

Investigation of NQR Parameters on the Tetrazole-Azide Tautomeric Equilibria: A DFT Study

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Abstract. A theoretical study was undertaken to reinvestigate whether NQR parameters such as quadrupole coupling constant, asymmetry factor, and NQR frequencies obtained from electric field gradient tensor can provide information to infer about the substituent effect on tautomeric forms of tetrazole-azide equilibria in a gas phase. For this purpose, ¹⁴N-NQR parameters of 5-R-tetrazolo [1, 5-a] pyridines and its corresponding tautomer, on the tetrazole-azide isomerization, were calculated at the B3LYP/6-31++G** level of theory and compared with each other, where R= H, CH₃, OH, Cl, OCH₃, NO₂. The results reveal that NQR parameters of nitrogen atoms of these compounds are highly sensitive to substituent effects. The influence of these groups on the transition state (TS) was also studied. Moreover, according to some plotted graphs reasonable relationship has been found between the values of the Hammett constant (σ_p) of mentioned substituents and their ¹⁴N-NQR parameter data. In general, it is observed that groups which stabilize the azide isomer lower the E_{act} of the isomerization reaction, and conversely, those that favor the tetrazole form, raise the E_{act} relative to the unsubstituted compound. The TS has a close resemblance to the tetrazole structure. Also, the energy differences between tautomeric forms, the graphs of σ_p versus energy values, and the graph of Hammett-constants versus E_{act} as well as the graph of r_{N3-N4} versus E_{act} have been analyzed. Finally, we have focused on some critical points in the plotted graphs of both E_Q^\pm (J) versus ν_Q^\pm (MHz) and E_Q^\pm (J) versus η .

Keywords: Tetrazole; Tautomeric equilibrium; ¹⁴N-NQR parameters; DFT; Hammett Constant.

Resumen. Se llevó a cabo un estudio teórico para reinvestigar si los parámetros de Resonancia Cuadrupolar Nuclear (RCN) tales como la constante de acoplamiento cuadrupolar, el factor de asimetría y las frecuencias RCN, obtenidos a partir del tensor gradiente del campo eléctrico, pueden proveer información para realizar inferencias sobre los efectos del sustituyente en las formas tautoméricas del equilibrio tetrazol-azida en fase gaseosa. Para este propósito, los parámetros ¹⁴N RCN del 5-R tetrazolo [1,5-a] piridinas y su tautómero correspondiente, en la isomerización tetrazol-azida, fueron calculados en el nivel de teoría B3LYP/6-31++G**, y fueron comparados uno con otro, donde R = H, CH₃, OH, Cl, OCH₃, NO₂. Los resultados revelan que los parámetros de los átomos de nitrógeno de estos compuestos son altamente sensibles a los efectos del sustituyente. La influencia de estos grupos en el estado de transición (ET) también fue estudiada. Además, de acuerdo a las gráficas, se encontró una relación razonable entre la constante de Hammett (σ_p) de los sustituyentes y sus datos derivados de los parámetros ¹⁴N-RCN. En general, se observa que grupos que estabilizan el isómero azida bajan la E_{act} de la reacción de isomerización, y complementariamente, aquellos que favorecen la forma de tetrazol, aumentan la E_{act} de la reacción, relativo al compuesto sin sustitución. El ET tiene similitud a la estructura del tetrazol. Las diferencias de energía entre las formas tautoméricas fueron evaluadas y las gráficas de σ_p contra los valores de energía, y la gráfica de constantes de Hammett contra E_{act} , así como la gráfica r_{N3-N4} versus E_{act} fueron analizadas. Finalmente, hemos enfocado algunos puntos críticos en el trazo de los gráficos de E_Q^\pm (J) versus ν_Q^\pm (MHz) y E_Q^\pm (J) versus η .

Palabras clave: Tetrazol, equilibrio tautomérico, parámetros ¹⁴N RCN, TFD, constante de Hammett

Introduction

The annular tautomerism of tetrazole became a subject of numerous experimental and theoretical studies. Heterocyclic azides are known to spontaneously cyclize to give the fused tetrazole form or more generally exist as an equilibrium mixture. This fact has been described in the literature as tautomerism, as an azido-tetrazole equilibrium [1-3].

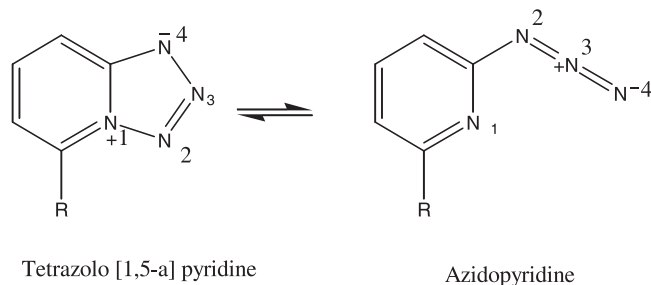
The tetrazole ring is the fragment of a number of modern drugs such as antibacterial, anti-allergic, anti-inflammatory, angiotensine II antagonists. The presence of several reaction centers and the possibility of prototropy in tetrazoles afford the conditions for their use in organic and bio-organic synthesis as reagents and catalysts.

The amount of publications devoted to the molecular structure, synthetic methods, chemical and physicochemical properties of tetrazoles constantly increases. Among the stable structures, this hetero-aromatic system contains the greatest

number of nitrogen atoms. That is why tetrazoles exhibit the extreme values of acidity, basicity, and complex formation constants. Also, these compounds have specific thermo chemical properties and exhibit multiple reactivity [4-7].

Moreover, on the basis of tetrazoles being highly effective explosives, rocket fuel and gas generating compositions were developed. The numerous possibilities of coordination of tetrazole ring with metal ions permit to use these compounds as effective complexones and as corrosion inhibitors [8-12].

The analysis of the published data permits to conclude that in spite of the relatively abundant experimental data on the acidity, basicity, and tautomerism of the neutral forms and conjugated acids of 5-substituted NH-tetrazoles, theoretical works evaluating the effect of substituents on the prototropic equilibria of tetrazoles are limited. Moreover, no attempt has been made to determine the tautomers on the basis of such parameters as NQR frequencies, quadrupole coupling constant or asymmetry parameters found from the ¹⁴N-NQR spectra and there are quite



R=H, CH₃, OH, OCH₃, NO₂

Fig. 1. Tetrazolo [1,5-a] pyridines and its corresponding azide isomer.

a few reports (all experimental works) on the tetrazole–azide equilibrium in tetrazolo [1, 5–a] pyridines (Fig. 1).

Since most studies have looked at the effect of substitution at the 8 position on the tetrazole–azide equilibrium [13–15], we were interested in systematically examining the effect of substitution at the 5–position on the tetrazole–azide equilibrium. The 5–position being nearest to the reaction center (the dissociating N₃–N₄ bond) could be expected to modulate the equilibrium reaction via an electronic and steric effect. This effect may be explained taking into account the fact that the chemical and physicochemical properties of 5R–tetrazoles are determined by the electronic structure of the whole ring and not only of the isolated reaction center [3].

Also, we have examined the influence of various substituents (R = CH₃, OH, Cl, OCH₃, NO₂) at the 5–position in tetrazolo (1, 5–a) pyridines on the stabilities of the tetrazole and azide isomers. These parameters can be used to gather a deeper insight about the conformational phenomena involved in the nitrogen containing heterocycles, which is an important issue nowadays. It is notable that often analysis of NQR parameters is restricted the quadrupole coupling constants and sometimes the asymmetry parameters, however, when the effects are so subtle it seems important to find out the quality of reproduction of all and not only selected NQR parameters.

Theoretical background

NQR spectroscopy deals with interactions between nuclear electric quadrupole moment and EFG at the site of quadrupolar nucleus $I = 1$. Nitrogen-14, with the spin of unity, exhibits in zero magnetic field three generally non-degenerate energy levels with the resonance (NQR) frequencies as below [13]:

$$\begin{aligned} v_+ &= \frac{3}{4} \frac{e^2 q Q}{h} \left(1 + \frac{\eta}{3}\right) \\ v_- &= \frac{3}{4} \frac{e^2 q Q}{h} \left(1 - \frac{\eta}{3}\right) \\ v_0 &= v_+ - v_- = \frac{1}{2} \eta \frac{e^2 q Q}{h} \end{aligned} \quad (1)$$

Its quadrupole moment is only $1.67 \times 10^{-30} \text{ m}^2$ [14,15]. Consequently, the corresponding coupling constants are small and seldom more than 6 Mc s^{-1} . A low ¹⁴N coupling constant is the main reason for the difficulty often encountered for acquiring data on nitrogen-14 nuclei. Hence, the intensities of nitrogen quadrupole resonance lines are very low and extremely sensitive spectrometers and much patience is required to get a result [16].

The ¹⁴N quadrupole coupling constant $e^2 q Q | h$ as well as the asymmetry parameter η of the electric field gradient (EFG) tensor strongly depends on the molecular structure and the electric charge distribution within the molecule as well as on the intermolecular interactions and molecular motions [17–19].

Furthermore, a notable point which is useful in this study is that the hybridization of the p-orbital with an s-orbital is indicated by the equation as below:

$$e^2 Q_{\text{mol}} = (1 - s + d - i - \pi) e^2 q Q \quad (2)$$

where $e^2 q Q$ at is the quadrupole coupling constant for occupancy of the p-orbital by a single electron, s is the fraction of s character employed by the atom in the bond to its neighbor, d is the fraction of d character in this bond, i is the fraction of ionic character in the bond, and π is the extent of π -bonding [13].

Computational details

All *ab-initio* molecular orbital calculations have been performed using the G98 program [20]. Since the NQR parameters are very sensitive to molecular geometry, it is necessary to obtain a good correlation between molecular geometry and NQR parameters for the conformational analysis. This requires the use of optimized geometries, so geometries of all structures were fully optimized at the B3LYP (three-parameter hybrid functional of Becke using Lee-Yang-Parr correlation functional) method using the 6-31++G** basis set. The optimization of molecular geometries using the minimization procedure of the energy gradient with respect to nuclear coordinates was possible for all SCF wave functions. Previous reports have shown that this computational level provides good results for a variety of molecules [21–23].

It is clear that more than one tautomers may exist in the gas phase, however, in this study, the transition states of only two tautomers displayed in Fig (1) have been considered and determined by varying the N₃–N₄ distance and optimizing the remaining structural parameters for each choice of the N₃–N₄ distance. All transition states have been characterized by checking vibrational frequencies. Ground states were confirmed by the presence of only one imaginary frequency.

Consequently, the optimized data of R-Piperazines R=H, CH₃, OCH₃, OH, NO₂ have been considered to compute the $e q_{xx}$, $e q_{yy}$, and $e q_{zz}$, the principal components of the electric field gradient tensor. From these quantities the values of NQR parameters such as quadrupole coupling constants, asymmetry parameter, and quadrupole frequencies of nitrogen atoms for

various optimized structures have been calculated and the influence of these groups on the NQR parameters of transition state (TS) have been also reported.

Since more than one tautomer may be present in the gas phase spectra, their calculated relative energies, and optimized inter-atomic distances and angles of the two tautomers have been considered in determining the relative concentrations of components in such mixtures.

For more investigation, the graphs of σ_p 's versus energy values have been analyzed. Moreover, in order to study more about substituent effect on the energy barrier, the graph of Hammett-constants versus E_{act} as well as the graph of r_{N3-N4} versus E_{act} have been analyzed.

Also we have discussed about some critical points in the plotted graphs of both E_Q^\pm (J) versus ν_Q^\pm (MHz) and E_Q^\pm (J) versus η .

Results and discussion

1. Substituent Effect on the ^{14}N -NQR parameters derived from the electric field gradients of tautomeric structures

Theoretical calculation of ^{14}N -NQR parameters has proven to be sensitive technique for the study of molecular structure of

the substituent effects produced in the conformational dynamics of nitrogen-containing heterocyclic compounds and can reveal many important facts closely related to their biological effects.

In this step, we supposed the theoretical NQR convention for magnitudes, namely $|q_{zz}| \geq |q_{yy}| \geq |q_{xx}|$ and we used the other conventions which have been discussed in the second section of our paper to derive NQR parameters of four nitrogen atoms and evaluate the substituent effect on their values. As different field gradients exist for non-equivalent nuclei in these molecules. So, we observed different NQR parameters for each type of nuclear environment. Moreover, through tautomeric equilibrium, the resonating quadrupolar nuclei of tetrazole ring feel the changes in the electric field gradient (EFG), which is reflected in the observed shifts of the NQR parameters. Values determined from theoretical calculation will thus provide a good indication of the components of each type in the field gradient principal axis frames, and will assist in the future assignment of such spectral data.

Since the use of a finite basis set is always a source of uncertainties in the EFG components, according to several papers in this field (21-23), the use of polarized basis set as 6-1++G** seems to be adequate for the prediction of the conformational preferences in these compounds. Moreover, it is notable that the sensitivity of ^{14}N nuclei to basis set is due to

Table 1. Theoretical NQR Parameters of four nitrogen atoms of R-Tetraazolo [1, 5-a] pyridine and its corresponding azide isomer and TS structure at the Level of B3LYP/6-311++G**.

NQR parameters	Atom's number	η			χ (MHz)			ν_0 (MHz)			ν_+ (MHz)			ν_- (MHz)		
		TETRA	TS	Azide	TETRA	TS	Azide	TETRA	TS	Azide	TETRA	TS	Azide	TETRA	TS	Azide
N ₁	H	0.401	0.429	0.113	5.369	6.168	5.449	1.077	1.326	0.309	4.564	5.289	4.242	3.476	3.963	3.932
	OH	0.417	0.325	0.157	5.515	6.458	7.026	1.152	5.368	0.747	4.711	5.386	5.643	3.561	4.319	4.895
	CH ₃	0.417	0.269	0.111	5.515	5.857	6.693	1.149	0.901	0.302	4.712	5.460	4.225	3.562	4.569	3.921
	OCH ₃	0.356	0.271	0.441	5.881	4.990	5.892	0.988	0.676	4.419	4.934	4.081	5.070	3.877	3.404	3.768
	NO ₂	0.283	0.682	0.025	6.250	8.046	0.923	0.804	2.744	0.055	5.129	7.407	0.698	4.245	4.662	0.686
N ₂	H	0.431	0.287	0.113	5.874	5.282	5.449	1.266	1.326	0.355	5.038	4.341	0.736	3.772	3.582	3.932
	OH	0.442	0.256	0.052	5.898	5.963	0.776	1.303	0.764	0.020	5.075	4.854	0.592	3.771	4.090	0.572
	CH ₃	0.430	0.340	0.646	5.857	5.894	0.812	1.262	0.586	0.303	5.024	4.713	4.225	3.762	4.127	3.921
	OCH ₃	0.441	0.975	0.442	5.892	8.057	5.892	1.299	7.957	4.419	5.154	10.021	5.070	3.833	4.127	3.921
	NO ₂	0.416	0.275	0.614	6.342	8.664	5.158	1.319	1.193	1.583	5.455	7.094	4.660	4.057	5.901	3.076
N ₃	H	0.359	0.402	0.643	4.988	5.164	4.917	0.895	1.038	0.259	4.188	4.392	0.736	3.295	3.354	3.354
	OH	0.271	0.451	0.151	5.100	5.912	2.416	0.691	0.667	0.183	4.169	5.101	1.903	3.480	3.766	1.710
	CH ₃	0.372	0.340	0.646	4.956	6.461	0.812	0.923	1.099	0.262	4.185	5.395	0.740	3.262	4.296	0.478
	OCH ₃	0.295	0.327	0.571	5.106	6.185	4.937	0.753	1.012	0.746	4.205	5.144	4.162	3.453	4.103	3.415
	NO ₂	0.275	0.454	0.241	5.193	6.234	1.116	0.714	1.418	0.134	5.251	5.384	0.905	3.537	3.966	0.837
N ₄	H	0.552	0.412	0.110	4.870	5.663	2.617	1.344	1.167	0.144	4.325	4.831	2.035	2.979	3.663	1.891
	OH	0.427	0.451	0.157	4.935	5.912	4.907	1.053	0.667	0.675	4.228	5.101	4.854	3.174	3.766	3.498
	CH ₃	0.527	0.215	0.087	4.920	6.693	5.431	1.296	0.676	4.136	4.338	5.049	4.231	3.041	4.373	4.042
	OCH ₃	0.571	0.248	0.571	4.937	5.127	5.882	1.409	0.636	4.411	4.407	4.163	4.935	2.998	3.527	3.887
	NO ₂	0.715	0.172	0.473	4.821	7.822	0.633	1.723	0.672	0.149	4.477	6.203	0.549	2.753	5.530	0.399

the core electrons. So, its EFG heavily depends on method and basis set. On the basis of the results of NQR study it is possible to conclude which tautomeric form is present in a given sample.

The parameters obtained by the B3LYP method in the extended basis set for two tautomeric forms and TS structure are collected in Table 1 to compare the quality of reproduction of such parameters. According to obtained results, nitrogen atoms of TS structures possess higher values of NQR parameters. The reason is due to the influence of the planarity of the TS ring on the charge distribution around nitrogen nucleus. This increases the component of the electric field gradient (EFG) in the direction of z axis, q_{zz} , for nitrogen. This reasoning is further substantiated by shorter N_3-N_4 bond length of 1.90 to 2.02 Å, encountered for TS and the $N_1-N_2-N_3$ angle which ranges from 116.980 to 125.3° and the $N_2-N_3-N_4$ angle varies from 94.9° to 99.4°. In the azides, the $N_1-N_2-N_3$ angle is on average 175°, showing that the azido group is linear and not bent; this is in agreement with an early reported MO calculation [24].

To go further in structural studies, Hammett-constants of mentioned substituents [25] have been used as the measure of the electronic effect and then the values of the $\chi^{14}N$ calculated in the present work satisfactorily correlated with σ_p -constants of substituents via plotting related graphs (Fig.2). According to the plotted graphs, it can be seen a direct relationship between σ_p and $\chi^{14}N$.

The optimized inter-atomic distances and angles of the two tautomers and TS structure are reported in Table 2. From these data it follows that on going from electron-donating substituents to electron-withdrawing ones, a significant shortening of the N_3-N_4 bond, while the C-N bonds are not considerably altered.

2. The relative energies of two tautomeric forms and TS structures

Investigation of a relative stability of tautomers requires the knowledge of differences in their total energies in the equilibrium geometries, determined under the assumption that the zero vibration energies are the same. A correct reproduction of such a subtle effect as the differences in the tautomers energy can be achieved only using the non-empirical methods with full optimization of geometry [26].

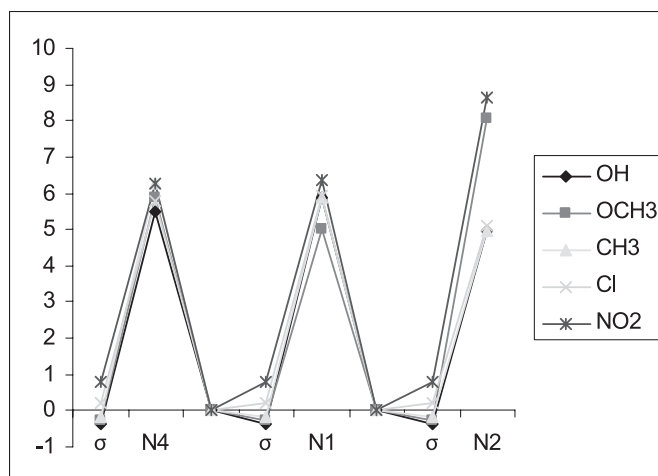


Fig. 2. The graph of Hammett constant of different substituents versus coupling constants of four nitrogen atoms of tetrazole ring.

Earlier studies have already shown that relative energies of the two tautomeric forms of tetrazole-azide pyridines are within a narrow range of a few Kcal/Mol [27].

The results of various calculations on absolute energies as well as relative energies are listed in Table 3.

According to the results, for the unsubstituted compound ($R=H$) and the molecule with CH_3 group, the tetrazole is predicted to be more stable. The effect of the Methyl group agrees with Messmer and Hajo's statement that the electron donating group enhance the stability of the tetrazole form [28]. For the other substituents such as OH, Cl, OCH_3 , and NO_2 favor the azido isomer. Among considered substituents, our data show that the NO_2 imposes the largest effect on the tautomeric equilibrium. However, the effect of the OH and OCH_3 groups goes against the Messmer and Hajo's opinion. The reason is that for these substituents, their inductive effect dominates the resonance effect.

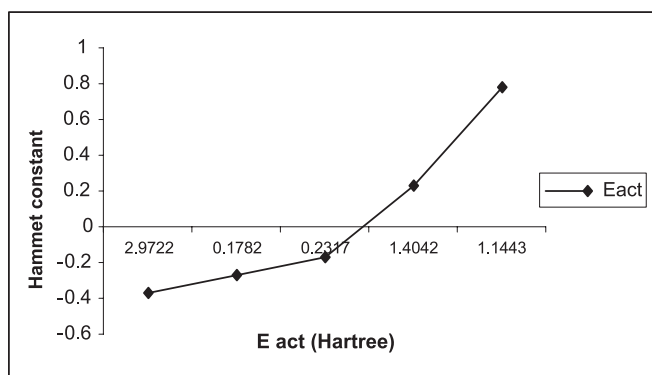
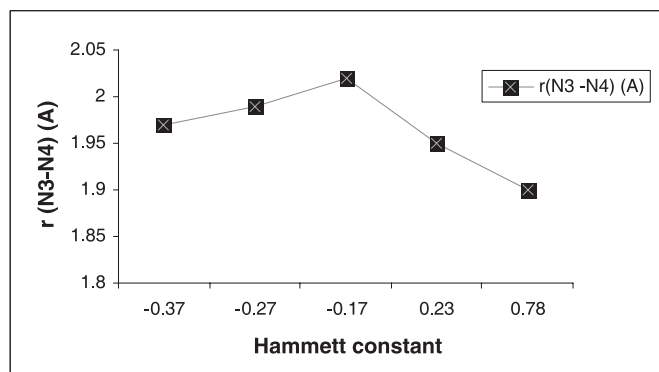
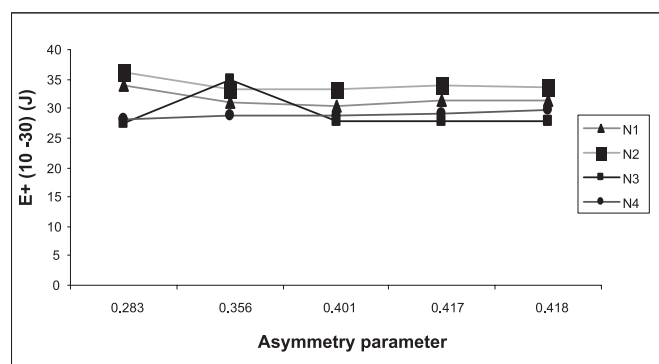
Considering the graph of σ_p 's versus E_{act} values, the minimum point has been observed for OCH_3 and CH_3 groups which predicted to stabilize the tetrazole isomer (Fig. 3). It is notable that a critical or maximum point has been found in the Fig. 4 for CH_3 substituent which has the maximum N_3-N_4 bond length. Regarding to this fact, we can suppose the N_3-N_4 bond as the more probable cleavage site in the tetrazole ring.

Table 2. Energies (Hartree) and geometries of TS and tetrazole isomer.

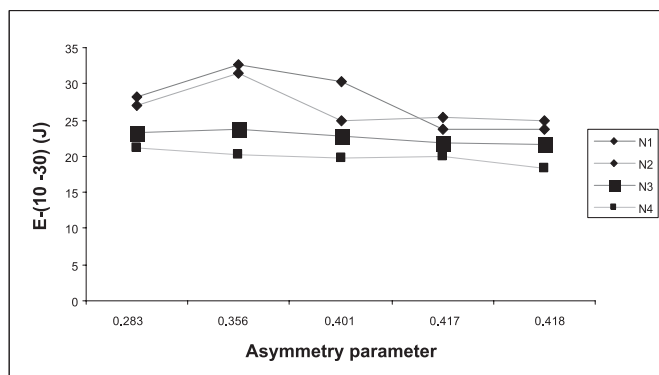
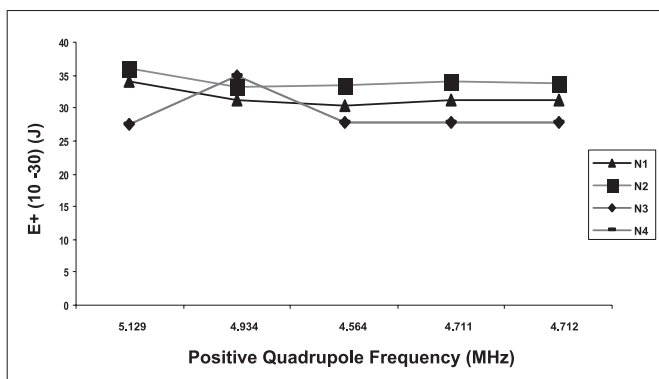
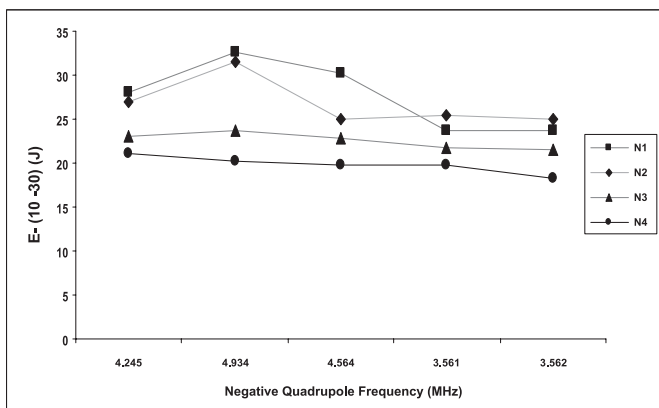
R	E_{TS}	$E_{act}(ET-ETS)$	N_3-N_4 (?)	$N_1-N_2-N_3$ (?)	$N_2-N_3-N_4$ (?)
H	-412.99144	0.1518	2.01(1.439)	125.3(113.04)	96.6 (111.247)
CH_3	-452.24343	0.2317	2.02(1.437)	123.3(112.90)	94.9(111.335)
OH	-412.21178	2.9722	1.97(1.441)	120.3(113.114)	95.8(111.017)
Cl	-870.21178	1.4042	1.95(1.440)	120.7(113.000)	96.7(111.114)
OCH_3	-527.52372	0.1782	1.99(1.441)	120.1(113.04)	95.3(113.063)
NO_2	-617.55179	1.1443	1.90(1.424)	116.980(109.130)	99.485(111.447)

Table 3. Energies (in terms of Hartree) of R-Tetrazolo [1, 5-a] pyridine and R-Azidopyridine at the Level of B3LYP/6-311++G**.

Substituent	R-Tetrazolo [1, 5-a] pyridine	TS	R-Azidopyridine
R=H	-413.1433088	-412.9914417	-411.9918161
R=CH ₃	-415.1840444	-452.2434314	-451.3234099
R=OH	-414.7593114	-412.2117847	-452.4752016
R=Cl	-871.61604341	-870.2117847	-872.7620568
R=OCH ₃	-527.7019435	-527.5237237	-527.9886799
R=NO ₂	-616.4074818	-617.5517899	-617.6930487

**Fig. 3.** The graph of Hammett constant versus E_{act} .**Fig. 4.** The graph of r_{N3-N4} (Å) versus Hammett constant.**Fig. 5.** The graph of E_Q^+ versus asymmetry parameters of four nitrogen atoms.

Finally, according to Figs. 5, 6 and 7 which evaluate the relationships between E_Q^\pm (J) versus v_Q^\pm and E_Q^\pm (J) and asymmetry parameter N_1 and N_2 atoms showed the similar behavior as well as N_3 and N_4 atoms which can emphasize the cleavage region on the tetrazole ring.

**Fig. 6.** The graph of E_Q^- versus asymmetry parameters of four nitrogen atoms.**Fig. 6.** The graph of E_Q^+ versus positive quadrupole frequencies of four nitrogen atoms.**Fig. 7.** The graph of E_Q^+ versus negative quadrupole frequencies of four nitrogen atoms.

Conclusions

- Theoretical calculations of ^{14}N -NQR parameters has proven to be a sensitive technique for the study of molecular structure of the substituent effects produced in the conformational dynamics of nitrogen-containing heterocyclic compounds and can reveal many important facts closely related to their biological effects.
- Quadrupole coupling constants afford a new source of information about the character of molecular bonds, a source which in some cases appears to give different and more reliable information than is otherwise available.
- Through going from electron-donating substituents to electron-withdrawing ones, a significant shortening of the 1–2 bond and a simultaneous elongation of the 2–3 one is observed, while the C–N bonds are not considerably altered.
- Nitrogen atoms of TS structures possess higher values of NQR parameters. The reason is due to the influence of the planarity of the TS ring on the charge distribution around nitrogen nucleus. This increases the component of the electric field gradient in the direction of z axis, q_{zz} , for nitrogen this reasoning is further substantiated by shorter N_3 - N_4 bond length of 1.90 to 2.02 Å, encountered for TS and the N_1 - N_2 - N_3 angle which ranges from 116.980 to 125.3° and the N_2 - N_3 - N_4 angle varies from 94.9° to 99.4°.
- According to the energy values, for the unsubstituted compound (R=H) and the molecule with CH_3 group, the tetrazole is predicted to be more stable.
- For the substituents such as OH, Cl, OCH_3 , and NO_2 favor the azido isomer and among considered substituents, our data show that the NO_2 imposes the largest effect on the tautomeric equilibrium.
- For the OH and OCH_3 , their inductive effect dominates the resonance effect which groups are against the Messmer and Hajo's opinion that the electron donating groups enhance the stability of the tetrazole isomer.
- In the tetrazole ring, N_1 and N_2 atoms showed the similar behavior as well as N_3 and N_4 atoms which can emphasize the cleavage region.

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