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The effects of isomerism and side chain mutation on binding energy and NMR/NQR tensors of L-methionylasparagine and L-asparagylmethionine

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ABSTRACT

Density functional theory methods(DFT) and natural bond orbital (NBO) analysis were used to investigate the effects of isomerism and side chain mutation at a microscopic level on the stability, binding energy and NMR/NQR tensors of structural isomers, L- methionylasparagine (Met-Asn) and L- asparagylmethionine (Asn-Met) in the gas phase. The results represented that the isomerism and side chain mutation were caused to change the relative stability, binding energy and the thermodynamics parameters of peptide bond in the considered compounds. Therefore, Asn-Met had higher binding energy and relative stability than Met-Asn. On the other hand, NMR and NQR calculations at B3LYP/6-311+G (d, p) level of theory on the optimized structures of Met-Asn and Asn-Met indicated that the isotropic chemical shielding (σ_{iso}) values of oxygen and nitrogen nuclei in two structures with similar positions were different considerably and nitrogen nuclei were more shielded than oxygen nuclei in both dipeptides. In addition, amino nitrogens (N_{10} nuclei) had the highest values of chemical shielding (σ_{iso}) and the nuclear quadrupole coupling constant (χ) among nitrogen nuclei and the order of chemical shielding values of nitrogen nuclei in two structural isomers was amino nitrogen> amidic nitrogen> peptide nitrogen (N_{10}>N_9>N_1). The mentioned order for chemical shielding values was exactly the opposite of the order of resonance energies values of nitrogen lone pair electrons in two dipeptides. In other words, by increasing contribution of nitrogen lone pair electrons in intra-molecular resonance interactions, NMR chemical shielding around nitrogen nuclei were decreased.

Keywords: binding energy; L-Methionylasparagine; L-Asparagyl methionine; Isomerism; NBO analysis

1. INTRODUCTION

Peptides are important organic compounds since they are structural components of proteins and have effective roles in the different physiological and biological processes in living organisms [1]. Among the biological activities of peptides, their functions as hormones and neurotransmitters are very interesting. In addition, they are components of several protein sequences that interfere with biological metabolism [2]. A dipeptide molecule contains two amino acids linked by a peptide bond. Dietary proteins are digested to dipeptides and amino acids and the dipeptides are absorbed more quickly than the amino acids because their analyses involve a separate mechanism. The formation of a peptide bond between two amino acids is an example of a condensation reaction. Two amino acids

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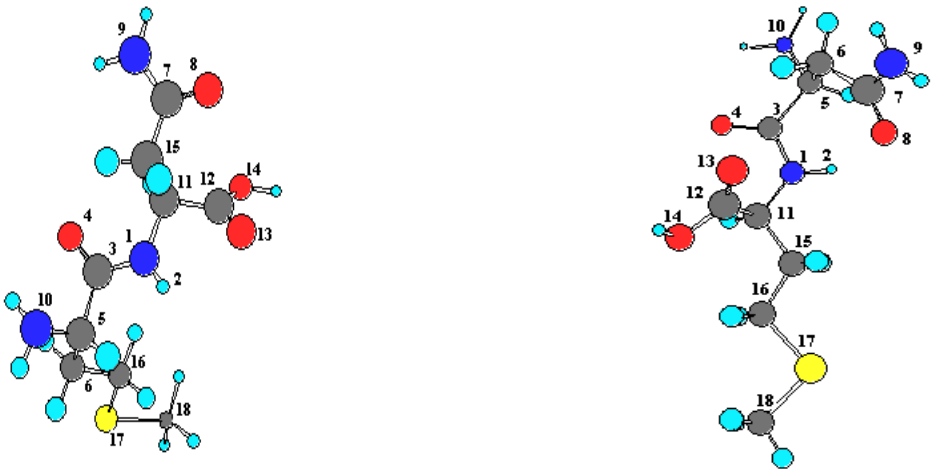
join covalently to form the bond together and to eliminate one water molecule. For the first time, the synthesis of peptides by Emile Fisher was performed with the synthesis and study of Glycyl-Glycine dipeptide in 1901[3]. Since glycine and alanine are the two simplest amino acids forming dipeptides and tripeptides, they are studied peptides using ab initio quantum mechanical calculations [4-8 and the references therein]. One important tool for studying peptides and proteins is vibrational spectroscopy so many studies have been conducted on the vibrational properties of peptides [9-13]. For example, vibrational properties of L- alanyl -L-alanine (Ala-Ala) have been studied at low and standard temperatures [14-17]. In another study on this dipeptide, Silva and his colleagues studied single crystals by Raman spectroscopy at low temperatures and determined normal modes [18]. In addition to vibrational spectroscopy, computational methods were used to study the conformational behavior and the vibrational spectrum of the glycyl-leucine cyclic dipeptide which is a biological active compound [19]. Similar studies have been conducted on the cyclic dipeptides such as Ala-Gly, Ala-Ala, Ser-Ser and Met-Met [20-25]. Furthermore, there are experimental and theoretical studies on dipeptides initiating with methionine. Methionine is one of two amino acids containing sulfur encoded by a single codon (AUG) in the standard genetic code. The AUG codon is also significant in protein synthesis and carries the start message for ribosome to begin protein translation from mRNA. Ivanova and his coworkers carried out a part of systematic studies on methionyl-histidine (Met-His) and hystidyl-methionine (His-Met) dipeptides and also methionyl-glycyl-glycine (Me-Gly-Gly) and glycyl-glycyl-methionine (Gly-Gly-Met) tripeptides based on structural and IR-spectral characterizations [26, 27]. On the other hand, Asparagine is a non-essential amino acid which contains an α-amino group (which is in the protonated $-NH^{+}_{3}$ form under biological conditions), an α-carboxylic acid group (which is in the deprotonated $-COO^{-}$ form under biological conditions), and a side chain carboxamide, classifying it as a polar (at physiological pH), aliphatic amino acid. Since the asparagine side-chain can form hydrogen bond interactions with the peptide backbone, asparagine residues are often found near the beginning of alpha-helices as asx turns and asx motifs, and in similar turn motifs, or as amide rings, in beta sheets. Its role can be thought as "capping" the hydrogen bond interactions that would otherwise be satisfied by the polypeptide backbone. Many studies have been conducted on asparagine residue, asparagine joined glycosyl and peptides containing asparagine due to the important roles they have in proteins and biosynthesis of glycoproteins [28-30].

In this study, dipeptides containing methionine and asparagine, L-methionylasparagine (Met-Asn) and L-asparagylmethionine (Asn-Met) were studied using theoretical methods due to their important roles in biological activities (see Fig.1). Met-Asn and Asn-Met are the structural isomers and have the same peptide framework, but their side chains were displaced. The effects of side chain mutation and isomerism at a microscopic level were investigated on the structure, binding energy and NMR/NQR tensors of Met-Asn and Asn-Met by using DFT methods. Furthermore, NBO analysis was used to compare the intra- molecular interactions and chemical reactivity indices of Met-Asn and Asn-Met dipeptides.



a)Met-Asn b) Asn-Met

Fig. 1. the optimized structures of structural isomers a) methionylasparagine (Met-Asn) and b) asparagylmethionine (Asn-Met) at B3LYP/6-311+G** level of theory.

2. COMPUTATIONAL DETAILS

Geometry optimizations were performed on Met-Asn, Asn-Met, Me, Asn and water molecules at B3LYP/6-311+G** level of theory [31-32]. The nature of the stationary points for the mentioned structures was verified by calculating the harmonic frequencies at the same level of theory. For minimum state structures, only real frequency values were accepted. The thermodynamic functions were calculated according to the following relations:

$E = E_0 + E_{vib} + E_{rot} + E_{trans}$, $H = E + RT$, $G = H - TS$, as defined in the output of the frequency calculation in GAUSSIAN manual . The binding energies, Δ H, ΔS and ΔG for two dipeptides were determined using the corresponding calculated thermodynamic data for initial and final states. In addition, Gauge including atomic orbital (GIAO) and Electric-field gradient (EFG) calculations were accomplished on optimized dipeptides in the gas phase using B3LYP/6-311+G** level of theory and the values of isotropic chemical shielding (σ_{iso}) and anisotropic chemical shielding ($\Delta\sigma$) were calculated by below formulas [33,34]:

$$\sigma_{iso} = \frac{1}{3}\left(\sigma_{11} + \sigma_{22} + \sigma_{33}\right) \quad (1)$$

$$\Delta\sigma = \sigma_{33} - \frac{1}{2}\left(\sigma_{11} + \sigma_{22}\right) \quad (2)$$

Often the NQR parameters are reported experimentally as the nuclear quadrupole coupling constant, and have the unit of frequency:

$$Q_{cc} = \chi(MHz) = e^2 Q q_{zz} / h \quad (3)$$

Asymmetry parameter is defined as $\eta_Q = \left|(q_{yy} - q_{xx}) / q_{zz}\right|, 0 \le \eta_Q \le 1$ since it measures the deviation of the field gradient tensor from axial symmetry. For a nucleus of unit spin (such as ^{14}N), we have three energy levels, so we get three nuclear quadrupole resonance frequencies [35, 36]:

$$\upsilon_+ = \frac{3}{4}\chi_{zz}\left(1 + \frac{\eta}{3}\right) \quad (4)$$

$$\upsilon_- = \frac{3}{4}\chi_{zz}\left(1 - \frac{\eta}{3}\right) \quad (5)$$

$$\upsilon_0 = \frac{1}{2}\chi_{zz}\eta \quad (6)$$

On the other hand, NBO analysis was performed on optimized structures using B3LYP/6-311+G** level of theory by NBO 3.1 program [37, 38]. Chemical reactivity parameters such as ionization energy (I), electron affinity energy (A), electronegativity (χ), chemical hardness (η) and chemical softness(S) were calculated using the following formulas [39]:

$$I = -E_{HOMO} \quad (7)$$
$$A = -E_{LUMO} \quad (8)$$
$$\chi = (I+A)/2 \quad (9)$$
$$\eta = (I-A)/2 \quad (10)$$
$$S = 1/2\eta \quad (11)$$

All calculations in present work were performed using the GAUSSIN software [40].

3. RESULTS AND DISCUSSION

In this study, geometrical optimizations of L-methionylasparagine (Met-Asn) and L-asparagylmethionine (Asn-Met) dipeptides and their amino acids were performed using B3LYP/ 6-311+G** level of theory. Met-Asn and Asn-Met dipeptides were formed by the amidic linkage between L-methionine and L-asparagine amino acids and were structural isomers of each other. They had identical backbones, but their side chains had been interchanged. Binding energies for dipeptides were calculated as the difference between the sum of the equilibrium energies from the two amino acids in the individual state and from the final state (dipeptide molecule + water). The results revealed that Asn-Met had higher binding energy and relative stability than Met-Asn (Table 1). The thermodynamics calculations also showed that Asn-Met had a higher Gibbs free energy than Met-Asn. Therefore, the formation of peptide bond in Asn-Met is preferable compared to its formation in Met-Asn thermodynamically. In addition, the performed calculations supposed a planar trans configuration of NH-CO amidic fragment in both isomeric structures of Met-Asn and Asn-Met (see Table 2 and Fig.2). The obtained values for bond lengths and angles were correlated significantly with crystallographic and theoretical data reported for other dipeptides containing methionine [12]. The data deviation of experimental values was in range of 0.01-0.04 A°. These results also indicated that B3LYP method overestimates the bond distances in most cases .The above mentioned deviations in the geometric parameters between the experimental and theoretical values can be due to the determined structure for the solid state which involves the inter-molecular interactions whereas the results of the calculations were applicable to the gas phase. The dipole moment is the first derivative of the energy with respect to applied electric field. It is a measure of the asymmetry in the molecular charge distribution. We reported dipole moment of Asn-Met and Met -Asn dipeptides in Table 1 at B3LYP/6-311+G** level of theory. The results revealed that Asn-Met had higher dipole moment than Met –Asn. This fact revealed that the charge distribution in Met –Asn was more symmetric than it was in Asn-Met.

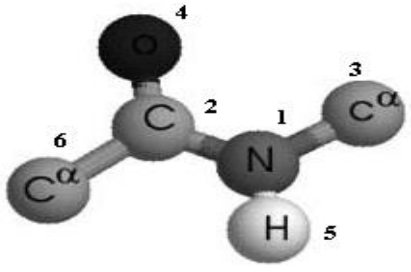


Fig. 2. The structure of the peptide framework of the studied dipeptides.

Table 1. Calculated electronic energies(E_{el}), binding energies (ΔE_{el}), thermodynamic functions of binding(enthalpies(ΔH), Gibbs free energies (ΔG) and entropies (ΔS)) and the dipole moment values (μ), for Met-Asn and Asn-Met dipeptides at B3LYP/6-311+G** level of theory in the gas phase

	$-E_{el}$	$-\Delta ZPE^{c}$	$-\Delta E_{el}$	$-\Delta E_0$	$-\Delta H$	$-\Delta G$	$-\Delta S$	μ
	Hartree	**kcal mol^{-1}**					**kcal mol^{-1} K^{-1}**	**Debye**
Met-Asn								
	1216.8706	0.9312	9.3358	10.2673	9.5971	6.4991	0.0104	4.2145
Asn-Met								
	1216.8712	0.0019	9.7425	10.1462	7.1084	10.9563	0.0101	4.0572

Table 2. The values of bond lengths(r in Å), bond angles (θ in degree) and dihedral angles(φ in degree) related to peptide backbone of Met-Asn and Asn-Met dipeptides at B3LYP/6-311+G** level of theory in the gas phase.

	r_{1-5}	r_{1-2}	r_{1-3}	r_{2-4}	r_{2-6}	θ_{215}	θ_{124}	θ_{126}	θ_{426}	φ_{5124}	φ_{3126}	φ_{5126}
Met-Asn												
	1.011	1.351	1.454	1.231	1.531	121.1	122.5	116.8	120.7	179.2	-0.64	-0.53
Asn-Met												
	1.016	1.361	1.450	1.223	1.537	116.8	122.9	115.4	121.7	-165.2	170.1	13.5

In this study, Effects of isomerism and side chain mutation on NMR and NQR tensors of ^{15}N and ^{17}O nuclei of structures of Met-Asn and Asn-Met dipeptides were investigated at B3LYP/6-311+G** Level of theory(see Table 3). As expected, the NMR and NQR tensors were severely affected by chemical environment (by what it was bonded to and by the type of bond to its neighbor) and intra-inter residual interactions such as resonance interactions. The results revealed that there were no identical chemical environments for nitrogen and oxygen nuclei in the considered structures. However, nitrogen and oxygen nuclei of structural isomers in Met-Asn and Asn-Met dipeptides presented different intra-molecular interactions, nuclear quadrupole coupling constant (χ), and isotropic chemical shielding values (σ_{iso}) as they were located in different positions in the two structures. Therefore, nitrogen and oxygen atoms with identical labels in the considered dipeptides revealed varying resonance energies, NQR tensors, and chemical shielding values around themselves. So that, nitrogen nuclei were more shielded than oxygen nuclei in both dipeptides. Table 3 showed that N_{10} (amino nitrogens) and O_{14} (acidic oxygens) nuclei had the highest chemical shielding (σ_{iso}), while N_1 (peptide nitrogens) and O_8 (amidic oxygens) ones had the lowest chemical shielding among nitrogen and oxygen nuclei in Met-Asn and Asn-Met structures. Comparison of the isotropic chemical shielding values around the nitrogen nuclei of two structural isomers represented that σ_{iso} around N_1 and N_{10} nuclei of Asn-Met was higher than it was around the identical nuclei of Met-Asn structure while N_9 nuclei in Met-Asn had higher chemical shielding than it had in Asn-Met. Moreover, the order of σ_{iso} values around nitrogen and oxygen nuclei of dipeptide structures was amino nitrogen >amidic nitrogen >peptide nitrogen (N_{10}> N_9> N_1) and O_{14}>O_4>O_{13}>O_8, respectively. In this regard, the EFG calculations indicated that N_{10} (amino nitrogens) and O_8 (amidic oxygens) nuclei in two isomers had the highest values of nuclear quadrupole coupling constant among nitrogen and oxygen nuclei (χ values of N_{10} and O_8 nuclei in Met-Asn isomer were

5.215472,9.804410 and in Asn-Met one were 5.278545 and 9.479568 MHZ, respectively.). Also, N_{10} nuclei in Asn-Met and O_8 nuclei in Met-Asn had the highest values of χ among nitrogen and oxygen nuclei of considered dipeptides (see Table 4). In addition, nitrogen nuclei in Asn-Met isomer had higher values of χ and q_{zz} in comparison to Met-Asn one. The order of χ values of nitrogen and oxygen nuclei in considered dipeptides was amino nitrogen > peptide nitrogen > amidic nitrogen (N_{10} > N_1 > N_9) and amidic oxygen > acidic oxygens > peptide oxygen (O_8>O_{14}>O_{13}>O_4).

Table 3. The calculated NMR parameters of ^{15}N and ^{17}O nuclei (isotropic, σ_{iso} and anisotropic, $\Delta\sigma$, chemical shielding (in ppm)) in structure of Met-Asn and Asn-Met dipeptides at B3LYP/6-311+G** level of theory in the gas phase

	N_1	**N_9**	**N_{10}**	**O_4**	**O_8**	**O_{13}**	**O_{14}**
Met-Asn							
σ_{iso}(ppm)	110.8185	145.8279	209.8154	-37.7915	-102.0491	-77.5625	124.2668
$\Delta\sigma$(ppm)	122.3902	119.5060	48.5102	585.8630	577.0469	540.1553	181.1605
Asn-Met							
σ_{iso}	113.3757	144.8615	220.7606	-57.6438	-74.1096	-75.6903	113.7278
$\Delta\sigma$	124.3307	138.1702	49.9072	638.9935	600.7447	528.4074	199.4805

Table 4. The NQR parameters calculated and principal components of the EFG tensors of nitrogen and oxygen nuclei in Met-Asn and Asn-Met dipeptides at B3LYP/6-311+G** level of theory in the gas phase

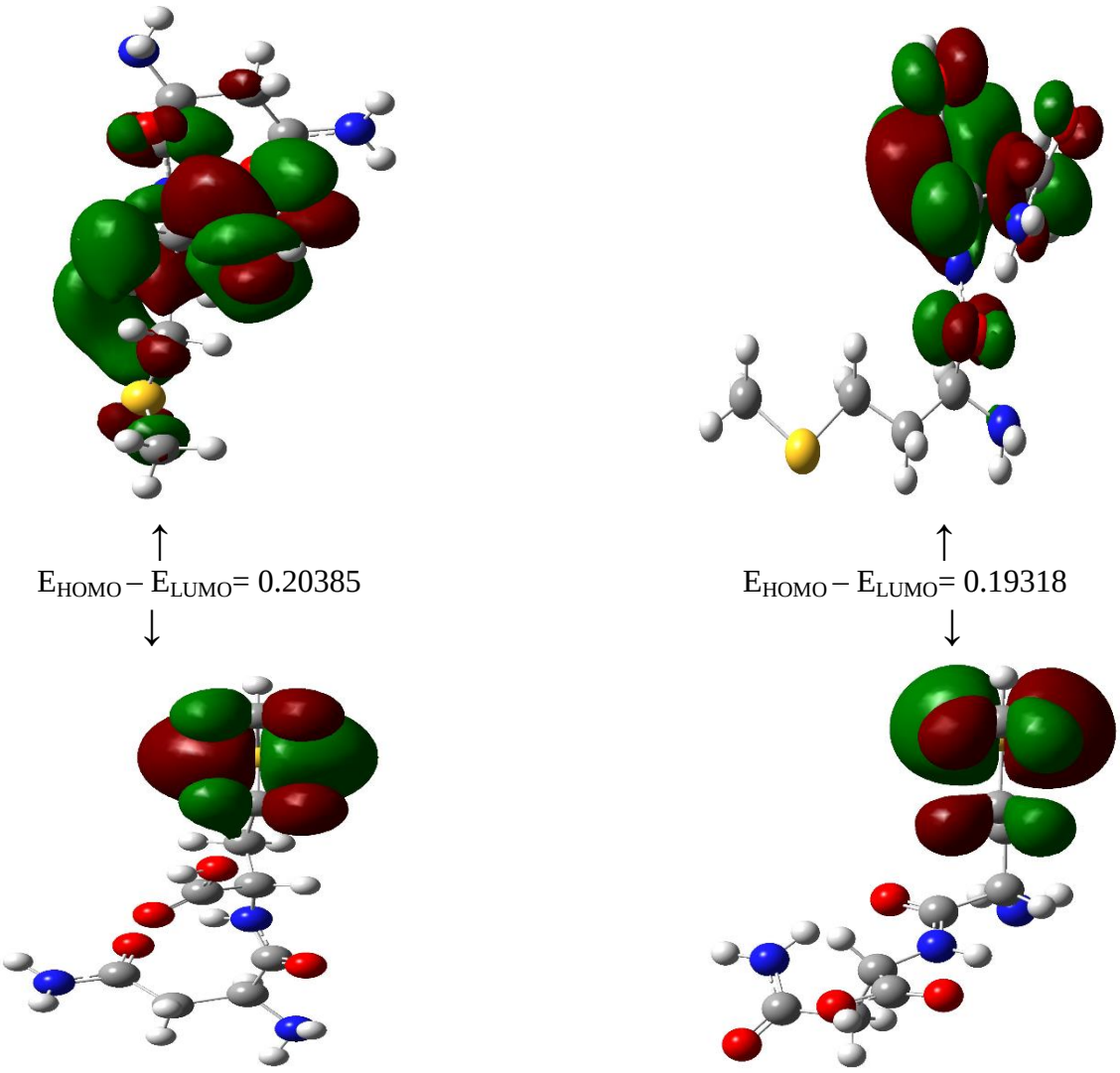
Tautomer	Nuclei	$q_{xx\ (Vm^{-2})}$	$q_{yy\ (Vm^{-2})}$	$q_{zz\ (V\ m^{-2})}$	$e^2\ q_{zz}\ Q/\ h$ (MHZ)	η_Q	ν_+ (MHZ)	ν_-(MHZ)	ν_0(MHZ)
Met-Asn									
	N_1	-3.346874	-5.299462	8.646336	4.273304	0.2259	3.446236	2.9637195	0.482516
	N_9	-3.145793	-5.012042	8.157825	4.031866	0.2288	3.715677	2.793307	0.922370
	N_{10}	-3.976346	-6.576314	10.552660	5.215472	0.2464	4.875345	3.590357	1.284988
	O_4	-5.769200	-8.895179	14.664378	9.070161	0.2132	7.285989	6.319254	0.966735
	O_8	-7.884903	-7.966587	15.851491	9.804410	0.0052	7.365940	7.340677	0.025263
	O_{13}	-6.515950	-8.316918	14.832868	9.174376	0.1214	7.159261	6.602300	0.556961
	O_{14}	3.7706972	11.283309	-15.054006	9.311153	0.4990	8.145034	5.821696	2.323338
Asn-Met									
	N_1	-3.173575	-5.690489	8.864064	4.3809121	0.2839	3.596670	2.974699	0.621971
	N_9	-4.107015	-4.681904	8.788910	4.343768	0.0654	3.470923	3.044729	0.426194
	N_{10}	-3.952247	-6.728041	10.680278	5.278545	0.2599	4.301881	3.615936	0.685945
	O_4	-7.034352	-7.938339	14.972691	9.261025	0.9040	7.085552	6.805983	0.279569
	O_8	-6.780816	-8.545470	15.326296	9.479568	0.1151	7.382545	6.836809	0.545736
	O_{13}	-6.401712	-6.451806	14.853507	9.187141	0.1313	7.191871	6.588843	0.603028
	O_{14}	3.566331	11.434715	-15.001048	9.278397	0.5245	8.175479	5.742115	2.433364

NBO analysis also showed that lone pair electrons of peptide nitrogens (N_1) had the highest values of resonance energies associated with LP(1)N→ σ^* or π^* interactions and they had the lowest values of negative charge and occupancy among nitrogen nuclei of two isomers. Moreover, lone pair electrons of acidic oxygens (O_{13} and O_{14} oxygens) had the highest values of resonance energy associated with LP O $\rightarrow\sigma^*$ or π^* interactions among oxygen nuclei (see Table 5) and the order of resonance energies values of nitrogen lone pairs was peptide nitrogen > amidic nitrogen > amino nitrogen (N_1> N_9> N_{10}) in the studied dipeptides. The mentioned order for resonance energy values of nitrogen atoms in two dipeptides was exactly the opposite of the order of the values of nitrogen lone pair occupancies, atomic charges and the chemical shielding values around nitrogen nuclei. In other words, by increasing contribution of nitrogen lone pair electrons in intra-molecular resonance interactions, NMR chemical shielding around nitrogen nuclei decreased. Furthermore, the results represented that the resonance energies related to the intra-molecular interactions of lone pair electrons of peptide and amidic nitrogens (LP N_1 and LP N_9) in Met-Asn were higher in comparison to Asn-Met, while the values of resonance energies related to the intra-molecular interactions of lone pair electrons of amino nitrogen (LP N_{10}) in Asn-Met was higher than it was in Met-Asn isomer.

In this study, chemical reactivity indices were also calculated using NBO analysis (Table 6). The results showed that the energy difference of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) orbitals in Asn-Met isomer was slightly higher than Met-Asn and the energy difference between them in two isomers was about 0.01 electron volts (Fig.3). NBO calculations also represented that other parameters calculated through HOMO and LUMO energies such as chemical potential, electron affinity, electronegativity, chemical hardness and chemical softness were very close to each other in the considered dipeptides. However, it could be deduced that isomerism and side chain mutation had not an effective role on the chemical reactivity of Met-Asn and Asn-Met dipeptides.

Table 5. Calculated natural atomic charges, lone pair orbital occupancies and total resonance energies (in kcal mol^{-1}) of nitrogen atoms in structure of Met-Asn and Asn-Met dipeptides at B3LYP/6-311+G** level of theory in the gas phase

	Met-Asn			**Asn-Met**		
Parameters	**Natural Charges**	**Occupancies**	**ΣE2 (kcal mol^{-1})**	**Natural Charges**	**Occupancies**	**ΣE2 (kcal mol^{-1})**
LP(1) N_1→ σ* or π*	-0.62816	1.68141	82.44	-0.64442	1.70728	68.69
LP (1) N_9 → σ* or π*	-0.82912	1.73696	62.46	-0.79459	1.74795	51.25
LP (1) N_{10} → σ* or π*	-0.84036	1.95388	11.1	-0.84388	1.95128	12.45
LP(1) O_4→ σ* or π*	-0.68864	1.97168	6.51	-0.64900	1.97859	-
LP(2) O_4→ σ* or π*		1.87388	45.59 52.1		1.86624	45.12
LP(1) O_8→ σ* or π*	-0.62445	1.97793	4.07	-0.66341	1.97449	5.24
LP(2) O_8→ σ* or π*		1.87060	44.61		1.87438	43.93
LP(1) O_{13}→ σ* or π*	-0.60768	1.97838	3.83	-0.60610	1.97849	3.89
LP(2) O_{13}→ σ* or π*		1.85003	51.64		1.84665	52.43
LP(1) O_{14}→ σ* or π*	-0.67153	1.97444	7.78	-0.69117	1.97666	7.23
LP(2) O_{14}→ σ* or π*		1.81455	47.85		1.82228	44.74



a) Asn-Met **b) Met-Asn**

Fig. 3. The representation of molecular orbitals HOMO and LUMO for a) Asn-Met and b) Met-Asn dipeptides.

Table 6. The calculated values of HOMO, LUMO energies (eV), HOMO-LUMO gap, ionization potential (I),electron affinity (A), absolute electronegativity (χ), chemical hardness(η) and chemical softness(S) of Met-Asn and Asn-Met dipeptides at B3LYP/6-311+G** level of theory in the gas phase.

	E_{HOMO}	E_{LUMO}	ΔE (eV)	I(eV)	A(eV)	η (eV)	χ(eV)	S(eV^{-1})
Met-Asn								
	-0.2320	-0.0388	-0.193۲	0.2320	0.0388	0.096٦	0.1354	0.048۳
Asn-Met								
	-0.228٦	-0.0247	-0.203۹	0.228٦	0.0247	0.1019	0.114۳	0.05۱۰

4. CONCLUSION

The mutation issue has been an important research tool for protein engineering at macroscopic level. The protein properties can be changed and new functionalities can be introduced. However, we investigated one of methionine and asparagines dipeptides, Met-Asn, and studied the effects of side chain mutation and isomerism on the structure and stability of its neutral configuration using quantum mechanics methods at a microscopic level. These small peptides can be considered as an example of a small model bio-molecule with mutation phenomena analogous to the effect of sequence mutation on protein conformation. The results represented that isomerism and changing the sequence of monomers in a dipeptide greatly affect the relative stability and binding energy. This phenomenon also affects the values of NMR and NQR tensors of electronegative nuclei of oxygen and nitrogen in the structure of two isomers. On the other hand, chemical reactivity indices calculated by NBO analysis indicated that changing the sequence of monomers in a dipeptide has a negligible effect on the chemical reactivity and the values of electron affinity energies, electronegativity, chemical hardness and softness of considered isomers were the same.

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