CONIINE, QUANTUM-CHEMICAL CALCULATION AND ITS APPLICATION IN AIR PURIFICATION

КОНИИН, КВАНТОВО-ХИМИЧЕСКИЙ РАСЧЕТ И ЕГО ПРИМЕНЕНИЕ В ОЧИСТКЕ ВОЗДУХА

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For the first time the geometric parameters, electronic and UV spectrum of the title compound were calculated by M062X/6-311+G* method. The intermolecular interaction between the molecules Coniine and CO has been explained. The Coniine is a powerful absorber of CO air has been found.

Впервые найдены геометрические параметры молекулы кониина, рассчитан электронный и УФ-спектр кониина неэмпирическим методом M062X/6-311+G*. Установлено межмолекулярное взаимодействие между молекулами кониина и CO воздуха. Установлено, что кониин является мощным поглотителем CO воздуха.

Keywords: Coniine, adsorption, DFT, non-bonded interaction, NBO analysis.

Ключевые слова: Кониин, адсорбция, метод функционала плотности, несвязанное взаимодействие, анализ НБО.

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In this work, the non-bonded interaction between $C_8H_{17}N$ with the CO was studied using DFT calculations in the gas phase and solvent water [Fig.]. The quantum chemical calculations have been carried out to optimized optimize the compound $C_8H_{17}N$ and complex $C_8H_{17}N$/CO using the DFT method (M062X) with the 6-311+G* basis set by Gaussian 09W software [1]. The Polarized Continuum Model (PCM) [] was used for the calculations of solvent effect. The adsorption energy (E_{ad}) [2,3] of the investigated molecular systems was calculated using the following equation:

$$E_{ad} = EC_8H_{17}N/CO – [EC_8H_{17}N + ECO] \quad (1)$$

Where, $EC_8H_{17}N$/CO, $EC_8H_{17}N$ and ECO are energies of the $C_8H_{17}N$ with the adsorbed CO, compound $C_8H_{17}N$ and the CO, respectively.

The molecular orbital (MO) calculations of the investigated compounds such as EHOMO, ELUMO, energy gap between LUMO and HOMO ($E_g=E_{LUMO}-E_{HOMO}$) were also performed. The optimized molecular structures, HOMO, LUMO and MEP surfaces were visualized using GaussView 05 program.

The other electronic properties of the title compounds such as the ionization potential ($I=-E_{HOMO}$), electron affinity ($A=-E_{LUMO}$), global hardness ($\eta=I-A/2$), electronegativity ($\chi=I+A/2$), electronic chemical potential ($\mu=-(I+A)/2$), electrophilicity ($\omega=\mu2/2\eta$) and chemical softness ($S=1/2\eta$) [4], natural charges and dipole moment were calculated.

Also, the interaction effects of the molecule CO with $C_8H_{17}N$ on the natural charge and the chemical shielding tensors [4] such as chemical shift isotropic (CSI) and chemical shift anisotropic (CSA) were investigated. The CSI and CSA parameters were calculated using following equations, respectively:

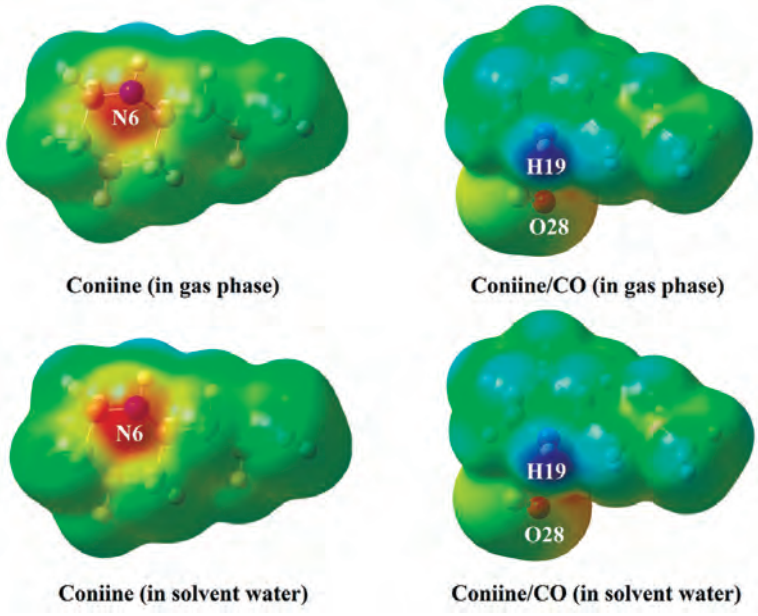
$$CSA\ (ppm) = (\sigma11 + \sigma22 + \sigma33)/3 \quad (2)$$

$$CSI\ (ppm) = \sigma33 - (\sigma11 + \sigma22)/2 \quad (3)$$

The three parameters such as σ11, σ22, σ33 show chemical shielding interaction in three dimensions. TD-DFT method [2] was used for the calculation of electronic transitions of the molecule $C_8H_{17}N$ and the complex $C_8H_{17}N$/CO in the gas phase and solvent water. The electronic structure of the mentioned compounds was also studied by using NBO analysis [3] at the M062X/6-311+G* level of theory in order to understand hyperconjugative interactions and charge delocalization.

At first, we have considered various states for interaction between the C8H17N with the CO. In the first step, all the states were computed by PM6 method. According to the calculated energies, we selected the most stable state for the

interaction between C8H17N and CO with the lowest energy value. Then, we have optimized the molecules C8H17N, CO and complex C8H17N/CO using M062X/6-311+G* level of theory in the gas phase and solvent water.



Figure–Molecular electrostatic potential (MEP) surfaces of the molecule $C_8H_{17}N$ and complex $C_8H_{17}N$/CO calculated using M062X/6-311+G method*

Geometrical parameters play an important role to interpret the non-bonded interaction between molecules. The theoretical bond lengths of optimized $C_8H_{17}N$ and complex $C_8H_{17}N$/CO in the gas phase and solvent water are reported in Table 1. As can be seen from Table 1, some geometrical parameters of $C_8H_{17}N$ are changed after the adsorption of CO over $C_8H_{17}N$ and the formation of the complex $C_8H_{17}N$/CO, although these changes are not significant.

The quantum molecular descriptors for the investigated compounds such as ionization potential (*I*), electron affinity (*A*), global hardness (η), electronegativity (χ), electronic chemical potential (μ), electrophilicity (ω) and chemical softness (*S*) are listed in the Table 4. The energy of HOMO is directly related to the ionization potential (*I*), while the energy of LUMO refers to the electron affinity (*A*). The global hardness (η) corresponds to the energy gap between HOMO and LUMO. A molecule with a small energy gap has high chemical reactivity, low kinetic stability and is a soft molecule, while a hard molecule has a large energy gap [].

As shown in Table 4, the global hardness values of the molecule $C_8H_{17}N$ and complex $C_8H_{17}N$/CO in the gas phase are 4.06 eV and 4.08 eV, respectively. After the adsorption of CO on the molecule $C_8H_{17}N$, the global hardness value of the complex is increased rather than isolated $C_8H_{17}N$; therefore, the complex has a low chemical activity, high chemical stability and it is a hard system. The global hardness values of the molecule $C_8H_{17}N$ and complex $C_8H_{17}N$/CO in the solvent water are 4.12 eV; on the other hand, the global hardness of the compound $C_8H_{17}N$ in the interaction with CO in the solvent water is not changed. Therefore, the complex $C_8H_{17}N$/CO in the gas phase has a high chemical activity, low chemical stability and it is a soft system rather than complex in the solvent water. Thus, it is found that the adsorption of the molecule carbon monoxide on $C_8H_{17}N$ in the gas phase and solvent solvent changes electronic properties of the complex.

After non-bonded interaction of carbon monoxide with $C_8H_{17}N$, the dipole moment value of $C_8H_{17}N$ are is increased from 0.93 to 1.30 in complex in the gas phase; and the dipole moment value of C8H17N are is increased from 1.55 to 1.70 in complex in the solvent water. The change of dipole moment after adsorption of CO over $C_8H_{17}N$ indicates a charge transfer between carbon monoxide and the $C_8H_{17}N$. The atomic charges have a significant role on physical properties such as molecular polarizability, dipole moment, electronic structure and related properties of molecular systems [2]. The charge distributions (NBO charges) for equilibrium geometry of the molecule $C_8H_{17}N$ and complex $C_8H_{17}N$/CO were calculated using M062X/6-311+G* level of theory.

NBO analysis is an important method for studying intra- and inter-molecular bonding and interaction between bonds in molecular systems [4]. The electron delocalization from donor orbitals (full NBOs) to acceptor orbitals (empty NBOs) describes a conjugative electron transfer process between them [3].The stabilization energy ($E^{(2)}$) describes the amount of the participation of electrons in the resonance between atoms of the molecular system [1].The bigger $E^{(2)}$, the more donation tendency from electron donors to electron acceptors [4].The NBO analysis for complex C8H17N/CO has been carried out by M062X/6-311+G* level of theory in the gas phase and solvent water. The results of NBO analysis are reported in Table 3. According to results of NBO analysis, the $\sigma\rightarrow\sigma^*$ transitions from $C_8H_{17}N$ to CO take place as σ(C1-H11)$\rightarrow\sigma^*$(C27-O28) interaction with stabilization energy ($E^{(2)}$) about 0.08 kcal/mol, in both pas phase and solvent water. The $n\rightarrow\sigma^*$ and $n\rightarrow\pi^*$ transitions from $C_8H_{17}N$ to CO also occur in complex $C_8H_{17}N$/CO. According to results, lone pairs (n) of the nitrogen atom (N6) in the compound $C_8H_{17}N$ overlaps with the anti-bonding orbital σ^* of CO that are including

n1(N6)→σ*(C27-O28) in the gas phase and solvent water with stabilization energies ($E^{(2)}$) of 0.12 kcal/mol and 0.13, kcal/mol, respectively. The electron charge transfer takes place from lone pairs of the N6 atom in the $C_8H_{17}N$ to the two anti-bonding orbital π* of CO that are including n1(N6)→π*(C27-O28) with stabilization energies ($E^{(2)}$) 0.35 kcal/mol, 0.84 kcal/mol in the gas phase and 0.28 kcal/mol, 0.68 kcal/mol in solvent water. The obtained results indicated that the n→σ* transitions from CO to $C_8H_{17}N$ take place in gas phase as n1(C27)→σ*(C1-H11), n1(C27)→σ*(C2-H13) interactions with resonance energies values ($E^{(2)}$) about 0.30 kcal/mol and 0.16 kcal/mol respectively; whereas in the solvent water, n1(C27)→σ*(C1-H11), n1(C27)→σ*(C2-H12), n1(C27)→σ*(C2-H13) transitions take place with stabilization energies ($E^{(2)}$) of 0.30, 0.06, 0.22 kcal/mol, respectively. Thus, $C_8H_{17}N$ and CO acts as both electron donor and electron acceptor; therefore, charge transfer takes place between $C_8H_{17}N$ and CO in the complex $C_8H_{17}N$/CO.

Molecular electrostatic potential (MEP) maps display the electronic density in the molecular systems and they are utilized to detect positions of positive and negative electrostatic potentials surfaces with different colors. In MEPs, the negative sites with the high electron density have red, orange or yellow colors that were related to electrophilic reactivity, whereas the positive regions with low electron density have blue color and they were related to nucleophilic reactivity and green color was used for neutral regions. The MEPs of the molecule $C_8H_{17}N$ and complex $C_8H_{17}N$/CO were obtained by theoretical calculations using the M062X/6-311+G* level of theory in the gas phase and solvent water and the charge distribution was studied by MEP calculations. As seen from the MEP maps of the $C_8H_{17}N$ in both gas phase and solvent water, the N6 atom with red color has the highest electron density; whereas after adsorption of the carbon monoxide on $C_8H_{17}N$, the N6 in complex $C_8H_{17}N$/CO has not red color due to the interaction between N6 of $C_8H_{17}N$ with CO. As seen from the MEP maps of the complex $C_8H_{17}N$/CO in both gas phase and solvent water, the H19 atom (N6-H19) of piperidine ring has the lowest electron density (blue) and it contains more electropositive atoms than the hydrogen ones; therefore, it is recognized as the acidic hydrogen atom. Also, the O28 atom of carbon monoxide at the complex $C_8H_{17}N$/CO has the highest electron density. Green color confirms the neutral part and zero potential of the title compound.

We have calculated the NMR parameters such as chemical shift isotropic (CS^I) and chemical shift anisotropic (CS^A) for atoms in the molecule $C_8H_{17}N$ and complex $C_8H_{17}N$/CO using the M062X/6-311+G* level of theory in the gas phase and solvent water. The electronic density affects the electrostatic properties of atoms. The adsorption of carbon monoxide over $C_8H_{17}N$ changes the electronic densities of atoms and NMR parameters. The results of the chemical shift tensors (ppm) are summarized in Table 5. The calculated results show that the values of the CS^I for the C1, C2, C4, N6, C7, H11, H16, H20, H23, H24 atoms of the molecule C8H17N in the gas phase are 158.85, 137.59, 153.85, 185.20, 143.32, 30.61, 31.10, 30.70, 30.82, 31.03 ppm, respectively, whereas after the adsorption of CO on $C_8H_{17}N$ was estimated about 159.08, 138.61, 154.28, 182.36, 143.89, 30.40, 30.99, 30.50, 30.77, 30.92 ppm, respectively. For the molecule $C_8H_{17}N$ in solvent water, the CS^I values of the C1, C2, C4, N6, C7, H11, H16, H19, H20, H22 atoms are 158.85, 137.58, 153.76, 185.79, 143.26, 30.74, 31.21, 31.30, 30.85, 31.09 ppm, respectively, but these values after the adsorption of carbon monoxide over Coniine, change to 159.38, 138.68, 154.02, 183.65, 143.67, 30.50, 31.17, 31.44, 30.73, 31.10 ppm, respectively. The change in the values of CS^I and CS^A for other carbon and hydrogen atoms of the compound $C_8H_{17}N$ also observed after a non-bonded interaction with CO.

We have calculated the UV spectra of the molecule $C_8H_{17}N$ and the complex $C_8H_{17}N$/CO in the gas phase and solvent water using TD-DFT calculations at M062X/6-311+G* level of theory with considering 20 excited states in order to investigate adsorption effect of the title carbon monoxide over $C_8H_{17}N$ on the λ_{max}. The computed results are represented in Tables 6,7, that indicate the λ_{max}, oscillator strength (f), and excitation energies (E).

The computed analysis of the UV spectrum for the molecule $C_8H_{17}N$ in the gas phase exhibits λ_{max} at 190 nm (f = 0.065) (see Table 6). The charge transfer at λ_{max} = 190 nm is related to the excited state $S_0 \rightarrow S_2$ with five electron configurations such as H→L+3 (80%), H→L (3%), H→L+2 (4%), H→L+7 (3%), H→L+8 (2%), in which the main transition is involved with the transition from HOMO to LUMO+3 [H→L+3 (80%)]. The other excited states of $C_8H_{17}N$ have very small intensity and do not play any role in the formation of electron spectrum of the title compound (Table 6). The calculated electronic absorption spectrum of $C_8H_{17}N$ in the gas phase is shown in Fig. 6. With the adsorption of carbon monoxide on the $C_8H_{17}N$ in the gas phase, λ_{max} observe at 195 nm (f = 0.086). The charge transfer at λ_{max} = 195 is related to the excited state $S_0 \rightarrow S_3$ and is defined by seven configurations including H→L+2 (10%), H→L+3 (14%), H→L+5 (46%), H→L (9%), H→L+1 (8%), H→L+10 (4%), H→L+11 (2%) (Table 6), in which the main transition is involved with the transition from HOMO to LUMO+5 [H→L+5 (46%)]. The other excited states of $C_8H_{17}N$/CO have very small intensity and do not play any role in the formation of electron spectrum of the title compound (Table 6). The calculated electronic absorption spectrum of the complex $C_8H_{17}N$/CO.

In the present work, the non-bonding interaction of the compound Coniine with carbon monoxide at the M062X/6-311+G* level of theory has been studied for the first time. The adsorption energy of CO over $C_8H_{17}N$ in the gas phase (-2.67 eV) is greater than solvent water (-1.33 eV). It is found that some geometrical parameters of $C_8H_{17}N$ are changed after adsorption process due to the formation of intermolecular non-bonded interaction. NBO analysis predicted a charge transfer from the molecule $C_8H_{17}N$ to CO and from CO to $C_8H_{17}N$. It was found that the electronic properties of the molecule $C_8H_{17}N$ are sensitive to the adsorption of the CO. As a result, the quantum molecular descriptors are changed at adsorption process. The complex $C_8H_{17}N$/CO in the gas phase has a high chemical activity, low chemical stability and it is a soft system rather than complex in the solvent water. The atomic charges and chemical shift tensors were changed by the adsorption of the CO over the compound $C_8H_{17}N$. The non-bonded interaction between the $C_8H_{17}N$ and CO is changed

the value of λ_{max}. Therefore, $C_8H_{17}N$ may be used for development of filters in order to adsorption of carbon monoxide as environmental pollution.

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РОЛЬ ШАПЕРОНОВ ПРИ САХАРНОМ ДИАБЕТЕ
THE ROLE OF CHAPERONES IN DIABETES MELLITUS

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Шапероны – уникальные ремоделирующие белки, участвующие во множестве внутриклеточных событий, вовлеченные в процессы коррекции структуры белков, предотвращения агрегации неправильно свернутых белков, разрушения белковых агрегатов, а также разворачивания нативных белков-мишеней для транслокации их через мембраны. Кроме того, шапероны участвуют, как в разборке активных олигомерных структур до состояния неактивных развернутых мономеров для их последующей протеолитической деградации, так и в формировании специфических комплексов и белковых ансамблей. В обзоре обобщены сведения о строении и функционировании молекулярных шаперонов Hsp70 и их роли в развитии сахарного диабета 2 и его осложнений.

Chaperones are unique remodeling proteins that participate in a variety of intracellular events and are involved in the protein structure correction process, preventing aggregation of incorrectly folded proteins, destroying protein aggregates, and deploying native target proteins to translocate them across membranes. In addition, chaperones are involved both in the disassembly of active oligomeric structures to the state of inactive expanded monomers for their subsequent proteolytic degradation, and in the formation of specific complexes and protein ensembles. The review summarizes information about the structure and functioning of Hsp70 molecular chaperones and their role in the development of diabeta type 2 and its complications.

Ключевые слова: Hsp70, сахарный диабет (СД), инсулин, β-клетки.

Keywords: Hsp70, diabetes mellitus (DM), insulin, β-cells.

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Сахарный диабет (далее − СД) и его осложнения являются одной из серьезнейших медико-социальных и экономических проблем современного здравоохранения. По данным Международной диабетической федерации, в настоящее время в мире СД болеют около 366 млн человек, и к 2030 г. эта цифра превысит 552 млн человек, в основном за счет больных СД2 типа (СД2). У больных с СД2 наблюдается уменьшенная экспрессия генов белка теплового шока HSP70, что коррелирует со сниженной чувствительностью к инсулину. Это стимулировало появление исследований с целью установления возможности использования препаратов и методов стимулирования экспрессии HSP70 для защиты от развития резистентности к инсулину [1]. Шапероны – уникальные ремоделирующие белки, участвующие во множестве внутриклеточных событий, вовлечены