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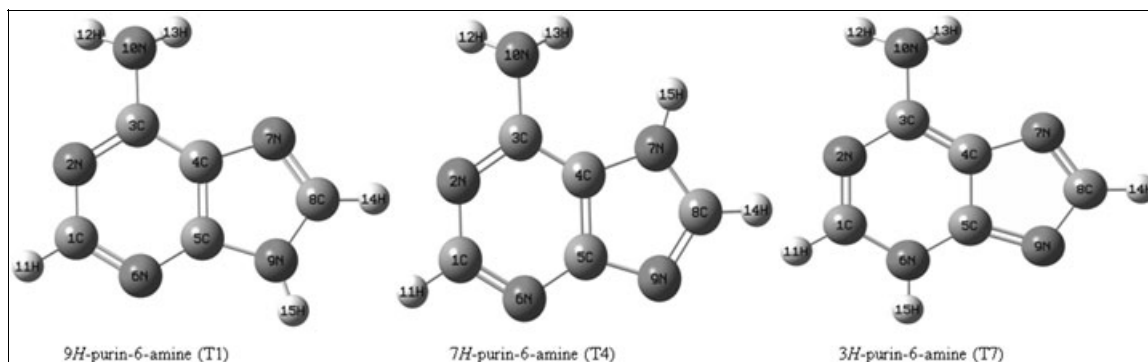
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The natural bond orbital (NBO) analysis, nucleus independent chemical shift (NICS), and ^{14}N NQR parameters of the most stable tautomers of adenine in the gas phase were predicted using density functional theory method. The NBO analysis revealed that the resonance interaction between lone pair of the nitrogen atom and empty non-Lewis NBO increases with increasing the p character of the nitrogen lone pair. The present investigation indicated the π clouds in both the considered heterocyclic rings containing six electrons, and these tautomers has the aromatic character. The NICS study utilizing the gauge-invariant atomic orbital method showed that there are diatropic currents in the heterocyclic rings of the tautomers, so we determined the order of overall aromaticity of these tautomers. The results of NQR parameter calculations showed three parameters are effective on nuclear quadrupole coupling constant; the p character value of lone pair electrons of nitrogens, and the related occupancies and whenever, the lone pair electrons of nitrogens participate in the formation of chemical bond and/or π system of the ring, the q_{zz} and consequently its χ decreases.

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INTRODUCTION

The purine and pyrimidine bases are known to occur in different tautomeric forms depending on the pH of the environment [1]. One of the purine derivatives is adenine that bind to thymine in DNA for stabilizing the nucleic acid structures and bind to uracil in RNA for protein synthesis. Also, when Adenine attached to ribose and deoxyribose creates adenosine and deoxyadenosine. When three phosphate groups attached to adenosine, forms adenosine triphosphate that plays important rules in cellular metabolism. On the other hand, when adenine binds with niacin and riboflavin (two B vitamins) makes essential cofactors nicotinamide adenine dinucleotide and flavin adenine dinucleotide, respectively [2]. Then adenine sometimes called vitamin B₄. In view of the fact that this molecule plays variety of important rules in biochemistry [3], tautomerization of adenine has stimulated a significant amount of theoretical and experimental research. The appearance of less stable tautomeric forms of purine and pyrimidine bases may lead

to the so-called point mutation, originating from changes in DNA taking place on the molecular level [4,5]. Adenine may exist in various tautomeric forms [6] differing from each other by the position of the hydrogens, which may be bound to either ring nitrogen atoms. Literature provides many experimental and theoretical works on the tautomerization of the adenine. Dreyfus et al. [7] reported an investigation of tautomerism of adenine in water using temperature jump relaxation technique. Their results indicated that two tautomeric forms (Fig. 1) T1 and hydroxy-amino T4 exist simultaneously. The equilibrium constant of T1 to T4 conversion was estimated 0.28 at 293.15 K with $\Delta H = 0.2$ kcal/mol. Eastman [8] using fluorescence method conclude that adenine in butanol at 170 K consist of 6% T4 and 94% T1. Chenon et al. [3] determined the quantitative tautomeric form of adenine from ^{13}C NMR data. Laxer et al. [9] reported the coexistence of the T1, T4, and T7 tautomers in aqueous solution. Hanus et al. [10] calculated the relative free energy of

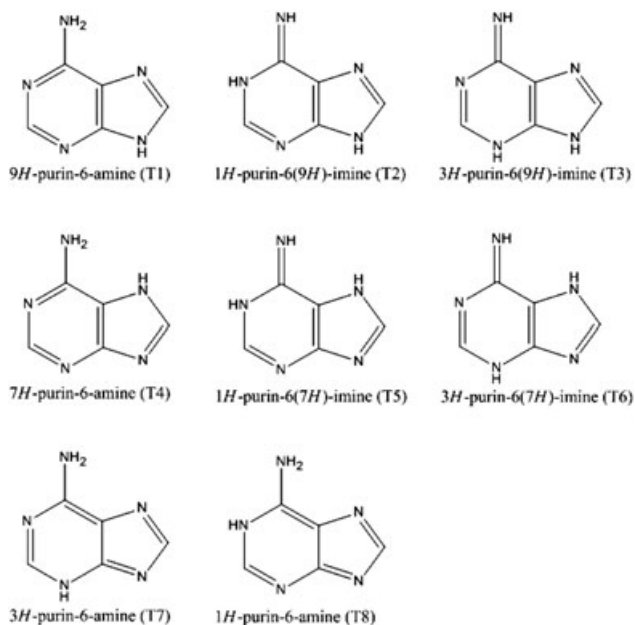


Figure 1. Structures of adenine tautomers.

T1, T4, and T7 in aqueous solution and demonstrated that T1 is more stable than other tautomers. Peng et al. [11] using ultraviolet photoelectron technique revealed that only T1 tautomers occur under the study conditions. Kim et al. [6] studied microsolvation of adenine in water by theoretical method and suggested that tautomerization of T1 to T4 and T7 facilitated by water. In any case, up to now experimental and theoretical studies indicated that the T1 tautomer is the most stable tautomer in the gas phase or aqueous solution. In contrast to the numerous studies on the thermodynamic stability or dynamic study of tautomerization of adenine in the gas phase and in solution, no attempt has been made to determine the some parameters such as NQR frequencies, quadrupole coupling constants or asymmetry parameters found from the ^{14}N spectra.

Nuclear quadrupole resonance (NQR), spectroscopy is well established as a versatile technique to study the details of the electronic and nuclear charge distribution about the nucleus of interest [12,13]. Nuclei with spin angular momentum, I , greater than one-half, $I > 1/2$, have the nuclear electric quadrupole moment, eQ , which interacts with the electric field gradient (EFG), tensor originated at the site of quadrupole nuclei [13]. The nuclear quadrupole coupling constant, QCC, and asymmetry parameter, η_Q are experimentally measurable NQR parameters of which the former indicates the amount of interaction of eQ with EFG tensor and the latter measures the symmetry of EFG tensor.

In a recent work, we calculate and compared ^{14}N EFG tensors for the most stable of the 5-methylcytosine

tautomers in the gas phase and justify these results with natural bond orbital analysis (NBO) and nucleus independent chemical shift (NICS) techniques [14]. In the present work, the same calculations performed for adenine tautomers in the gas phase.

COMPUTATIONAL ASPECTS

Geometry optimizations for all eight tautomers of adenine (Fig. 1) in the gas phase were performed with Gaussian 03 software package [15]. All calculations have been carried out at the B3LYP/6-311++G(d,p) level of theory. This corresponds to the approximation method that makes use of Becke-style 3-parameter density functional theory (DFT) with the Lee-Yang-Parr correlation functional. The triple- ζ basis set adds three sizes of s and p functions to the atoms and adds a d function to heavy atoms and a p function to hydrogens, respectively, as well as diffuse functions on heavy atoms and hydrogens. Geometry optimizations were performed without any symmetry constraints. The nature of the stationary points was verified by computations of the harmonic frequencies at the same level of theory. EFG, NBO analysis, and nuclear magnetic resonance (NMR) calculations have been accomplished for optimized stable tautomers in the gas phase.

The electrostatic interaction of a nuclear electric quadrupole moment and the electron charge cloud surrounding the nucleus can give rise to the observation of pure NQR [16]. The Hamiltonian of this interaction is given [17]:

$$H_Q = e^2 Q q_{zz} / 4I(2I - 1) \left[2I_z^2 - I^2 + \frac{\eta}{2} (I_+^2 + I_-^2) \right] \quad (1)$$

Quantum chemical calculations yield principal components of the EFG tensor, q_{ii} , in atomic units ($1 \text{ au} = 9.717365 \times 10^{21} \text{ Vm}^{-2}$) [13], with $|q_{zz}| \geq |q_{yy}| \geq |q_{xx}|$. q_{xx} , q_{yy} , and q_{zz} are the components of EFG in the directions of x , y , and z , respectively. The calculated q_{ii} values were used to obtain the nuclear quadrupole coupling constants, χ_{ii} :

$$\chi_{ii}(\text{MHZ}) = e^2 Q q_{ii} / h, i = x, y, z \quad (2)$$

where Q is the nuclear quadrupole moment of the ^{14}N nucleus. The standard values of quadrupole moment, Q , reported by Pyykkö [18] were used in Eq. 1, $Q(^{14}\text{N}) = 20.44 \text{ mb}$. Often the NQR parameters experimentally are reported as the “nuclear quadrupole coupling constant,” and have the unit of frequency:

$$QCC = \chi(\text{MHZ}) = e^2 Q q_{zz} / h \quad (3)$$

Asymmetry parameters are defined as $\eta_Q = |q_{yy} - q_{xx}| / |q_{zz}|$, $0 \leq \eta_Q \leq 1$ because it measures the deviation of the field gradient tensor from axial symmetry.

Table 1
Energies and relative stabilities of adenine tautomers.^a

	<i>E</i>	R.E
T1	-467.4515073	0.000
T2	-467.4325464	11.898
T3	-467.4014667	31.401
T4	-467.4383029	8.013
T5	-467.4251601	16.553
T6	-467.424464	16.970
T7	-467.4386075	8.094
T8	-467.4217498	18.673

^a*E*, absolute energy (in Hartree); R.E, relative energy (in kcal/mol).

For a nucleus of unit spin (such as ¹⁴N), we have three energy levels, so we get three NQR frequencies [17]:

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

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

$$v_0 = \frac{1}{2}\chi_{zz}\eta \quad (6)$$

The quadrupole coupling constant (χ_{zz}) and asymmetry parameter (η) are usually calculated from the nuclear quadrupole frequencies as follows:

$$\chi_{zz} = 2(v_+ + v_-)/3 \quad (7)$$

$$\eta = 3(v_+ - v_-)/(v_+ + v_-). \quad (8)$$

In the NICS study, the gauge-invariant atomic orbitals (GIAO) method was applied to estimate the diamagnetic ring current intensity on the optimized geometries in the gas phase. Magnetic properties of organic molecules arise from the diamagnetic ring currents of aromatic systems [19]. The NICS was defined by Schleyer et al. [20] as the negative value of the absolute magnetic shielding computed in centers of rings or 1 Å above the molecular plane.

NICS at an empty point in space equals zero and in principle does not require reference molecules and calibrating (homodesmotic) equations for evaluation of aromaticity. Negative values of NICS indicate shielding-presence of induced diatropic ring currents understood as aromaticity at specific point. On the contrary, its positive values are interpreted as deshielded-paratropic ring currents and antiaromaticity. Schleyer et al. [21] after studies on an extensive set of heterocyclic compounds, proved that there are very good linear correlations between geometric, energetic, and magnetic properties providing straightforward interpretation of the electronic structures and properties of organic molecules.

RESULTS AND DISCUSSION

Relative stability. The energies and relative stabilities of adenine structures in the gas phase are given in Table 1. The obtained relative stabilities at the DFT level revealed the T1 tautomer to be at the lowest energy. Moreover the results indicate that a substantial amount of the T4 and T7 can be present in the gas phase. This is in agreement with the previous studies [6–10]. Ball/stick structures and numbering system of the most stable tautomers of adenine are presented in Figure 2.

NBO analysis. Delocalization of electron density between the filled (bonding or lone pair) Lewis type NBOs and empty (antibonding and Rydberg) non-Lewis NBOs leads to loss of occupancy from the localized NBOs of the idealized Lewis structure into the empty non-Lewis orbitals (and thus, to departures from the idealized Lewis structure description), they are referred to as “delocalization” corrections to the zeroth-order natural Lewis structure to a stabilizing donor–acceptor interaction. The energies of these interactions can be estimated by the second order perturbation theory [22]. For each donor NBO(*i*) and acceptor NBO(*j*), the stabilization energy (*E*₂) associated with *i* → *j* delocalization, is explicitly estimated by the following equation [23]:

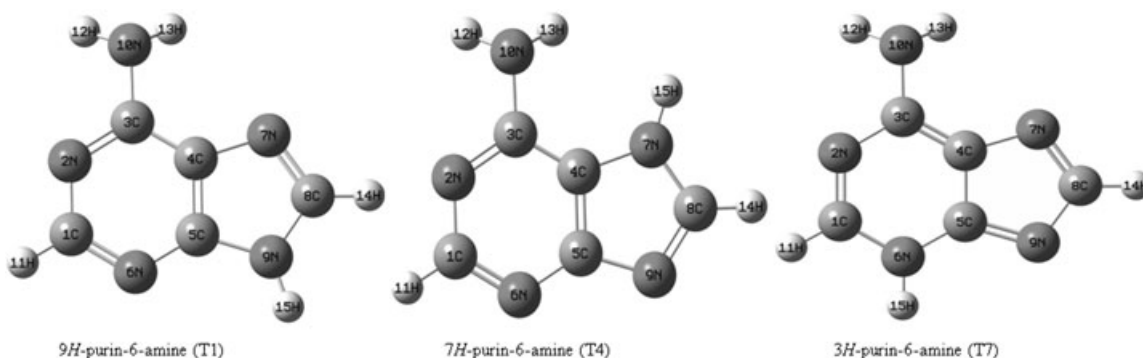


Figure 2. Structure and numbering system of the most stable tautomers of adenine.

Table 2

Calculated natural hybrids (NHOs), occupancies and selected large quantities interaction energy of nitrogen lone pair for the most stable tautomers of adenine in the gas phase.

Tautomer	Lewis-type NBOs			Non-Lewis NBOs		
	Type	Hybrid	Occupancy	Type	Interaction energy E_2 (kcal/mol)	
T1	LP N ₂	sp ^{2.39}	1.90597	BD*(1)	27.59	35.92
				BD*(2)	0.00	
				RY*	8.33	
	LP N ₆	sp ^{2.18}	1.91003	BD*(1)	25.85	35.22
				BD*(2)	0.00	
				RY*	9.37	
	LP N ₇	sp ^{1.95}	1.92720	BD*(1)	16.14	24.86
				BD*(2)	0.00	
				RY*	8.72	
	LP N ₉	p	1.60687	BD*(1)	0.00	89.74
BD*(2)				82.54		
RY*				7.20		
LP N ₁₀	p	1.74915	BD*(1)	0.00	60.20	
			BD*(2)	55.44		
			RY*	4.76		
T4	LP N ₂	sp ^{2.38}	1.90401	BD*(1)	27.76	36.29
				BD*(2)	0.00	
				RY*	8.53	
	LP N ₆	sp ^{2.25}	1.90652	BD*(1)	27.01	36.67
				BD*(2)	0.00	
				RY*	9.66	
	LP N ₇	p	1.62479	BD*(1)	0.00	80.03
				BD*(2)	73.27	
				RY*	6.76	
	LP N ₉	sp ^{1.90}	1.91805	BD*(1)	17.55	27.39
BD*(2)				0.00		
RY*				9.84		
LP N ₁₀	sp ^{0.79}	1.81588	BD*(1)	0.70	39.44	
			BD*(2)	34.40		
			RY*	4.34		
T7	LP N ₂	sp ^{2.44}	1.90056	BD*(1)	28.07	35.85
				BD*(2)	0.00	
				RY*	7.78	
	LP N ₆	p	1.56362	BD*(1)	0.00	113.21
				BD*(2)	105.71	
				RY*	7.5	
	LP N ₇	sp ^{1.88}	1.93102	BD*(1)	16.06	24.78
				BD*(2)	0.00	
				RY*	8.72	
	LP N ₉	sp ^{1.83}	1.92889	BD*(1)	15.79	25.46
BD*(2)				9.67		
RY*				0.00		
LP N ₁₀	p	1.72475	BD*(1)	0.00	55.27	
			BD*(2)	50.38		
			RY*	4.89		

$$E_2 = \Delta E_{ij} = q_i [F_{(i,j)}^2 / (\epsilon_i - \epsilon_j)] \quad (9)$$

where q_i is the donor orbital occupancy, ϵ_i and ϵ_j are diagonal elements (orbital energies) and $F_{(i,j)}$ is the off-diagonal NBO Fock matrix elements. The natural hybrids, occupancies and delocalization of electron density for lone pair electrons of nitrogens calculated by the NBO method for the optimized geometries of three tautomers of adenine are tabulated in Table 2. The NBO analysis of donor-acceptor interactions showed that the total resonance

energy for LP(N) $\rightarrow \sigma^*$, π^* and RY* delocalization increases with increasing p character of nitrogen lone pair and in exceptional cases other parameters such as occupancy of the lone pair of nitrogen and orbital energies are important, in such a manner that the occupancy of the LP (N) decreases with increasing p character of the lone pair of nitrogen. The hybrid composition of the LP(N) (in the ring) shows that for the T1 tautomer, the electrons of LP (N₉), in the T4 tautomer, the electrons of LP(N₇) and in the T7 tautomer, the electrons of LP(N₆) occupy p orbitals.

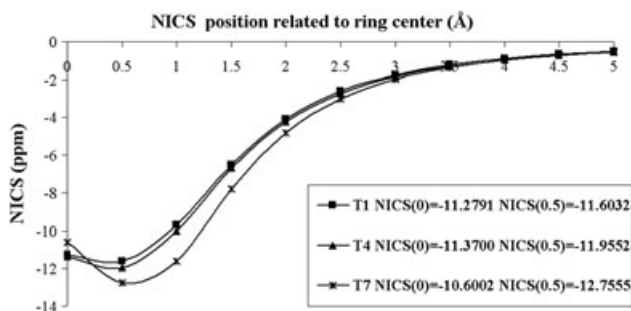


Figure 3. Aromaticity of five-membered ring of adenine tautomers estimated as a function of NICS (negative value of magnetic tensor shielding) versus distance from ring geometric center. NICS(0) and NICS(1) denotes values estimated at ring geometric center and 1 Å above, respectively.

The overlap of the p orbitals in the rings, gives rise to π electron clouds. The π electron clouds contain a total of six electrons, the aromatic sextet. In other words, in addition to six-membered rings, in the T1 and T4 tautomers the five-membered rings are aromatic and in T7, the six-membered ring is aromatic, too. Deep attention to the occupancies of the lone pair of tetravalent nitrogens (in the ring) leading to possibility of the aromaticity of the five-membered ring of T4 is more than the five-membered ring of T1, whereas, the aromaticity of the five-membered ring of T1 is more than the six-membered ring of T7. This view has been analyzed in the next section using NICS technique.

NICS study. In the NICS study, the GIAO method was applied to estimate the magnetic shielding tensor. For all studied tautomers, the sets of points lying below and above the both rings' geometric centers were used. Their locations correspond to distances from -5 to 5 Å with 0.5 Å steps. Since NICS plots of all tautomers were symmetrical along the molecule plane, only the points above the plane were presented in Figures 3–5. This feature is rather expected due to ring planarity and insignificant influence on magnetic shielding of non planar side groups. The minima of NICS values were located at the distance of 0.5 – 1.5 Å below and above the plane. The NICS 0 Å values calculated at the centre of the ring were influenced by σ bonds, whereas the NICS 1 Å values calculated at the 1 Å above the plane were more affected by the π -system [24]. On the basis of NICS plots (Figs. 3 and 4), five- and six-membered rings in all stable tautomers of adenine show considerable aromaticity. Interesting, for all three stable tautomers of adenine NICS values at the minimum point of five-membered rings are more negative (i.e., indicating more aromaticity) than six-membered rings. Notably, the most negative values of NICS plots in each rings containing tetravalent nitrogen indicate that aromaticity of five-membered ring of T4 is more than the five-membered ring of T1, whereas, the aromaticity of the five-membered

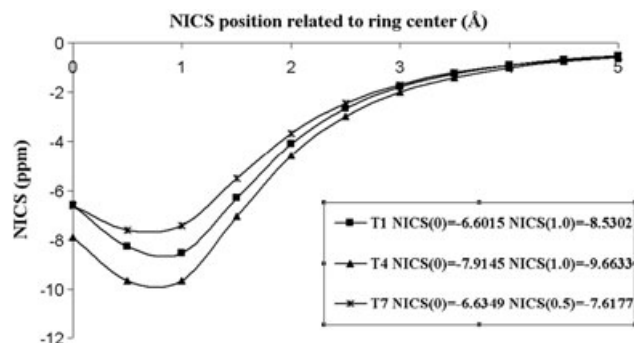


Figure 4. Aromaticity of six-membered ring of adenine tautomers estimated as a function of NICS (negative value of magnetic tensor shielding) versus distance from ring geometric center. NICS(0) and NICS(1) denotes values estimated at ring geometric center and 1 Å above, respectively.

ring of T1 is more than the six-membered ring of T7, and this is in agreement with the NBO results. It should be noted that the overall aromaticity of tautomers is better indicated by its Σ NICS value (Fig. 5). The strongest aromatic quality was found for the T4 tautomer. The T7 tautomer was also characterized by significant relative aromaticity, but less compared to the T4 tautomer. The T1 tautomer had the least aromaticity. It is clear that the order of relative aromaticity of the different tautomers is not similar to the relative energies.

^{14}N -NQR parameters. Our studies were based on the distortion of the charge distributions around nitrogen atoms. Any charge distributions may be interpreted by EFGs. Since the EFG around a nitrogen nucleus is symmetric in N_2 free molecule, the calculated values of NQR parameters for N_2 molecule are $\eta_Q = 0$ and $\nu_Q^{\text{cal}} = 4184.546\text{kHz}$. The calculated NQR frequencies of nitrogen atoms in the most stable adenine tautomers in the gas phase are listed in Table 3. The differences between the frequencies of nitrogens in these tautomers can be attributed to the direct participation of the electron pairs of some N atoms during chemical bond formation

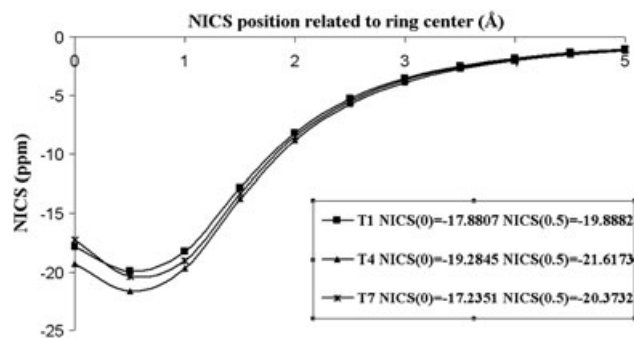


Figure 5. Overall aromaticity of adenine tautomers estimated as a function of NICS (negative value of magnetic tensor shielding) versus distance from ring geometric center. NICS(0) and NICS(1) denotes values estimated at ring geometric center and 1 Å above, respectively.

Table 3

The NQR parameters calculated and principal components of the EFG tensors for the most stable tautomers of adenine in the gas phase.

Tautomer	Nuclei	ν_+ (MHz)	ν_- (MHz)	ν_0 (MHz)	$e^2Q q_{zz}/h$ (MHz)	η_Q	q_{zz} (10^{21}V/m^2)	q_{yy} (10^{21}V/m^2)	q_{xx} (10^{21}V/m^2)
T1	-N ₍₂₎ =	3.33755	2.95544	0.38211	4.19533	0.18216	8.48608	-5.01595	-3.47013
	-N ₍₆₎ =	3.17334	2.89270	0.28063	4.04403	0.13879	8.18004	-4.65622	-3.52383
	-N ₍₇₎ =	3.16437	3.05846	0.10591	4.14856	0.05106	8.39148	-4.40999	-3.98149
	-N ₍₉₎ H-	2.52231	2.40894	0.11337	3.28750	0.06897	6.64978	-3.55421	-3.09557
	-N ₍₁₀₎ H ₂	3.68435	3.39653	0.28781	4.72059	0.12194	9.54854	-5.35648	-4.19206
T4	-N ₍₂₎ =	3.29267	3.09189	0.20077	4.25638	0.09434	8.60957	-4.71090	-3.89868
	-N ₍₆₎ =	3.53850	3.24470	0.29380	4.52214	0.12994	9.14713	-5.16787	-3.97925
	-N ₍₇₎ H-	2.76323	2.60951	0.15371	3.58183	0.08583	7.24513	-3.93350	-3.31164
	-N ₍₉₎ =	3.18873	3.15667	0.03206	4.23027	0.01516	8.55675	-4.34325	-4.21349
	-N ₍₁₀₎ H ₂	3.78415	3.45250	0.33165	4.82444	0.13749	9.75861	-5.55018	-4.20843
T7	-N ₍₂₎ =	3.41936	2.92862	0.49074	4.23199	0.23192	8.56025	-5.27278	-3.28746
	-N ₍₆₎ H-	2.13136	2.03098	0.10038	2.77490	0.07235	5.61291	-3.00950	-2.60341
	-N ₍₇₎ =	3.08645	2.72012	0.36633	3.87105	0.18927	7.83014	-4.65611	-3.17403
	-N ₍₉₎ =	3.06577	2.49945	0.56631	3.71015	0.30528	7.50469	-4.89789	-2.60680
	-N ₍₁₀₎ H ₂	3.51106	3.18369	0.32737	4.46317	0.14670	9.02785	-5.17613	-3.85172

or diatropic current in the ring. The calculated η_Q presents that the charge distributions around the N(7) and N(9) in the T1, and N(2), N(7), and N(9) in the T4 and N(6) in the T7 are approximately cylindrical and for the other nitrogens are deviated from axial symmetry. The nitrogen atoms in these tautomers are located in the electric field of the other nuclei, therefore the symmetry of the EFG around them changes. This change brings about the splitting of the energy levels of ^{14}N nuclei, consequently three NQR frequencies for ^{14}N will be observed. The calculated χ for nitrogen atoms in N_2 free molecule is 5579.395 (kHz) [14]. From the results reported in Table 3, it is obvious that the χ values for nitrogen atoms are reduced compared with N_2 free molecule. The EFG around a given nucleus arises from charge distribution of the surrounding atoms, and the contribution of nonbonding electrons is more than bonding electrons. Whenever the lone pair electrons of nitrogen participate in the formation of π bond, the q_{zz} and consequently its χ decreases. In the amino groups of stable tautomers, the p character of nitrogen atoms are about 100% and nuclear quadrupole coupling constant is in the order $\text{T4} > \text{T1} > \text{T7}$. We attribute these trends to the high degree of occupancy for lone pair electrons of nitrogen of T4 form in comparison with T1 and T7, respectively. Also, we compared χ value of N(9) in T1 with N(7) in T4 and N(6) in T7. The examination of NBO and NQR results show that the χ value of N(7) with 100% p character in lone pair electrons for T4 is larger than the χ value of N(9) in T1 and N(6) in T7 with the same p character, due to the occupancy of lone pair electrons of N(7) in T4 being greater than the occupancies of N(9) in T1 and N(6) in T7, respectively. Comparative examination of nitrogens with 100% p character in each tautomers show that the resonance frequencies of nitrogen of amino groups are

very larger than other nitrogen. In the other words resonance frequencies of N(10) is larger than N(9), N(7), and N(6) in the T1, T4, and T7, respectively. The reason is due to conjugation of the lone pair electrons of N(9), N(7), and N(6) in the T1, T4, and T7 with the π -system of the ring. In the nitrogens with fractional p character χ value is depend to the both of degree of p character and occupancy of lone pair electrons of nitrogen.

CONCLUSION

- NBO analysis revealed that the resonance between LP(N) and empty (σ^* , π^* and RY*) non-Lewis NBO increases with increasing p character of nitrogen lone pair.
- Occupancy of the LP(N) decreases with increasing p character of lone pair electrons.
- NBO analysis showed that in these tautomers the π clouds in the both considered heterocyclic heterocycle rings contained six electrons, and these tautomers are aromatic.
- NICS study showed that diatropic currents exist in the heterocycle rings of all of the three tautomers, so these tautomers are aromatic.
- NICS calculation results revealed that the order of aromatic character is: $\text{T4} > \text{T7} > \text{T1}$
- Whenever the lone pair of nitrogen atoms participates in the formation of chemical bond, the q_{zz} and consequently its χ decreases.
- NQR results show that although q_{zz} is the component of EFG in the direction of z axis and lone pair electrons of nitrogen, the nuclear quadrupole coupling constant depends on these factors: the p character value of lone pair electrons of nitrogen, their occupancy and the portion of lone pair electrons involved in magnetic currents of ring.

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