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 кониина 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 C₈H₁₇N 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 C₈H₁₇N and complex C₈H₁₇N/CO using the DFT method (M062X) with the 6-311+G* basis set by Gaussian 09W software [1]. The Polarized Continuum Model (PCM) [2] 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 = EC₈H₁₇N/CO – [EC₈H₁₇N + ECO]

Where, EC₈H₁₇N/CO, EC₈H₁₇N and ECO are energies of the C₈H₁₇N with the adsorbed CO, compound C₈H₁₇N and the CO, respectively.

The molecular orbital (MO) calculations of the investigated compounds such as EHOMO, ELUMO, energy gap between LUMO and HOMO (Eg=ELUMO-EHOMO) 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 (η=I-A/2), electronegativity (χ=I+A/2), electronic chemical potential (µ=(I+A)/2), electrophilicity (ω=µ²/2η) and chemical softness (S=1/2η) [4], natural charges and dipole moment were calculated.

Also, the interaction effects of the molecule CO with C₈H₁₇N 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) = (σ₁₁ + σ₂₂ + σ₃₃)/3

CSI (ppm) = σ₃₃ - (σ₁₁ + σ₂₂)/2

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 C₈H₁₇N and the complex C₈H₁₇N/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.

![Molecular electrostatic potential (MEP) surfaces](image)

Figure—Molecular electrostatic potential (MEP) surfaces of the molecule C8H17N and complex C8H17N/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 C8H17N and complex C8H17N/CO in the gas phase and solvent water are reported in Table 1. As can be seen from Table 1, some geometrical parameters of C8H17N are changed after the adsorption of CO over C8H17N and the formation of the complex C8H17N/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 ($\eta$), electronegativity ($\chi$), electronic chemical potential ($\mu$), electrophilicity ($\omega$) and chemical softness ($S$) are listed in 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 ($\eta$) 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 C8H17N and complex C8H17N/CO in the gas phase are 4.06 eV and 4.08 eV, respectively. After the adsorption of CO on the molecule C8H17N, the global hardness value of the complex is increased rather than isolated C8H17N; therefore, the complex has a low chemical activity, high chemical stability and it is a hard system. The global hardness values of the molecule C8H17N and complex C8H17N/CO in the solvent water are 4.12 eV; on the other hand, the global hardness of the compound C8H17N in the interaction with CO in the solvent water is not changed. Therefore, the complex C8H17N/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 C8H17N in the gas phase and solvent solvent changes electronic properties of the complex.

After non-bonded interaction of carbon monoxide with C8H17N, the dipole moment value of C8H17N are increased from 0.93 to 1.30 in complex in the gas phase; and the dipole moment value of C8H17N are increased from 1.55 to 1.70 in complex in the solvent water. The change of dipole moment after adsorption of CO over C8H17N indicates a charge transfer between carbon monoxide and the C8H17N. The atomic charges have a significant role on physical properties such as molecular polarizability, dipole moment, electronic structure and related properties of molecular systems. The change of dipole moment after adsorption of CO over C8H17N indicates a charge transfer between carbon monoxide and the C8H17N. The atomic charges have a significant role on physical properties such as molecular polarizability, dipole moment, electronic structure and related properties of molecular systems.

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NBO analysis is an important method for studying intra- and inter-molecular bonding and interaction between bonds in molecular systems. The electron delocalization from donor orbitals (full NBOs) to acceptor orbitals (empty NBOs) describes a conjugative electron transfer process between them. The stabilization energy ($E(2)$) describes the amount of the participation of electrons in the resonance between atoms of the molecular system. The bigger $E(2)$, the more donation tendency from electron donors to electron acceptors. 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 C8H17N to CO take place as $\sigma$(C1-H11)$\rightarrow\sigma^*$(C27-O28) interaction with stabilization energy ($E(2)$) about 0.08 kcal/mol, in both gas phase and solvent water. The $n\rightarrow\sigma^*$ and $n\rightarrow\pi^*$ transitions from C8H17N to CO also occur in complex C8H17N/CO. According to results, lone pairs (n) of the nitrogen atom (N6) in the compound C8H17N overlaps with the anti-bonding orbital $\sigma^*$ 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 C8H17N 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 C8H17N 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, C8H17N and CO acts as both electron donor and electron acceptor; therefore, charge transfer takes place between C8H17N and CO in the complex C8H17N/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 C8H17N and complex C8H17N/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 C8H17N 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 C8H17N, the N6 in complex C8H17N/CO has not red color due to the interaction between N6 of C8H17N with CO. As seen from the MEP maps of the complex C8H17N/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 C8H17N/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 (CSI) and chemical shift anisotropic (CSA) for atoms in the molecule C8H17N and complex C8H17N/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 C8H17N 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 CSI 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 the carbon monoxide on C8H17N, the N6 in complex C8H17N/CO has not red color due to the interaction between N6 of C8H17N with CO. As seen from the MEP maps of the complex C8H17N/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 C8H17N/CO has the highest electron density. Green color confirms the neutral part and zero potential of the title compound.

We have calculated the UV spectra of the molecule C8H17N and the complex C8H17N/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 C8H17N on the λ<sub>max</sub> of the computed results are represented in Tables 6,7, that indicate the λ<sub>max</sub>, oscillator strength (f), and excitation energies (E). The computed analysis of the UV spectrum for the molecule C8H17N in the gas phase exhibits λ<sub>max</sub> at 190 nm (f = 0.065) (see Table 6). The charge transfer at λ<sub>max</sub> = 190 nm is related to the excited state S<sub>2</sub>→S<sub>1</sub> with five electron configurations such as H→L+3 (80%), H→L (3%), H→L+2 (4%), H→L+1 (3%), H→L-1 (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 C8H17N 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 C8H17N in the gas phase is shown in Fig. 6. With the adsorption of carbon monoxide on the C8H17N in the gas phase, λ<sub>max</sub> observe at 195 nm (f = 0.086). The charge transfer at λ<sub>max</sub> = 195 is related to the excited state S<sub>12</sub>→S<sub>11</sub> 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 C8H17N/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 C8H17N/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 C8H17N in the gas phase (-2.67 eV) is greater than solvent water (-1.33 eV). It is found that some geometrical parameters of C8H17N are changed after adsorption process due to the formation of intermolecular non-bonded interaction. NBO analysis predicted a charge transfer from the molecule C8H17N to CO and from CO to C8H17N. It was found that the electronic properties of the molecule C8H17N are sensitive to the adsorption of the CO. As a result, the quantum molecular descriptors are changed at adsorption process. The complex C8H17N/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 C8H17N. The non-bonded interaction between the C8H17N and CO is changed.
the value of $\lambda_{\text{max}}$. Therefore, $\text{C}_8\text{H}_{17}\text{N}$ may be used for development of filters in order to adsorption of carbon monoxide as environmental pollution.

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THE ROLE OF CHAPERONES IN DIABETES MELLITUS

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Shaperones 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 and their role in the development of diabetic type 2 and its complications.

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, вовлеченные