A quantum-chemical study on 3,3'-bi(4H-1,2,4-triazole)

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The conformational analysis of 3,3'-bi(4H-1,2,4-triazole) molecule is performed by semiempirical methods such as MNDO, AM1 and PM3, and the planar trans conformation is found to be the most stable conformation of the molecule. Moreover, the electronic properties of 3,3'-bi(4H-1,2,4-triazole) and the effect of conformational change on electronic and geometric properties have also been investigated. The electronic properties and conformations of monoprotonated species derived from the molecule have also been studied. The proton affinity for the different nitrogens atoms of the molecule have been calculated and the possible protonation centers determined. Furthermore, the complex formation ability of the molecule with metal cations have been evaluated and discussed.

The quantum-chemical investigation of 3,3'-bi(1H-1,2,4-triazole) and 3,4'-bi(4H-1,2,4-triazole) systems have recently been reported by us[1,2]. In continuation of our interest in the quantum-chemical study of bitriazole systems, we wish to report the results related for the investigation of 3,3'-bi(4H-1,2,4-triazole) molecule. It is obvious that tautomeric equilibriums are established by a lot of heterocyclic compounds. In the investigation of the physical and chemical properties of such compounds, it is important to take into consideration of the tautomeric interconversion. In fact, the stability and related properties of the tautomers of a selected molecule are important from the point of some chemical aspects such as substitution, cyclocondensation, alkylation and complex formation. In this connection, the relative stability of 1H-1,2,4-triazole and 4H-1,2,4-triazole tautomers has not been definitely determined yet[3]. However, 1H-tautomer of 1,2,4-triazole molecule has been found to be less stable than 4H-tautomeric form according to calculation by MNDO, AM1 and PM3 methods[4-6]. For this reason, it appeared interesting to investigate the relative stability of 3,3'-bi(4H-1,2,4-triazole) (A) and 3,3'-bi(1H-1,2,4-triazole) (B) tautomers. On the other hand, the metal complexes of 1,2,4-triazole and its derivatives have been known[7-9]. Hence, the complex formation of the 3,3'-bi(1,2,4-triazole) molecule is also possible. The complexing ability

of the ligands is essentially related to their ionisation potentials and proton affinities[10]. But, the conformation assumed upon complexation for a flexible molecule often does not correspond to the equilibrium conformation of the free ligand[11]. For this reason, it appeared important to investigate the conformations and electronic properties of 3,3'-bi(1,2,4-triazole) system containing various competing protonation sites. The experimental determination of the protonation centers of the molecules having heteroatoms different from each other in position is generally difficult[12,13]. In fact, the experimental investigation of the conformational behaviour of such a molecule only gives some evidence about the stable conformations. Hence, it appeared important to perform the conformational analysis and to determine the protonation parameters of 3,3'-bi(1,2,4-triazole) molecule theoretically. The selectivity of complex formation ability of 3,3'-bi(1,2,4-triazole) molecule containing competing coordination centers can be theoretically evaluated and the stability of the complexes predicted. On the other hand, the effect of conformational change on the electronic properties can be revealed by the theoretical investigation of the molecule. Due to the effect of the interactions between the two 1,2,4-triazole rings on the properties of the 3,3'-bi(1,2,4-triazole) system, the theoretical investigation of the bitriazole system is also important. In addition, the
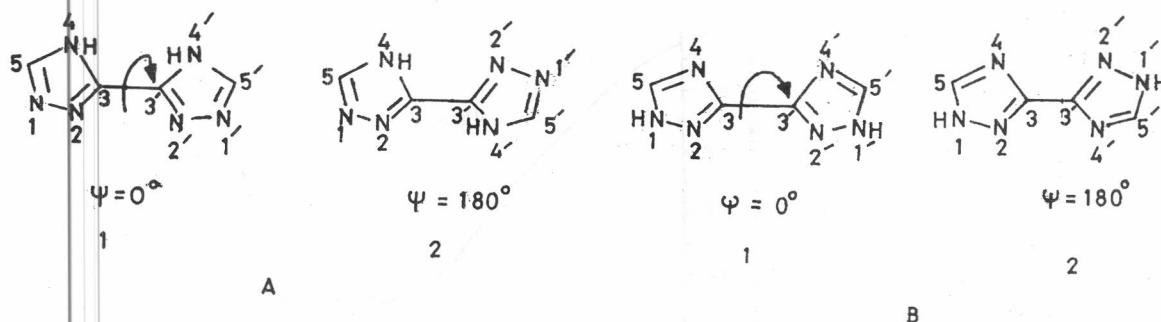
Scheme I

formation mechanisms of the complexes formed by a flexible ligand such as 3,3'-bi(1,2,4-triazole) with various metal cations also appeared interesting to investigate theoretically. It is known that semiempirical methods as well as ab initio methods have been used widely for the conformational analysis and for the calculations of the protonation parameters of heterocycles and biheterocycles[4-6,11,14-33]. Also, PM3 and AM1 methods are generally used as reliable routes to calculate the proton affinities of various heterocyclic compounds[21-30]. In our previous study, the conformations and electronic properties of 3,3'-bi(1H-1,2,4-triazole) (tautomeric form B) have been studied (Scheme I)[1]. In the present study, the semiempirical methods MNDO[34], AM1[35] and PM3[36] have been used for the detailed investigation of the conformations and electronic properties of 3,3'-bi(4H-1,2,4-triazole) molecule (tautomeric form A) (Scheme I). The proton affinity of the molecule was calculated by AM1 and PM3 methods for different nitrogen atoms. The electronic properties of the Fe^{2+} and Zn^{2+} complexes of the tautomers A and B of 3,3'-bi(1,2,4-triazole) molecule were investigated using ZINDO/1[37] and PM3 methods. Moreover, the stability and mechanism of formation of these complexes were also studied. All calculations related to the study were performed using HyperChem 4.5 program with a IBM PC/AT 486 DX4-100 computer.

Results and Discussion

3,3'-bi(4H-1,2,4-triazole) molecule may exist in different conformations due to its flexibility (Scheme I-A). For this reason, the conformational analysis of the molecule was performed with full geometry optimization using MNDO, AM1 and PM3 methods. According to the results obtained by the three methods, it seems that the planar trans conformation of the molecule (ρ = 180 °) is the most stable conformation (Scheme 1-A2). In order to investigate the effect of internal rotation to the energy of molecule, the potential curves for internal rotation around the central C_3-C_3, bond are drawn in Figure 1 using the three semiempirical routes with geometry optimization. It is easy to see that the energy maximum of the molecule corresponds to the planar *cis* conformation (φ=0°) (Scheme I-A1). The results obtained for the 3,3'-bi(4H-1,2,4-triazole) molecule by semiempirical routes in the present study are in confirmity with the results obtained for the conformations of some conjugated biheterocyclic systems by semiempirical and *ab initio* methods[11,16,19]. The calculated total energies (E_{tot}), the heats of formation (ΔH_f^o), the length of C_3-C_3, single bond (r_{c-c}) and the distances between the hydrogen atoms of NH groups ($r_{H....H}$) for the *cis* (A1) and *trans* (A2) conformations of the molecule are given in Table I. As seen from Table I, the total energy difference between the *cis*- and *trans* conformations is found to be 8.464 kcal/mol, 8.731 kcal/mol and 11.308 kcal/mol according to MNDO, AM1 and PM3, respectively.

The stability effect of the conjugation between the triazole rings of 3,3'-bi(4H-1,2,4-triazole) system is almost the same in the *trans* and *cis* conformations. In order to explain the difference between the stabilities of these conformations, it is necessary to take into account the steric and electronic interactions between ortho-groups. In fact for 3,3'-bi(4H-1,2,4-triazole) molecule, the repulsive interactions between N....N and NH....HN ortho-groups exist in *cis* conformation. In contrast, the *trans* conformation involves the attractive interactions between NH....N ortho-
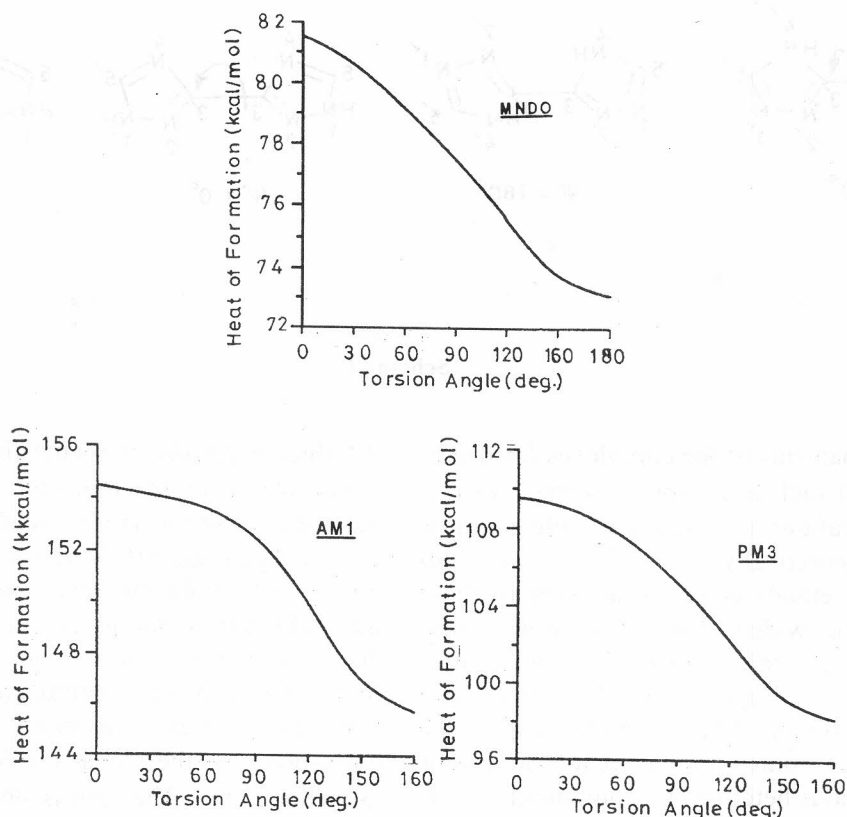
Figure 1 — Internal rotational potential curves of 3,3′-bi(4H-1,2,4-triazole) obtained by MNDO, AM1 and PM3 methods

Table I—Total energies, heats of formation, bond lengths and distances between the hydrogen atoms of NH groups

Method	Structure	E_{tot} (kcal/mol)	ΔH_f^o (kcal/mol)	R_{c-c} (Å)	$R_{H\ldots H}$ (Å)
MNDO	A1	−41730.423	81.593	1.445	2.615
	A2	−41738.887	73.092	1.443	4.843
AM1	A1	−41617.634	154.483	1.447	2.472
	A2	−41626.365	145.752	1.445	4.803
PM3	A1	−34735.041	109.552	1.442	2.567
	A2	−34746.349	98.243	1.436	4.823

groups (Scheme I-A). In other words, there exist lone pair-lone pair and hydrogen-hydrogen interactions in cis and lone pair-hydrogen interactions in trans conformations. Since the calculated $r_{H\ldots H}$ values (Table I) are nearly equal to the sum of van der Waals radii of hydrogen atoms (~ 2.4 Å), the steric interaction between the hydrogen atoms may be possible in cis conformation.

Furthermore, the repulsive interactions between the NH hydrogens must be considered due to these atoms possess positive charge (Q_H=+0.217). The results obtained from the three semiempirical

routes indicate that the length of C_3-C_3, covalent bond in trans conformation is shorter than that of in cis conformation (Table I).

In our previous study, the conformational analysis of the tautomeric system B has been performed by MNDO, AM1 and PM3 methods and the stable conformations have been determined[1]. A comparison of the results obtained from the three methods reveals that 3,3′-bi(4H-1,2,4-triazole) (tautomer A) is more stable than 3,3′-bi(1H-1,2,4-triazole) (tautomer B). Because the 1,2,4-triazole molecule generally exist in 1H- and 4H forms in gas and liquid phases[38], it is possible to consider that 3,3′-bi(1,2,4-triazole) molecule involves tautomeric forms A and B in the same media. In order to investigate the electronic properties and to find out the reaction contents, cis (A1) and trans (A2) conformations of 3,3′-bi(4H-1,2,4-triazole) system were studied using MNDO, AM1 and PM3 methods. The energies of frontier molecular orbitals (E_{HOMO} and E_{LUMO}, in eV) and dipole moments (μ, in Debye) of the two conformations were calculated. For example, according to

MNDO, the calculated values of A1 and A2 structures were respectively found as −9.574 and −9.572 (E_{HOMO}), −0.641 and −0.597 (E_{LUMO}), and 9.518 and 0.0 (μ). The results obtained from the three methods indicate that the ionisation potential (IP=-E_{HOMO}) of *cis* conformation is relatively higher than that of *trans* conformation. Experimental ionization potential of 1,2,4-triazole molecule has been reported to be 10.00 eV[39]. The ionisation potential of 4*H*-1,2,4-triazole was calculated using MNDO, AM1 and PM3 routes and was found to be 10.025 eV, 10.033 eV and 10.215 eV, respectively. A comparison of the values calculated for 3,3'-bi(4*H*-1,2,4-triazole) and 4*H*-1,2,4-triazole molecules in the present study reveals that the bitriazole molecule has a relatively lower ionisation potential than that of 4*H*-1,2,4-triazole, Moreover, the ionisation potential of 3,3'-bi(1*H*-1,2,4-triazole) (B) calculated by the three semiempirical methods is also lower than that of 3,3'-bi(4*H*-1,2,4-triazole) (A) tautomer[1].

According to E_{HOMO} values calculated for *cis* and *trans* conformations of tautomers A and B by each method (Scheme 1), tautomer B posseses more electron-donor character than the other tautomer. On the other hand, the electron-donor character of *cis* conformations of tautomers A and B is lower than that of the *trans* conformations.

The analysis of the frontier orbitals (HOMO·and LUMO) of 3,3'-bi(4*H*-1,2,4-triazole) molecule reveals that these orbitals in two conformations are formed by the P_Z atomic orbitals of carbon and nitrogen atoms. In the case of HOMO, the electron density (q_i) is highest at $C_5(C_{5'})$, $C_3(C_{3'})$, $N_2(N_{2'})$, $N_1(N_{1'})$ atoms for trans conformation. (According to MNDO, 0.164, 0.149, 0.105 and 0.076, respectively). However, $N_4(N_{4'})$ and $N_1(N_{1'})$ atoms have the highest atomic charges (Q_i) in the molecule, as shown in Scheme II.

The results so obtained show that the electronic properties of 3,3'-bi(4*H*-1,2,4-triazole) molecule depend on its conformational structure.

The determination of protonation sites of 3,3'-bi(4*H*-1,2,4-triazole) molecule containing different proton-acceptor centers is important for the investigation of the basicity and finding out the coordination centers. The N-4 and N-4' atoms are predicted to be the main centers of the bitriazole molecule for the electrophilic attack of hydrogen in accordance with the negative charge distribution on
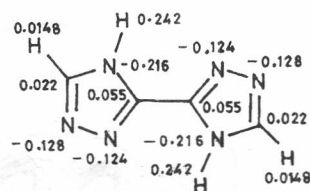
Scheme II

nitrogen atoms (Scheme II). However, negative atomic charges are also high on N-1 and N-1' atoms. In order to find out the way of approach and the center of attack of hydrogen to 3,3'-bi(4*H*-1,2,4-triazole) molecule, the electrostatic potentials (MEP) (in kcal/mol) of the two conformations were calculated by the three semiempirical methods. The electrostatic potential contour maps (Figure 2) indicates that the electrophilic attack of proton predominantly occurrs on N-2/N-2' and N-1/N-1' atoms in *cis* and *trans* conformations, respectively.

To determine the exact protonation centers of 3,3'-bi(4*H*-1,2,4-triazole), the proton affinities for the different nitrogen atoms of the molecule were calculated by means of AM1 and PM3 routes. The stable conformations for the monocations formed by the protonation of each nitrogen atom of the molecule were determined, and the heats of formation (ΔH_f^o, in kcal/mol) were calculated with full geometry optimization by AM1 and PM3 methods. For example, the ΔH_f^o values of protonated forms of A1 and A2 were respectively found as 317.078 and 308.932 for N-1, 311.892 and 311.431 for N-2, and 352.368 and 339.068 for N-4, using AM1 method. The results reveal that the *cis* conformations of the monocations are more stable than the others. The conformational analysis of these monoprotonated species indicates that these monocations have planar structures. In spite of the fact that the total energy difference between the two conformations of the neutral molecule is relatively high, the difference between the total energies of *cis* and *trans* conformations of the N-2 protonated species is very low (0.43 kcal/mol by AM1 method and 0.59 kcal/mol by PM3 method).

The proton affinity (PA) values (in kcal/mol) for the different nitrogen atoms of 3,3'-bi(4*H*-1,2,4-triazole) molecule were calculated using the equation given below.

$$PA = 367.2 + \Delta H_f^o(B) - \Delta H_f^o(BH^+)$$

Here, PA is proton affinity, $\Delta H_f^o(B)$ is the heat of formation for the molecule, $\Delta H_f^o(BH^+)$ is the heat
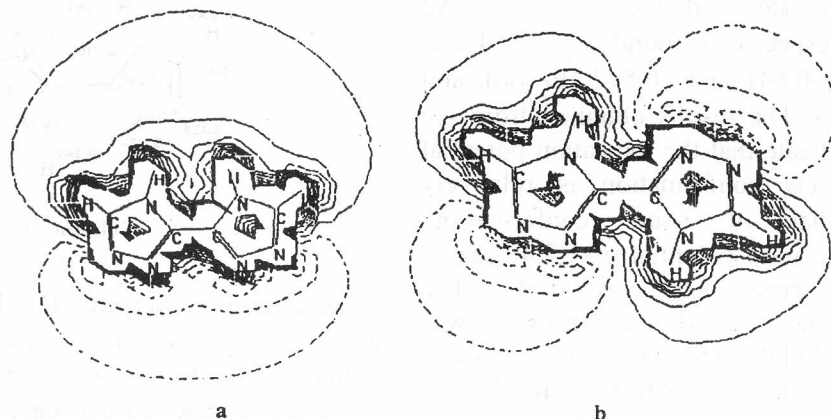
Figure 2 — Electrostatic potential contour maps of the cis (a) and trans (b) conformations calculated by means of MNDO

of formation for the cation and 367.2 is the heat of formation for the proton (kcal/mol)[40].

The results obtained indicate that the proton affinities of 3,3′-bi(4H-1,2,4-triazole) molecule calculated for N-2 atom in *cis* conformation (according to AM1 and PM3, 209.79 and 213.37, respectively) and for N-1 atom in *trans* conformation (according to AM1 and PM3, 204.02 and 206.65, respectively) are higher than those of the other nitrogens. Hence, 3,3′-bi(4H-1,2,4-triazole) molecule is predicted to protonate at N-2 and N-1 atoms in *cis* and *trans* conformations, respectively.

The proton affinity values of the bitriazole molecule calculated for N-1 and N-2 atoms are relatively higher in *cis* conformation than those of in *trans* conformation. It is easy to see from the results that the proton affinity values of the molecule calculated for N-1 atom in *cis* conformation are nearly equal to those of in *trans* conformation. But, the values obtained for N-2 atom in *cis* conformation are relatively different from the others. As a result of the interaction between the lone pair electron orbitals of N-2 and N-2′ atoms through space during the conversion of the molecule from trans conformation to *cis* form, the individual protonation centers join in a common system. Hence, the MEP gradient (Figure 2) and proton affinity of the bitriazole molecule increase when trans form changes to *cis* conformation. This behaviour indicates that the reactivity of the molecule increases and it becomes a more basic molecule in *cis* conformation.

In our previous study[1] the proton affinity values of 3,3′-bi(1H-1,2,4-triazole) molecule have been calculated for the different nitrogen atoms in *cis* and *trans* conformations by AM1 and the proton affinity related to N-4 atom (Scheme I-B) has been determined as the highest value : 219.7 kcal/mol (*cis*) and 217.64 kcal/mol (*trans*). Comparing these values with those of 3,3′-bi(4H-1,2,4-triazole) molecule, it seems that the tautomeric form B of 3,3′-bi(1,2,4-triazole) molecule is more basic than A. Thus, the monocation formed by N-4 protonation of 3,3′-bi(1H-1,2,4-triazole) in *cis* conformation is more stable than the one formed by N-2 protonation of 3,3′-bi(4H-1,2,4-triazole) molecule in *cis* form.

In accordance with the proton affinity values of 3,3′-bi(4H-1,2,4-triazole) molecule containing several nitrogen atoms differing from each other in position, the electrophilic attack of metal ions to the molecule probably occurs at N-1/N-1′ and N-2/N-2′ atoms in *cis* and *trans* conformations, respectively. The complex formation ability of the bitriazole molecule in *cis* conformation is relatively higher than that of in *trans* form according to the proton affinity values. On the other hand, it is plausible to consider that the complex formation ability of 3,3′-bi(4H-1,2,4-triazole) molecule is relatively lower than that of 3,3′-bi(1H-1,2,4-triazole) in accordance with proton affinities. In other words, the tautomeric form B of 3,3′-bi(1,2,4-triazole) has a higher complex formation ability than tautomer A and its metal complexes are more stable than those of tautomer A.

In order to confirm the results obtained, the electronic properties of the predicted metal complexes of tautomers A and B (Scheme I) were investigated using ZINDO/1 and PM3 methods, and the formation mechanism of the complexes were theoretically studied. In this connection, the electronic properties of $Fe(3,3'-Bi-4H-Tr)^{2+}$ type complexes formed by tautomer A with Fe^{2+} ion were investigated with full geometry optimization using ZINDO/1 method. Total energies (E_{tot}, in kcal/mol), heats of formation (ΔH_f^o, in kcal/mol), positive charge densities of iron (Q_{Fe}) and bond lengths (r_{Fe-N}, in Å) for the complexes containing Fe^{2+} ion attached to N-1/N-2 (I) and N-2/N-2' (II) (Scheme I-A) were calculated. The complex I having Fe^{2+} ion attached to N-1/N-2 may exist in cis and trans form. The cis form of complex I is 2.124 kcal/mol more stable than the other. But, complex II is 78.452 kcal/mol more stable than the cis form of complex I (For complexes I-cis, I-trans and II, E_{tot} values were found as −71891.159, −71889.035 and −71969.611). ΔH_f^o and Q_{Fe} values of the same complexes were respectively calculated as −2576.985, −2574.904, −2655.980 and 1.090, 1.073, 0.915. All the complexes have approximately planar structures. The $Fe-N_1$ and $Fe-N_2$ bond lengths of complexes I-cis and I-trans were found as 2.038, 2.017 and 1.977, 1.989, respectively. The $Fe-N_2$ ($Fe-N_2'$) bond length of the complex II was calculated as 2.007. Complex II corresponding to the cis form of the bitriazole molecule is the most stable one among the $Fe(3,3'-Bi-Tr)^{2+}$ type complexes.

It is reasonable that 3,3'-bi(4H-1,2,4-triazole) molecule may predominantly exist in trans conformation due to the more stability of this form than cis conformation. Obviously, each of the two conformations (Scheme I, A1 and A2) found in an equilibrium may participate in the complex formation with metal cations. It is possible to consider that complex I (trans) initially formed is converted to complex I (cis) because of the stability of the latter. Furthermore, it is also possible to take into consideration that complex I (cis) rearranges to give complex II due to much more stability of the latter. Hence, the formation of the most stable complex can be considered to occur via two different mechanisms. One of these routes is the direct attachment of Fe^{2+} ion to the N-2/N-2' atoms of cis conformation of the bitriazole molecule (Scheme I-A1). The other route involves the attachment of Fe^{2+} ion to the N-1/N-2 atoms of trans conformation (Scheme I A-2), subsequently the conversion into cis form and finally the rearrangement the latter complex to afford complex II.

The total energy difference between cis and trans conformations of 3,3'-bi(1H-1,2,4-triazole) molecule (tautomer B) has been reported to be ~ 0.958 kJ/mol[1]. These conformations exist in approximately the same proportions in normal conditions[4]. For this reason, the two conformations can participate in the complex formation with metal ions. According to the proton affinity values of 3,3'-bi (1H-1,2,4-triazole) molecule having several nitrogen atoms differing from each other in position (Scheme I-B)[1], a complex containing M^{2+} ion attached to N-4/N-4' atoms is predicted to be more stable than those having the metal ion attached to N-2/N-2' or N-4/N-2' atoms. In order to determine the relative stability of the Fe^{2+} complexes of the molecule in cis and trans conformations, their electronic properties were investigated with full geometry optimization in the present study using ZINDO/1 method. Total energies (E_{tot}, in kcal/mol), heats of formation (ΔH_f^o, kcal/mol) positive charge densities of iron (Q_{Fe}) and bond lengths (r_{Fe-N}) for the $Fe(3,3'-Bi-1H-Tr)^{2+}$ type complexes containing Fe^{2+} ion attached to N-4/N-4' or N-2/N-2' in cis form and N-4/N-2' in trans form (complexes III, IV and V, respectively) were calculated. E_{tot} values of the complexes III, IV and V were found as −71989.675, −71977.893 and −71963.889, respectively. ΔH_f^o and Q_{Fe} values of the same complexes were respectively calculated as −2675.545, −2663.762, −2649.759 and 0.874, 0.875, 0.872. The $Fe-N_4$ ($Fe-N_4'$) bond length of complex I and $Fe-N_2$ ($Fe-N_2'$) bond length of complex II were found as 1.988 and 1.997, respectively. The $Fe-N_4$ and $Fe-N_2'$ bond lengths of complex III were respectively calculated as 1.993 and 1.990.

The results obtained indicate that the complexes have approximately planar structures and complex III is the most stable one among the $Fe(3,3'-Bi-1H-Tr)^{2+}$ type complexes. This situation reveals that 3,3'-bi(1H-1,2,4-triazole) molecule (tautomer B) has a higher complex formation ability with the metal ions in cis conformation, and the N-4/N-4'

atoms act as coordination centers. Moreover, it is easy to see that complex III is more stable than complex II. In other words, the tautomer B of 3,3'-bi(1,2,4-triazole) system can form more stable complexes with metal ions than tautomer A (Scheme I).

In addition, the electronic properties of Fe(3,3'-Bi-4H-Tr)$_2^{2+}$ (VI) and Fe(3,3'-Bi-1H-Tr)$_2^{2+}$ (VII) complexes formed by tautomers A and B of 3,3'-bi(1,2,4-triazole)molecule with Fe^{2+} ion were also investigated with full geometry optimization using ZINDO/1 method. The results obtained indicate that complexes VI and VII have pseudotetraedric structures. The average length of Fe-N bond in complexes VI and VII is 2.071 Å and 2.101 Å, respectively. The total energies (E_{tot}, in kcal/mol), heats of formation (ΔH_f^o, in kcal/mol) and positive charge densities of iron (Q_{Fe}) for the complexes VI and VII were found as −130525.332 and −130529.124, −5823.129 and −5820.982, and 0.225 and 0.201, respectively. E_{HOMO} (in eV) and E_{LUMO} (in eV) values of the same complexes were respectively calculated as −15.048, −15.0253 and −5.056, −4.828. The results indicate that, complex VII is 3.853 kcal/mol more stable than the other. Furthermore, the electronic properties of Zn(3,3'-Bi-4H-Tr)$_2^{2+}$ (VIII) and Zn(3,3'-Bi-1H-Tr)$_2^{2+}$ (IX) complexes formed by tautomers A and B with Zn^{2+} ions were also studied with full geometry optimization using PM3 route. So, it was found that complexes VIII and IX have also pseudotetraedric structures and complex VIII is 7.505 kcal/mol less stable than the other. The results obtained from the theoretical investigation of A and B tautomers of 3,3'-bi(1,2,4-triazole) molecule and their metal complexes indicate that tautomer A is more stable than tautomer B. Also, it has a higher proton affinity and complexing ability than the other tautomer. Tautomer B forms more stable metal complexes according to tautomer A.

Acknowledgement

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