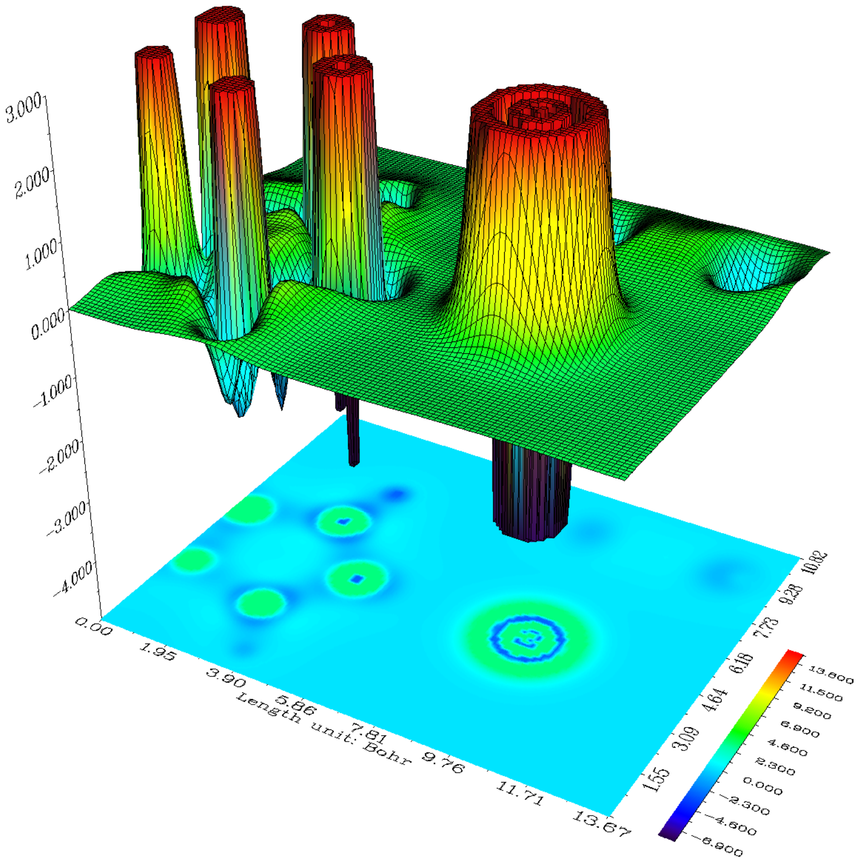

Figure 5: Plot of Laplacian electron density of in the studied complex in the Sn-$C_{carbene}$–N2 plane in the Cp_2Sn=NHC complex.

Energy density

The total energy density (H) is equal to:

H= G + V

In this equation G and V areLagrangian kinetic energy and Virial energy density, respectively.

Energy density of in bond critical point (BCP) of Sn-$C_{carbene}$ bond in the basis of the QTAIM calculations is-0.00792 a.u.

QTAIM results reveal V values is -0.03601 a.u. On the other hand, G values is0.02808a.u. The negative values of H for Sn-$C_{carbene}$ bond is directly connected with relative grater predominance of |V| magnitude over the G magnitude. As expected for shared interactions, the obtained energy density (H) values are negative. Therefore, previous studies have confirmed similar findings for the M–C bonds in organometallic complexes [57] and transition metal carbonyl clusters [58], where the characteristics of the metal–ligand bonding is a combination of the properties of closed-shell and shared interactions.

Electron localization function (ELF) analysis

Spherically averaged like spin conditional pair probability has direct correlation with the Fermi hole and then suggested electron localization function (ELF) [59]):

$$ELF(r) = \frac{1}{1 + [\frac{D(r)}{D_0(r)}]^2}$$

Where:

$$D(r) = \frac{1}{2}\sum_i \eta_i |\nabla\varphi_i|^2 - \frac{1}{8}[\frac{|\nabla\rho_\alpha|^2}{\rho_\alpha(r)} + \frac{|\nabla\rho_\beta|^2}{\rho_\beta(r)}]$$

$$D_0(r) = \frac{3}{10}(6\pi^2)^{\frac{2}{3}}[\rho_\alpha(r)^{\frac{5}{3}} + \rho_\beta(r)^{\frac{5}{3}}]$$

for close-shell system, since:

$$\rho_\alpha(r) = \rho_\beta(r) = \frac{1}{2}\rho$$

Therefore, D(r) and D_0(r) terms can be simplified as:

$$D(r) = \frac{1}{2}\sum_i \eta_i |\nabla\varphi_i|^2 - \frac{1}{8}[\frac{|\nabla\rho|^2}{\rho(r)}]$$

$$D_0(r) = \frac{3}{10}(3\pi^2)^{\frac{2}{3}}.\rho(r)^{\frac{5}{3}}$$

This is a direct relationship between ELF values and electron localization, which indicates the existence of a covalent bond, a lone pair or inner shells of the atom.

ELF values of Sn-$C_{carbene}$ bond is 0.28533 a.u. Figure 6 presents plot of ELF of in the studied complex in the Sn-$C_{carbene}$–N2 plane.

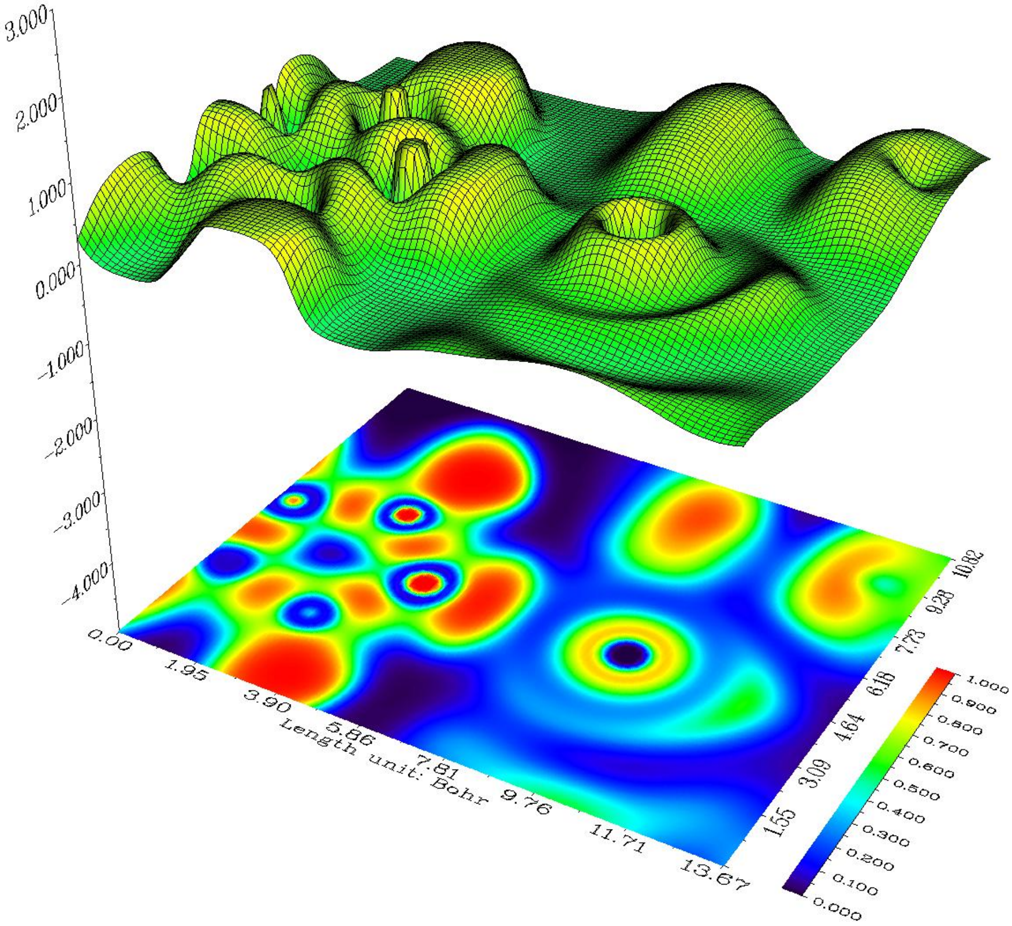

Figure 6: Plot of ELF of in the studied complex in the Sn-$C_{carbene}$–N2 plane in the Cp_2Sn=NHC complex.

Localized orbital locator (LOL)

Localized orbital locator (LOL) is another function for locating high localization regions Likewise ELF, defined by [60]:

$$LOL(r) = \frac{\tau(r)}{1+\tau(r)}$$

Where:

$$\tau(r) = \frac{D_0(r)}{\frac{1}{2}\sum_i \eta_i |\nabla\varphi_i|^2}$$

LOL values of Sn-$C_{carbene}$ bond is 0.38728 a.u.Figure 7 presents plot of LOL of in the studied complex in the Sn-$C_{carbene}$–N2 plane.

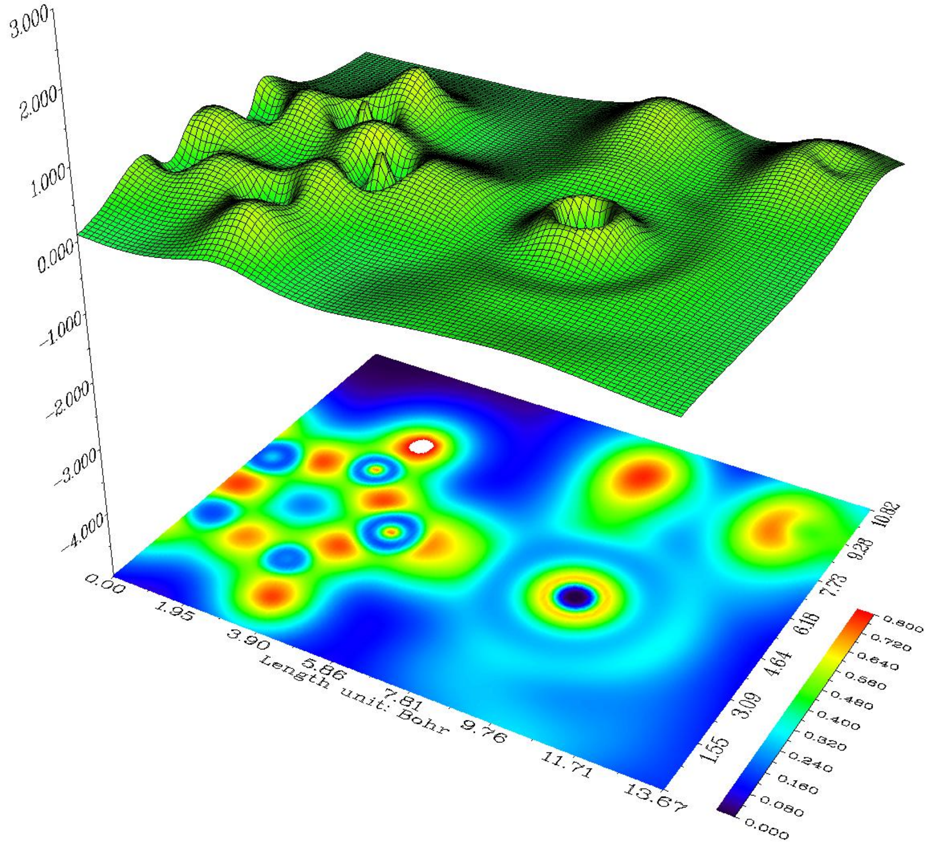

Figure 7: Plot of LOL of in the studied complex in the Sn-$C_{carbene}$–N2 plane in the Cp_2Sn=NHC complex.

Conclusion

In this study natural bond orbital (NBO) and quantum theory of atoms in molecules (QTAIM) analyses were used for exploring of structure and bonding in Cp_2SnNHC. QTAIM analysis shows that Sn-$C_{carbene}$ bond had a mix of the closed-shell and shared parameters. Also, electron localization function (ELF) and localized orbital locator (LOL) parameters were calculated for this bond. NBO analysis revealed the largest negative charges were located on nitrogen atoms. Also, our studies explored, the electron configuration of Sn was [core]5s(1.87)5p(1.04)5d(0.01)6p(0.01).

Acknowledgements

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