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A Quantum-Chemical Investigation on 3-(4H-1,2,4-Triazol-4-yl)-1H-1,2,4-Triazole

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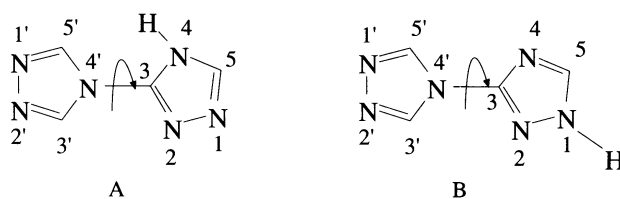
The molecular conformations and electronic properties of the 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole molecule containing various reaction centers were investigated by the semiempirical methods MNDO, AM1 and PM3. The most stable conformation of the molecule was determined to be the planar conformation. The total energies, heats of formation, dipole moments, rotational barriers, geometric parameters, ionization potentials, full atomic charges, energies of frontier molecular orbitals (E_{HOMO} and E_{LUMO}) and their electron densities were calculated and discussed. In order to determine the protonation sites of the 3,4'-bitriazole system, the molecular electrostatic potential (MESP) of the molecule has also been calculated. The conformations and electronic properties of mono- and di-protonated species were also performed by AM1 and PM3 treatments. The proton affinities for the different nitrogens of the molecule were calculated using AM1 and PM3, and possible protonation sites were determined. The complex forming ability of the bitriazole molecule with metal cations was also discussed. The geometry and electronic properties of the complex formed by Mg^{2+} ions were investigated using PM3.

Introduction

We have recently reported the quantum-chemical investigations of 3,3'-bi(1H-1,2,4-triazole) and 3,4'-bi(4H-1,2,4-triazole) molecules^{1,2}. In continuation of our interest in the quantum-chemical study of bitriazole systems, we wish to report the results obtained from the investigation of the 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole molecule, because the 3,4'-bi(4H-1,2,4-triazole) (A) and 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole (B) systems are tautomers (Scheme 1), and so it seemed appealing to investigate the relative stabilities of these molecules. According to X-ray results, the tautomeric form B is preferred by the molecule in crystalline state³. In fact, the relative stabilities of the 1H- and 4H- tautomeric forms of the 1,2,4-triazole molecule have not yet been conclusively determined. However, the 4H-tautomer of 1,2,4-triazole has been found to be more stable than 1H-1,2,4-triazole, according to the results obtained from investigations using MNDO, AM1 and PM3 methods^{4,5}. Hence, quantum-chemical investigation of tautomers A and B of the flexible 3,4'-bi(1,2,4-triazole) molecule, and the determination of their stable conformations would be important. On the other hand, the 3-(4H-1,2,4-triazol-4-yl)1H-1,2,4-triazole molecule containing 1H-1,2,4-triazole and 4H-1,2,4-triazole rings and having several nitrogen atoms may have basic properties

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and may form various metal complexes. The complexing ability of ligands is essentially related to their ionization potentials and proton affinities⁶. But the experimental determination of the protonation centers of the molecule containing heteroatoms differing from each other in position is generally difficult^{7,8}. For this reason, the theoretical calculations of protonation parameters and the conformational analysis of the 3,4'-bi(1,2,4-triazole) system also appear important. According to the results obtained, the selectivity of complex formation ability of 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole molecule containing competing coordination centers can be theoretically evaluated and the stability of the complexes can be predicted. Since the interactions between the two heterocycles affect proton affinity and other properties, the theoretical investigation of the 3,4'-bitriazole system is also important. On the other hand, the effect of tautomeric change on electronic properties can be evaluated by the theoretical investigation of the molecule. It is clear that ab initio methods as well as semiempirical methods have been used widely for the calculations of the protonation parameters and for the conformational analyses of heterocycles and biheterocycles^{4,5,11-32}. Furthermore, AM1, and PM3 methods have been found to be reliable for calculating the proton affinities of various heterocyclic compounds^{20,23,24,29}. In the present study, the semiempirical methods MNDO³³, AM1³⁴, PM3³⁵ were used for a detailed investigation of the electronic properties and conformations of the 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole molecule (Scheme 1-B)



Scheme 1

For the different nitrogen atoms, the proton affinity of the bitriazole molecule was calculated using AM1 and PM3 methods. The geometry and electronic properties of the Mg^{2+} complex of the bitriazole molecule were investigated by PM3 treatment. The results so obtained were compared with those of the Mg^{2+} complex of tautomer A².

All calculations related to the study were made with the HyperChem 4.5 program on an IBM PC/AT-Pentium-133 computer.

Results and Discussion

It is reasonable for the flexible 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole molecule to exist in various conformations due to the rotation of the 1,2,4-triazole rings around the $C_3-N_{4'}$ single covalent bond (Scheme 1-B). In order to determine the most stable conformation, the conformational analysis of the molecule was made with full geometry optimization using MNDO, AM1 and PM3 methods. In all cases geometries were optimized using the Fletcher-Reeves algorithm. From the conformational analysis results obtained by the three methods, it is clear that the planar conformation of the molecule with maximum conjugation between the two triazole rings is the most stable. Thus, a minimum was found at the conformation corresponding to $\varphi = 0^\circ$ or $\varphi = 180^\circ$. According to X-ray results, the internal rotation angle of the 3,4'-bitriazole molecule is 8.5° in crystalline state³. In order to investigate the effect of internal rotation on the energy of the molecule, the potential function of internal rotation around the $C_3-N_{4'}$ single bond was calculated. For this reason, the φ angle was varied in the range $0-180^\circ$ by a step of 30° and calculations were performed with geometry optimization using the three semiempirical treatments. According to the results of the three

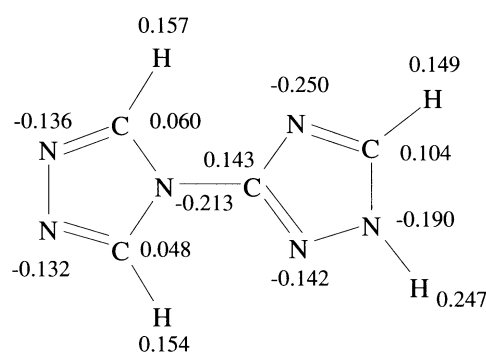
methods, the two 1,2,4-triazole rings are perpendicular to each other in the conformation corresponding a maximum ($\varphi = 90^\circ$). In this conformation, the conjugation between the two triazole rings is minimum and the length of $C_3-N_{4'}$ is maximum 1.402 Å (MNDO), 1.401 Å (AM1) and 1.420 Å (PM3). The results obtained for the conformations of the 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole (B) molecule by semiempirical methods in the study are in agreement with the results obtained for the conformations of some conjugated molecules involving lone pair - hydrogen and lone pair - lone pair interactions by semiempirical and ab initio methods^{9-12,14,15,32}. The calculated total energies (E_{tot}) internal rotation barriers (ΔE), internal rotation angles (φ_{min} and φ_{max}) and length of the $C_3-N_{4'}$ bond (r_{C-N}) are given in Table 1.

Table 1. Total energies (in kJ/mol), internal rotation barriers (kJ/mol), internal rotation angles (in degree) and the length of $C_3-N_{4'}$ (in Å) for 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole (A).

Methods	E_{tot}	ΔE	φ_{min}	φ_{max}	r_{C-N}
MNDO	-174561.551	7.517	0	90	1.396
AMI	-174066.182	13.984	0	90	1.395
PM3	-145333.089	11.602	0	90	1.417

A comparison of the results shown in Table 1 and the reported values² reveals that the calculated internal rotation barrier of 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole (B) is higher than that of 3,4'-bi(4H-1,2,4-triazole) tautomer (A). The MNDO and AM1 results indicate that tautomer A is more stable than the other tautomer in gas phase. However, the results obtained by PM3 are in agreement with the published X-ray results³ and indicate tautomer B to be more stable in gas phase. Hence, structures A and B are taken into consideration in a tautomeric equilibrium in gas and liquid phases.

In our other study, the electronic properties of 3,4'-bi(4H-1,2,4-triazole) molecule (tautomer A) were investigated². In order to determine the reaction centers of 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole molecule (tautomer B), its electronic structure and properties were investigated with the aid of the semiempirical methods in the present study. The values for the heats of formation (ΔH_{f°), dipole moments (μ) and the energies of frontier molecular orbitals (E_{HOMO} and E_{LUMO}) are given in Table 2. As seen from the results in Table 2, the ionization potential values $IP = -E_{HOMO}$ related to the three methods are in conformity with each other. The atomic charges (Q_i) of the atoms in the molecule are shown in Scheme 2.



Scheme 2. Full atomic charge of 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole (MNDO)

In order to investigate the basicity and to find out the coordination centers, it is important to determine the protonation sites of the 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole (B) molecule having various proton-acceptor centers. Thus the N-4 atom is predicted to be the main basic site of the 3,4'-bitriazole system according to the negative charge distribution on nitrogen atoms (Scheme 2). However, negative atomic

charges are high on other nitrogen atoms as well. To determine the possible protonation centers of the 3,4'-bitriazole molecule, the molecular electrostatic potential (MESP) (in kJ/mol) of the system was calculated by the three semiempirical routes. The electrostatic potential contour maps of the molecule indicate that the electrophilic proton attack predominantly occurs on N-1' and N-2' atoms. Apart from this, the probability of proton attack on an N-4 atom is also high. Figure 1 shows the MESP contour map according to MNDO.

Table 2. Heats of formation (ΔH_{f°) (in kJ/mol), dipole moment (in Debye) and energies of frontier molecular orbitals (in eV) of the 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole molecule.

Methods	ΔH_{f°	μ	E_{HOMO}	E_{LUMO}
MNDO	379,719	7.777	-10.083	-0.384
AM1	708.360	7.908	-10.061	-0.419
PM3	456.688	8.707	-9.995	-0.861

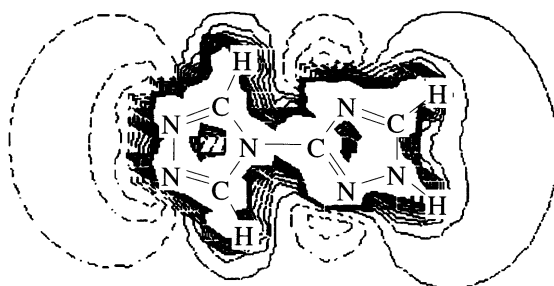


Figure 1. Electrostatic potential contour map of 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole(MNDO)

In order to determine the correct protonation sites of the 3,4'-bitriazole molecule, the proton affinity (PA) values for the different nitrogen atoms of the molecule were calculated using AM1 and PM3 methods. For this reason, the heats of formation (ΔH_{f°) for the cations formed by the protonation of each nitrogen atom of the molecule were calculated with full geometry optimization and their stable conformations were determined (Table 3).

Table 3. Heats of formation (in kJ/mol) for the protonated forms of 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole.

Protonated Nitrogens→	N-1	N-2	N-4	N-1'	N-2'
AM	1529.244	1466.664	1409.146	1362.909	1364.469
PM3	1295.592	1238.272	1177.223	1099.070	1099.911

Conformational analysis of the protonated 3,4'-bi(1,2,4-triazole) molecule by AM1 and PM3 methods revealed the stable conformations of the cations to have planar structures. The cation formed by the protonation of N-1' or N-2' atoms of the 4H-1,2,4-triazole ring may exist in cis or trans conformation in accordance with the position of NH groups to the $C_3-N_{4'}$ central bond. According to Scheme 1, the protonation of N-1' and N-2' atoms leads to the formation of trans and cis conformations, respectively. The results obtained show that the trans conformation is relatively more stable and the total energy difference between the two conformations is relatively small (1.560 kJ/mol for AM1 and 0.844 kJ/mol for PM3).

The proton affinity (PA) values calculated for the different nitrogen atoms of the 3,4'-bi(1,2,4-triazole) molecule given in Table 4 were calculated using the equation cited below:

$$PA = \Delta H_f^\circ(H^+) + \Delta H_f^\circ(B) - \Delta H_f^\circ(BH^+)$$

Here, PA is the proton affinity, $\Delta H_{f^\circ}(\text{B})$ is the heat of formation for the molecule, $\Delta H_{f^\circ}(\text{BH}^+)$ is the heat of formation for the cation and $\Delta H_{f^\circ}(\text{H}^+)$ is the heat of formation for the proton³⁶.

Table 4. Proton affinities (in kJ/mol) of 1H-1,2,4-triazole(1), 4H-1,2,4-triazole(2) and 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole (3) calculated for different nitrogens.

Protonated Nitrogens→	N-1	N-2	N-4	N-1'	N-2'
AM1					
1	731.99	810.65	880.02		
2				863.33	863.33
3	715.46	778.06	835.59	881.82	880.23
PM3					
1	713.75	792.70	866.63		
2				866.72	866.72
3	697.47	754.79	815.84	893.99	893.16

By comparison of the results shown in Table 4, it is easy to see that the proton affinities of the 3,4'-bi(1,2,4-triazole) molecule calculated for N-1' and N-2' atoms are higher than the others. According to Scheme 1-B, the protonation of N-1' atom results in the formation of anti conformation of the cation, and hence the proton affinity of the molecule corresponding to N-1' atom is higher than that of N-2' (Table 4). For this reason, the bitriazole molecule is predicted to protonate at N-1'. In other words, the electrophilic attack of the proton on the N-1' atom of 4H,1,2,4-triazole ring placed in anti position according to the NH group of the 1H-1,2,4-triazole ring is easier. The results obtained indicate that the proton affinities calculated for nitrogen atoms increase when the nitrogens are as far inward as the central C₃-N_{4'} bond.

In is possible that the interactions between the two 1,2,4-triazole rings of the 3,4'-bi(1,2,4-triazole) affect the basicity of the molecule. For this reason, the proton affinities of the 3,4'-bi(1,2,4-triazole), 1H-1,2,4-triazole and 4H-1,2,4-triazole molecules were calculated for the same nitrogens in position (Table 4). Comparing the results obtained for the same nitrogens in position, we find that the proton affinity of the 3,4'-bi(1,2,4-triazole) system is relatively lower than that of 1H-1,2,4-triazole ring and is relatively higher than that of 4H-1,2,4-triazole molecule. As a result, the 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole molecule is predicted to be more basic than 4H-1,2,4-triazole, according to the data obtained for proton affinities. In other words, the complex formation of the 3,4'-bi(1,2,4-triazole) molecule containing several competitive coordination centers involves the attachment of metal cations to the N-1' and N-2' atoms.

In our previous study², the proton affinity values of 3,4'-bi(4H-1,2,4-triazole) molecule (A) were calculated for the different nitrogens in position and the proton affinity for the N-2' atom (Scheme 1-A) was determined to be the highest value : 851.946 kJ/mol (AM1) and 866.590 kJ/mol (PM3). A comparison of these values with those of the 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole molecule (B) calculated for N-1' atom (Table 4) reveals that tautomer B is a more basic molecule than tautomer A. Furthermore, the cation formed by N-1' and N-2' diprotonation of tautomer B was found to be, 46.790 kJ/mol (AM1) and 60.739 kJ/mol (PM3) more stable than the one formed by N-2' and N-1' diprotonation of tautomer A. According to the results, the tautomeric form B 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 Mg²⁺ complex of tautomer B were studied by PM3 and were compared with those of tautomer A. In this connection, the complex involving the attachment of Mg²⁺ ion to the N-1'/N-2' atoms of tautomer B was found to have an

approximately planar structure, and the bond lengths r_{Mg-N_1} and r_{Mg-N_2} , were determined to be 1.871 Å and 1.873 Å, respectively.

In addition, the geometries of the complexes having an Mg^{2+} ion attached to N-1' and N-2' atoms of tautomers A and B (complexes IA and IB) were optimized by PM3. They are shown in Figure 2.

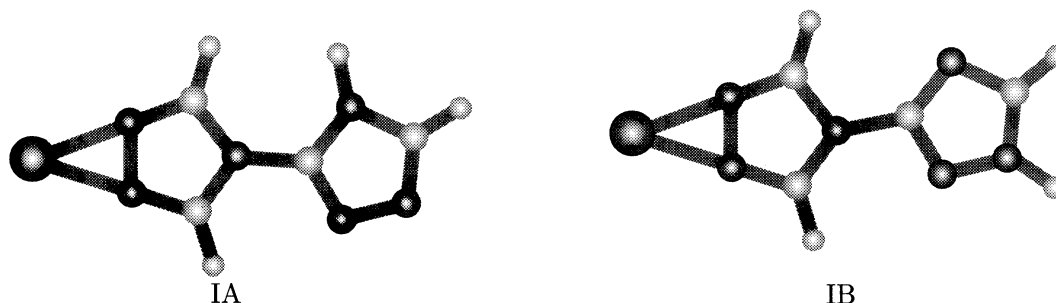


Figure 2. Geometries of the complexes IA and IB by PM3.

The calculated total energies (E_{tot}), heats of formation (ΔH_{f°), positive charge densities of magnesium (Q_{Mg}) and energies of frontier molecular orbitals (E_{HOMO} and E_{LUMO}) for the complexes IA and IB are given in Table 5.

Table 5. Total energies (in kJ/mol), heats of formation (in kJ/mol), positive charge densities on magnesium and energies of frontier molecular orbitals (in eV) of complexes of IA and IB (PM3)

Methods	E_{tot}	ΔH_{f°	Q_{Mg}	E_{HOMO}	E_{LUMO}
IA	-145894.528	2217.763	1.212	-16.745	-10.837
IB	-145953.330	2158.961	1.210	-16.939	-10.708

As seen in Table 5, complex IB is 14.043 kJ/mol more stable than complex IA. From the theoretical investigation of the complexes IA and IB, it is evident that tautomer B forms more stable complexes than tautomer A. The results obtained from the theoretical investigation of 3-(4H-1,2,4-triazol-4-yl)-1H-1,2,4-triazole and 3-4'-bi(4H-1,2,4-triazole) tautomers and also their metal complexes indicate that the energy difference between the two tautomers is low and their stable conformations have planar structures. Tautomer B has a higher proton affinity and complexing ability than the other tautomer. The complexes formed by metal ions with tautomer B are more stable than those formed by the same ions with tautomer A.

Acknowledgement

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