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A Quantum-Chemical Investigation on 5,5′-BI(1H-1.2,4-Triazole))

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The conformational analysis of flexible 5,5′-bi(1H-1,2,4-triazole) molecule containing various reaction centers has been performed by the semiempirical methods MNDO,AM1 and PM3, and the internal rotation barrier calculated. The most stable conformation of the molecule has been determined to be the planar trans conformation. According to the three methods, 5,5'-bi(1H-1,2,4-triazole) molecule (C) has been found to be relatively more stable than its tautomer 3,3'-bi(1H-1,2,4-triazole)(B) and to be less stable than its other tautomer 3,3'-bi(4H-1,2,4-triazole)(A). Moreover, the electronic properties of 5,5'-bi(1H-1,2,4-triazole) molecule and the effect of conformational changing on electronic and geometric properties have also been investigated. To determine the protonation sites of the 5,5'- bitriazole system, the molecular electrostatic poential (MESP) of the molecule has been calculated. The electronic properties and conformations of the monoprotonated species formed from the protonation of the molecule have also been studied using AM1 and PM3 routes. The proton affinity of the 5,5'-bitriazole molecule has been calculated for the different nitrogens using AM1 and PM3 methods and the possible protonation centers have been determined. The electronic properties and the geometry of Fe^{2+} complex of the bitriazole system have been investigated by ZINDO/1 method and its formation process has been searched theoretically. According to proton affinity values, the complex formation ability of A, B and C tautomers of bi(1,2,4-triazole) system have been evaluated and the stabilities of their Fe^{2+} complexes have been determined by ZINDO/1 route. It has been found that tautomer B has a higher complex formation ability and forms more stable metal complexes relative to the other tautomers.

Keywords. 1,2,4-triazol, conformational analysis, protonation affinity, tautomerism, electronic properties

Introduction

In our previous studies, the quantum-chemical investigation of 3,3'-bi(1,2,4-triazole) and 3,4'-bi(1,2,4-triazole) systems have been reported [1−3]. In continuation of our interest in the quantum-chemical study of bi(1,2,4-triazole) systems, we wish to report the results obtained from the investigation of 5,5'-bi(1H-1,2,4-triazole) molecule. It is important that the tautomeric interconversion must be taken into consideration to investigate the physical and chemical properties of the compounds which exist in a tautomeric equilibrium.

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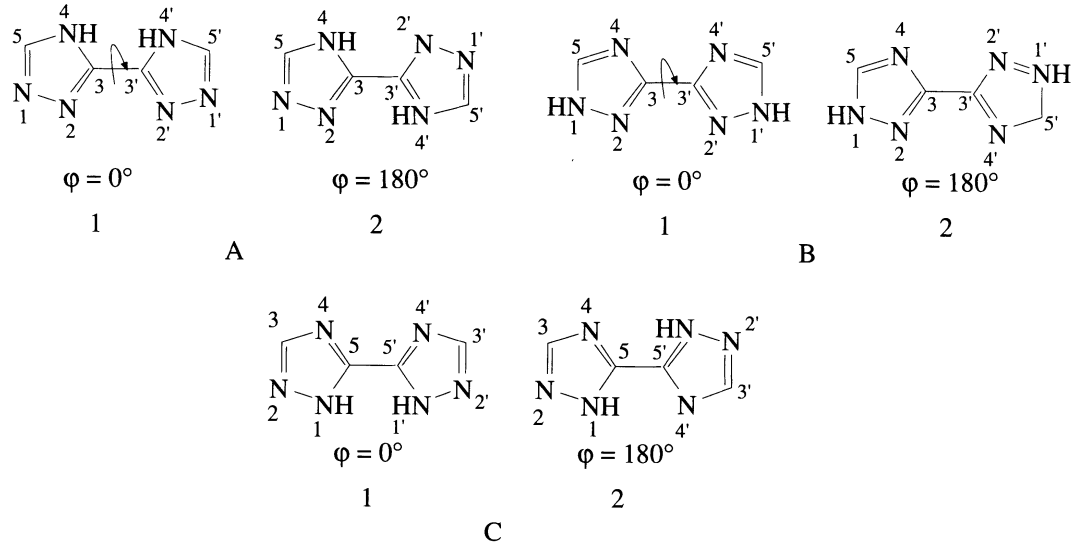
Obviously, a bi(1,2,4-triazole) molecule containing 1H and/or 4H forms of 1,2,4-triazole ring may exist in different tautomeric forms. Since the relative stability of 1H-1.2.4-triazole and 4H-1,2,4-triazole tautomers has not been defineitely determined yet, it apears interesting to investigate the relative stabilities of the tautomeric forms of a bi(1,2,4-triazole)[4]. However, it has been reported that 4H-tautomer of 1,2,4-triazole molecule is more stable than 1H-tautomer according to the calciulation MNDO, AM1 and PM3 semiempirical methods[5–7]. In order to determine the relative stabilities of the tautomeric forms of a bi(1,2,4-triazole) molecule, their quantum-chemical investigation and the determination of stable conformations appear to be important. On the other hand, a bi(1,2,4-triazole) molecule having 1H-1,2,4-triazole and 4H-1,2,4-triazole rings and containing several nitrogen atoms may have basic properties and may form various metal complexes. The complexing ability of a ligand essentially depends on its ionization potential and proton affinity[8]. But the conformation assumed upon complexation for a flexible molecule generally does not correspond to the equilibrium conformation of the free ligand[9]. Hence, it appears important to investigate the conformations and the electronic properties of a flexible bi(1,24-triazole) system having various competing protonation centers. However, the experimental determination of the protonation sites of the molecules containing hetero atoms differing from each other in position is often difficult[10,11]. In fact, some evidence about the stable conformations may be obtained from the experimental investigation of the conformational behavior of such a molecule[9]. For this reason, the conformational anaysis of the tautomeric forms of a bi(1,2,4-triazole) molecule and the theoretical calculation of the protonation parameters also appear important. According to the results obtained, the selectivity of the complexing ability of a bi(1,2,4-triazole) molecule having competing coordination centers can be theoretically evaluated and the stability of the metal complexes can be prognosticated. It is clear that conformational or tautomeric changing affects the electronic properties of the molecule, and this situation can be evaluated by the theoretical investigations. It also appears interesting to investigate the formation mechanism of the complexes formed by a flexible ligand such as a bi(1,2,4-triazole) with various metal ions. It is konwn that modern semiempirical methods as well as ab initio methods have been widely used for the conformatonal analyses and for the calculations of protonation parameters of heterocycles and biheterocylcles[5–7,9–23]. Moreover, AM1 and PM3 routes have been also used as reliable methods to calculate the proton affinities of various heterocyclic compounds [18,22].

In our previous studies, the electronic properties and conformations of 3,3'-bi(1H-1,2,4-triazole) (B) and 3,3'-bi(4H-1,2,4-triazole)(A) tautomers have been studied (Scheme 1). In the present study, our quantum-chemical studies on the bitriazole systems have been continued and the semiempirical methods MNDO[24], AM1[25], and PM3[26] have been used for the detailed investigation of the conformations and electronic properties of 5,5'-bi(1H-1,2,4-triazole) molecule (tautomer C) (Scheme 1). By using AM1 and PM3, the proton affinity of the bitriazole molecule has been calculated for the nitrogen atoms differing from each other in position. Furthermore, the stability and electronic properties of the Fe^{2+} complex of the 5,5'-bi(1H-1,2,4-triazole) molecule have been investigated by ZINDO/1 [27] method and he complex formation mechanism has been searched. All calculations were performed using HyperChem 3.0 program with a IBM PC/AT DX4-100 computer.

Results and Discussion

It is obvious that the 5,5'-bi(1H-1,2,4-triazole) molecule may exist in various conformational forms because of its flexibility. In order to determine the conformations of the molecule with minimum and maximum energy, its conformational analysis was performed by the aid of MNDO, AM1 and PM3 routes using Monte Carlo Multiple Minimum (MCMM) scheme[23]. According to the three methods, the conformation of the molecule

corresponding to the global minimum is planar trans conformation having an internal rotation angle (φ) of 180° (Scheme 1-C2). But the conormation with maximum enrgy which corresponds to the saddle point of the internal rotational potential curve of the bitriazole molecule is planar cis conformation (Scheme 1-C1) in accordance with the methods used. The results obtained for the conformations of 5,5'-bi(1H-1,2,4-triazole) molecule (C) by semiempirical methods in the study are in agreement with those obtained for the conformations of some conjugated biheterocyclic systems by semiempirical and ab initio methods[9,14,15]. The calculated total energies (E_{tot}) for cis (C1) and trans (C2) conformations of the moleule, the heats of formation (ΔH_f°), the lengths of C_5-$C_{5'}$ covalent bond (r_{C-C}), the distances between the hydrogens of NH groups ($r_{H\cdots H}$) and internal rotation barriers (ΔE) are given in Table 1.



Scheme 1.

In fact, the stability of biheterocyclic systems depends on the conjugation between the heterocyclic rings and the interactions between the atoms or groups found in o-position of the rings. The conjugation between the triazole rings of 5,5'-bi(1H-1,2,4-triazole) system is almost the same in the planar cis and trans conformations. Trans conformation is more stable than cis form, and the steric and electronic interactions between ortho groups play an important role on the stabilities of conformations. Thus, the 5,5'-bi(1H-1,2,4-triazole) molecule involves the repulsive interactions between N···N and NH···HN ortho groups in cis conformation and attractive interactions between NH···N ortho groups in trans conformation (Scheme 1-C). In other words, lone pair-lone pair and hydrogen-hydrogen interactions in cis and lone pair-hydrogen interactions in trans conformations must be taken into consideration. Because the calculated values of $r_{H\cdots H}$, shown in Table 1, are nearly equal to the sum of van der Walls radii of hydrogen atoms (~2.4 Å), steric interaction between the hydrogen atoms may exist in cis conformation. At the same time, repulsive interactions between the hydrogens of NH groups may be possible due to these atoms possess positive charge (Q_H =+0.217). According to the three sememprical methods, the calculated length of C_5-C_5, covalent bond in cis form is longer than that of in trans conformation (Table 1). In our previous studies, the conformational analyses of A and B tautomers of bi(1,2,4-triazole) system have been performed by MNDO, AM1 and PM3 methods and their stable conformations have been determined. The tautomerization energy values of the bi(1,2,4-triazole) system (Scheme 1) are presented in Table 2. As seen from Table 2, tautomer A is the most stable one among the tautomers of the bi(1,2,4-triazole) system. Tautomer C is relatively more stable than tautomer B. Since the 1,2,4-triazole molecule involves a tautomeric equilibrium of 1H- and 4H- forms in gas and liquid phases [29], it is plausible to consider that the bi(1,2,4-triazole) molecule exist in tautomers A, B

and C in the same media.

Table 1. Total energies, heats of formation, bond lengths, distances between the hydrogen atoms of NH groups and internal rotation barriers.

Method	Structure	E_{tot} (kcal/mol)	ΔH_f°(kcal/mol)	r_{c-c}(Å)	$r_{H\cdots H}$(Å)	Δ E(kcal/mol)
MNDO						
	C1	-41722.094	89.873	1.451	2.628	7.346
	C2	-41729.440	82.527	1.448	4.886	
AM1						
	C1	-41608.827	163.290	1.453	2.469	7.266
	C2	-41616.093	156.024	1.450	4.489	
PM3						
	C1	-34735.359	109.233	1.444	2.699	10.545
	C2	-34745.904	99.389	1.439	4.901	

Table 2. Tautomerization energies of 3,3'(or 5,5')-bi(1,2,4-triazole) system (kcal/mol)

Method	A-B	A-C	C-B
MNDO	-11.917	-9.447	-2.470
AM1	-15.737	-10.272	-5.365
PM3	-9.639	-0.545	-9.194

In order to investigate the electronic properties, to find out the reaction centers and to determine the reactivity of 5,5'-bi(1H-1,2,4-triazole) system, cis (C1) and trans (C2) conformations have been studied using MNDO, AM1 and PM3 routes. Ionization Potentials (IP), dipole moments and the energies of frontier molecular orbitals (E_{HOMO}) and (E_{LUMO}) of C1 and C2 conformations have been calculated and given in Table 3.

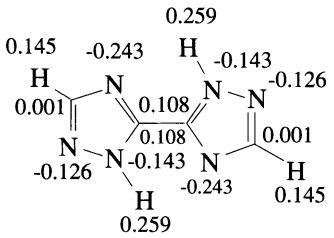
Table 3. The energies of frontier molecular orbitals and dipole moments for cis (C1) and trans (C2) conformations of 5,5'-(1,2,4-triazole)

Method	Structure	E_{HOMO}	E_{LUMO}	μ(Debye)
MNDO				
	C1	-10.122	-0.771	3.443
	C2	-10.050	-0.727	0.0
AM1				
	C1	-9.957	-0.746	3.628
	C2	-9.867	-0.686	0.0
PM3				
	C1	-9.993	-1.075	4.057
	C2	-9.919	-1.015	0.0

The results obtined from the three semiempirical methods indicate that the ionization potential (IP=-E_{HOMO}) of cis conformation is relatively higher than that of trans form. The experimental ionization potentials of 1,2,4-triazole molecule has been reported to be 10.00 eV. By using MNDO, AM1 and PM3 routes, the ionization potential of 1H-1,2,4-triazole has been calculated and found to be 10.30 eV, 10.27

eV and 10.396 eV, respectively[30]. By comparison of the values calculated for 5,5'-bi(1H-1,2,4-triazole) and 1H-1,2,4-triazole molecules, it is clearly seen that the bitriazole molecule has a relatively lower ionization potential than that of 1H-1,2,4- triazole. Among the tautomeric forms of 3,3' (or 5,5')-bi(1,2,4-triazole) molecule, tautomer B has a lowest ionization potential while tautomer C has the highest one. According to the E_{HOMO} values calculated for cis and trans conformations of the tautomers of 3,3'(or 5,5')-bi(1,2,4-triazole) system by each semiemprical method, tautomer B has a highest electron-donor character while tautomer C has a lowest one. At the same time, the trans forms of three tautomers possess more electron-donor character than the other conformations.

The analysis of the frontier molecular orbitals (HOMO and LUMO) of 5,5'-bi(1H-1,2,4-triazole) molecule indicates that these orbitals in two conformations are essentially 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 $N_2(N_2)$, $C_5(C_5)$ and $C_3(C_3)$ atoms (Table 4), as also shown in Figure 1 for trans conformation. However, $N_4(N_4)$, $N_1(N_1)$, $N_2(N_2)$, atoms have the higest atomc charges (Q_i) in the bitriazole molecule (Table 4), as presented in Scheme 2. The values shown in Table 4 were calculated usng MNDO method.



Scheme 2.

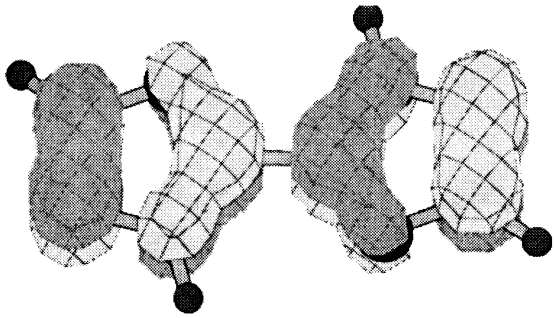


Figure 1. Electron density distribution (HOMO) of the bitriazole molecule in trans conformation

Table 4. The values of electron densities (q_i) (HOMO) and full atomic charges (Q_i), for the conformations of 5,5'-(1,2,4-triazole)

	Structure	N_1	N_2	N_4	C_3	C_5
q_i						
	C1	0.056	0.178	0.040	0.095	0.130
	C2	0.063	0.172	0.032	0.105	0.128
Q_i						
	C1	-0.186	-0.124	-0.184	-0.003	0.114
	C2	-0.143	-0.126	-0.0243	0.001	0.108

The results so obtained reveal that the electronic properties of 5,5'-bi(1H-1,2,4-triazole) molecule are related to its conformational structure.

In order to investigate the basicity and to find out the possible coordination centers, the determination of the orientation sites of 5,5'-bi(1H-1,2,4-triazole) molecule containing various proton-acceptor centers for electrophilic proton attacks is important. In accordance with the negative charge distribution on nitrogen atoms (Table 3 and Scheme 2), the N-4 and N-4' atoms are predicted to be the main sites of the molecule for the electrophilic attack of hydrogen. In fact, the determination of the exact protonation centers acording to the negative charge distribution is difficult because the negative atomic charges are also high on the other nitrogen atoms.

To find out the possible way of approach and the center of attack for hydrogen to 5,5'-bi(1H-1,2,4-triazole) molecule, the molecular electrostatic potentials (MESP) (in kcal/mol) of the two conformations were calculated by the three semiemprical methods. According to the electrostatic potential contour maps (Figure 2), the electrophilic attatck of proton may predominantly occur at N-4 and N-4' atoms in cis and trans conformations. Moreover, Figure 2 indicates that the attack of proton at N-2 and N-2' atoms is also possible in trans conformation.

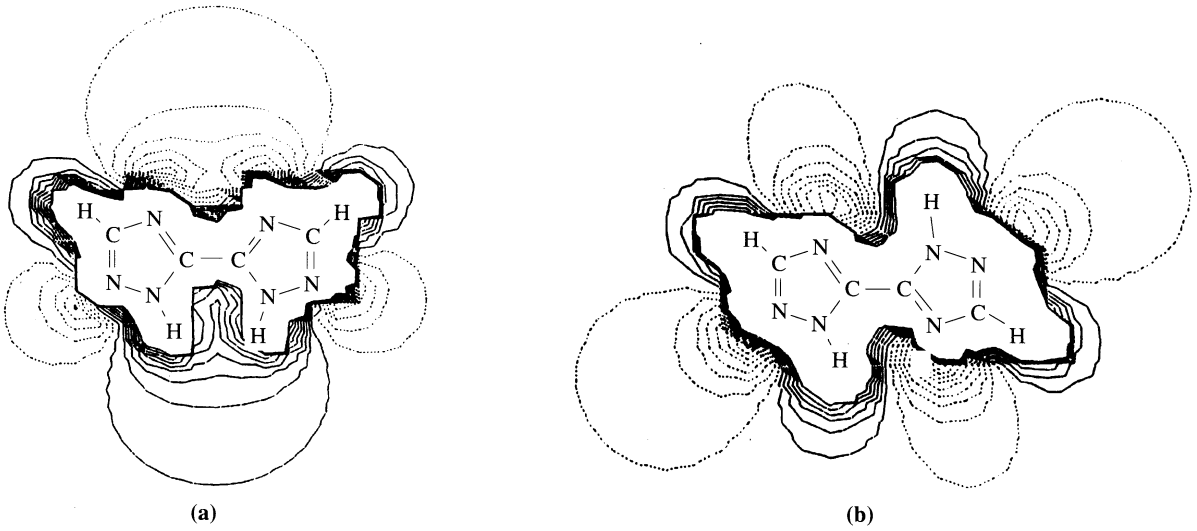


Figure 2. Electrostatic potential contour map of the cis(a) and trans(b) conformations (The maps are drawn in the x, y plane and the intervals between the contours are 0.03 kcal/mol) (MNDO).

For the determination of the exact protonation centers of 5,5'-bi(1H-1,2,4-triazole) system, the proton affinities for the different nitrogens of the molecule in cis and trans conformations were calculated by AM1 and PM3 methods. Hence, the stable conformations for the monocations formed by the protonation of different nitrogens of the molecule were determined with full geometry optimization and the heats of formation (ΔH_f°) were calculated using AM1 and PM3 routes (Table 5).

The conformational analysis performed by the two semiempirical methods indicates that the monocations have planar structures. Cis conformations of the momocations resulting from N_1 or N_2 protonation of the bitriazole molecule are more stable than the trans forms. In spite of the fact that the trans conformation of the neutral molecule is more stable than cis conformation, the cis form of the monocation resulting form N_4 protonation is relatiely more stable than the other form in accordance with the two methods.

The proton affinity values for the different nitrogens of 5,5'-bi(1H-1,2,4-triazole) molecule were calculated by the equation given below. The results obtained are shown in Table 6.

$$\mathbf{PA = 367.2 + \Delta\ H_f^\circ(B) - \Delta\ H_f^\circ(BH^+)}$$

Table 5. Heats of formation (ΔH_f°) for the protonated forms of cis (C1) and trans C(2) conformations of 5,5'-bi(1H-1,2,4-triazole) (in kcal/mol)

Method	Structure	Protonated Nitrogens		
		N1	N2	N4
AM1				
	C1	358.635	339.897	318.866
	C2	347.195	330.847	319.176
PM3				
	C1	307.021	287.451	264.554
	C2	293.141	276.149	264.987

Here, PA is proton affinity, $\Delta H_f^\circ(B)$ is the heat of formation for the molecule, $\Delta H_f^\circ(BH^\circ)$ is the heat of formation for the cation and 367.2 is the hea of formation for the proton (kcal/mol)[31]. As seen from the results presented in Table 6, the molecule possess the highest poroton affinity for N-4 (N-4') atom in towo conformations. In other words, 5,5'-bi(1H-1,2,4-triazole) moolecule is predicted to protonate at N-4 (N-4') atom in two comformations. The proton affinity value calculated for N-4 atom of cis form of the molecule is higher than that of trans conformation. But, the proton affinity for N-2 atom of cis conformation of the molecule is lower than that of trans form. Although, the difference between the protn affinity values calculated for N-2 atom in cis and trans conformations is low, the corresponding difference between those calculated for N-4 atom is sufficiently high (Table 6). As a result of the interaction between the lone pair electron orbitals of N-4 and N-4' atoms through space during the conversion of the molecule from trans form to cis comformation, the individual protonation centers join in a common system. For this reason, the MESP gradient (Figure 2) and proton affinity of the bitriazole molecule increase during the conversion of trans conformation to cis form. This behavior indictes that the basicity and the reactivity of the molecule increases in cis conformation.

Table 6. Proton afinities (PA) of 5,5'-bi(1H-1,2,4-triazole) calculated for different nitrogens (in kcal/mol)

Method	Structure	Protonated Nitrogens		
		N1	N2	N4
AM1				
	C1	171.854	190.593	211.624
	C2	176.029	192.377	204.048
PM3				
	C1	169.412	188.982	211.879
	C2	173.448	190.440	201.599

In our previous studies, the proton affinities of tautomers A and B of the bi(1,2,4-triazole) molecule have been calculated [1,3]. A comparison of the results obtained indicates that tautomer B has the highest proton affinity among the tautomers of the bitriazole molecule. The proton affinity values of tautomers A and C are near to each other. Tautomer C involves a relatively higher proton affinity than tautomer A according to AM1 method. But in accordance with PM3 route, tautomer A has a relatively higher proton affinity than form C. These results reveal that tautomer B of the bi-(1,2,4 triazole) molecule has the highest basic properties among the tautomers. On the other hand, cis forms of the three tautomers have higher proton affinity values than trans conformations.

According to the proton affinity values of 5,5'-bi(1H-1,2,4-triazole) molecule involving several nitrognes differing from each other in position, the electrophilic attack of metal ions to the molecule is predicted to occur at N-4 and N-4' atoms in cis and trans conformations. If we consider the proton affinity values on Table 6, it is apparent that the complexing ability of the bi-(1,2,4-triazole) molecule with metal cations in cis conformation is higher than that of in trans form. On the other hand, it is easy to see that the complex formation ability of tautomer B is the highest among the tautomeric forms of the bitriazole systems, and its metal complexes are more stable than those of tautomers A and C. The complexing abilty of tautomers A and C and the stability of their complexes are almost the same.

The predicted Fe^{+2} complexes of tautomers A and B have been investigated from the point of electronic properties and of he formation mechanisms in a previous study[3]. For the purpose of confirming the results obtained, the electronic properties and the stability of the predicted Fe^{+2} complexes of tautomer C were investigated with full geometry optimization using ZINDO/1 method. Fe[5,5'-bi(1H-1,2,4-triazole)]$^{2+}$ type complex formation of 5,5'-bi(1H-1,2,4-triazole) molecule containing several competitive coordination centers involves the attachment of 5,5'-bi(1H-1,2,4-triazole) ion to the N-4 and N-4' atoms.

It is likely that 5,5'-bi(1H-1,2,4-triazole) molecule may predominantly exist in trans form under the normal condition owing to the more stability of this conformation than cis form[32]. Obviously, the two conformations (Scheme 1 C1 and C2) found in an equilibrium may participate in a complex formation with metal cations. Hence, the formation mechanism of Fe[5,5'-bi(1H-1,2,4-triazole)]$^{2+}$ type complex appears to be interesting. A way for the formation of Fe[5,5'-bi(1H-1,2,4-triazole)]$^{2+}$ complex is the attachment of Fe^{2+} ion to the N-4/N-4' atoms of cis conformation of the bi-(1,2,4-triazole) in the plane of molecule.

As mentioned above, the cis form of the monocation resuting from N-4(or N-4') protonation is more stable than trans form, whilst the trans conformation of 5,5'-bi(1H-1,2,4-triazole) molecule is more stable than the other. For this reason, the conversion of the monocation formed by N-4 protonaiton of the trans form into cis conformation may be possible. Similarly, the cation formed by the coordination of Fe^{2+} ion with N-4 or N-4' center of the trans conformation may changes to cis form. After this, the Fe^{2+} may be attached to the other coordination center (N-4' or N-4) in order to form the Fe[5,5'-bi(1H-1,2,4-triazole)]$^{2+}$ complex. This may be considered as a second way for the formation of the Fe[5,5'-bi(1H-1,2,4-triazole)]$^{2+}$ complex.

The calculated total energies (E_{tot}), heats of formation ($\Delta\ H_f^\circ$), positive charge densities of iron (Q_{Fe}) and the lengths of Fe-N bonds for the Fe^{2+} complexes of tautomers A, B and C of 3,3'(or 5,5')-bi(1H-1,2,4-triazole) system - Fe[3,3'-bi(1H-1,2,4-triazole)]$^{2+}$ (1A), Fe[3,3'-bi(1H-1,2,4-triazole)]$^{2+}$ (1B) and Fe[5,5'-bi(1H-1,2,4-triazole)]$^{2+}$ (1C), respectively - are calculated using ZINDO/1 method and given in Table 7.

Table 7. Total energies, heats o formation, positive charge densities of iron and the Fe-N bond lengths of complexes 1A, 1B and 1C (ZINDO/1)

Complexes	E_{tot}(kcal/mol)	(ΔH_f° (kcal/mol)	Q_{Fe}	r(Å)			
				Fe-N_4	Fe-N_4	Fe-N_2	Fe-$N_{2'}$
1A	-71969.611	-2655.480	0.915			2.007	2.007
1B	-71989.675	-2675.545	0.874	1.988	1.988		
1C	-71970.632	-2656.502	0.875	2.002	2.002		

The results obtained indicate that complexes 1A, 1B and 1C have approximately planar structures (Figure 3) and complex 1B is the most stable one. The stabilities of complexes 1A and 1C are approximately the same.

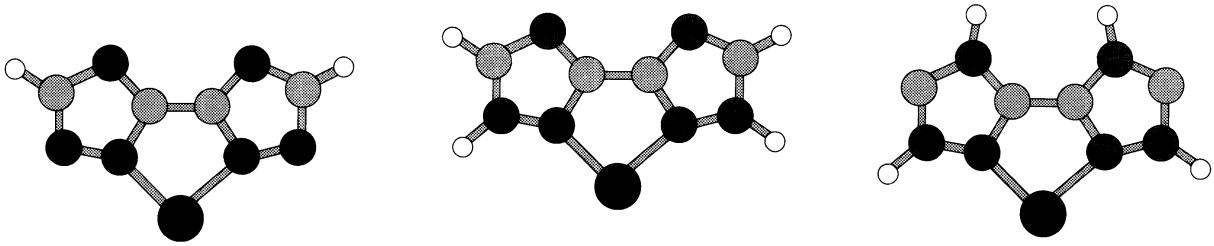


Figure 3. Geometries of the complexes 1A, 1B and 1C by ZINDO/1

The positive charge on the Fe^{2+} ion is partially transferred to the ligand in the three complexes. The results obtained from the theoretical investigation of the tautomers of the 3,3'(or 5,5')-bi(1,2,4-triazole) system revel that tautomer A is the most stable molecule according to MNDO, AM1 and PM3 methods. Tautomer B has the highest proton affinity among the tautomeric forms and its complex formation ability with metal cations is higher than those of the other tautomers. The complexes formed by tautomer B are more stable than those foremed from forms A and C. While tautomer A is more stable than other, the complex formation of the 3,3'(or 5,5')-bi(1,2,4-triazole) molecule essentially proceeds via tautomer B.

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