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Gas Phase Computational Studies of C-Substituted Tetrazoles

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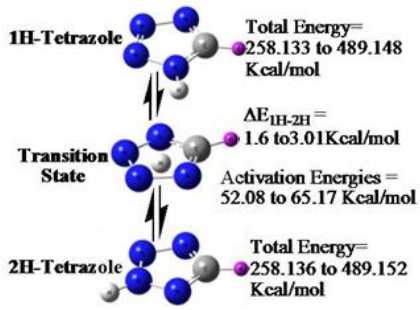
Abstract: *A DFT (B3LYP) with basis sets 6-31G, 6-31+G*, 6-311++G** and cc-pVTZ were incorporated to study tetrazole and its substituted tautomers. The results predict 2H-tautomer to be more energetic over 1H-tautomer. E_{1H-2H} between unsubstituted tautomers compares fairly well with experimental value, 6.95 ± 1.50 kJ mol^{-}. Activation barrier for all the species were predicted as 60.0±6.0kcal mol^{-1}. Geometry based degree of aromaticity show 62.38 to 98.35 for ground state and -99.0 to 79.17 for transition state isomers.*



I. Introduction

N-Heterocycles are found to have distinct and interesting chemical properties, especially when nonsymmetrically substituted, distinguishable properties can arise for these molecules. The presence of several reaction centers and the possibility of prototropy in tetrazole afford the conditions for their use in organic and bio-organic synthesis as reagents and catalysts. Among the stable structures, this hetero-aromatic system contains the greatest number of nitrogen atoms, which is why tetrazole exhibit the extreme values of acidity, basicity, and complex formation constants. Moreover, being highly energetic nitrogen rich compounds, explosives materials, rocket fuel and gas generating compositions were developed from a number of tetrazole derivative[1-3]. The tetrazole ring is a fragment from a number of modern drugs such as anti-bacterial,

Computational details

All calculations in this work were performed using Density Functional Theory since it is a promising choice because it is able to efficiently predict atomic and molecular properties for a variety of systems[6,7]. Since aromaticity parameters are highly sensitive to molecular geometry, all the structures are fully optimized at the B3LYP (three–parameter hybrid functional of Becke using Lee-Yang-Parr correlation functional) method using the standard 6-31G, 6-31+G*, 6-31**G++ and cc-pVTZ basis sets to obtain desirable geometries and energies. Diffuse and polarization functions were known to predict quality results and low computational cost in case of geometrical optimization and for systems with large electron density[8-13]. The 6-311++G** is triple- zeta quality for the valence electron anti–allergic, anti–inflammatory, angiotensine II antagonists[4]. The numerous possibilities of coordination of tetrazole ring with metal ions permit to use these compounds as effective complexones and as corrosion inhibitors[5]. The degree of aromaticity of the ring systems between the two tautomers are examined using different simple parameters like Harmonic Oscillator Model of Aromaticity, Bird Index and Nuclear Independent Chemical Shift, and the value corresponding to the degree of aromaticity is found to show fluctuation under the influence of various substituents. The purpose of this work is to obtain computational data relating to substituent effects on the structures and chemical properties of the tetrazole by investigating the substituted tautomers. and reported to produce significantly higher computational efficiency and satisfying geometries[14,15]. In order to examine the influence of basis sets regarding the degree of consistency and reliability in terms of various parameters, we have compared the total energies, relative energies, activation energies and degrees of aromaticity arising from the calculated result on various selected theoretical levels with standard basis set. Substitution was made at the Carbon atom of the tetrazole

ring with seven selected functional groups,

viz., OH-, CH3, C_2H_5-, NO_2-, NH_2-, COOH- and C_6H_5-.
The study focus towards the electronic structures base on the Density functional theory of calculation, and all the geometry optimizations were performed using Gaussian03W and GaussView3.7 software packages.

II. Results And Discussions

Optimised geometries of 1H- and 2H- Isomers

Our calculations of the parent (unsubstituted) and substituted isomers between B3lyp/6-31G and B3lyp/6-31+G (d) levels predicts close values for 1H-and 2H- isomers. Differences in the values of calculated bond length on the substituted and unsubstituted isomers are usually small for all the ring systems. Regarding N-H bond length we obtained result close to the normal N-H bond length (1.01 Å) with B3lyp/6-31+G (d) level for both the isomers.

There are no significance changes in bond lengths of the optimised geometries of the tetrazole isomers even upon substitution. The electron withdrawing and donating effect of substituents imparts more or less the same effect on the ring, and all the

Energetic Properties

Among all the tetrazole isomers, 2H-Isomer is reported to be the more energetically preferred tautomer in the gas phase [17-19]. Enthalpy differences between the two tautomers are mostly predicted as 2 kcal mol^{-1} on average[18,19]. According to Susana C.S.Bugalho et al, experimental result in enthalpy between the two tautomers, i.e. E_{1H-2H} is reported as 6.95 ± 1.50 kJ mol^{-1} (1.65 ± 0.35kcal/mol)[20]. Our results in Table.1 show good agreement with experimental result for most substituents where the calculated relative energies fall within the range of 0.2 to 2.9 kcal mol^{-1} energies[19]. We

Table 1: Total energies (in Hartrees) and relative energies E_{1H-2H} (in kcal/mol) of ground state isomers.

Isomers	B3lyp/6-31G		
	1H	2H	E1H–2H
Tetrazole	-258.133	-258.136	1.8
5-HydroxyTz	-333.324	-333.325	0.2
5-MethylTz	-297.450	-297.452	1.5
5-EthylTz	-336.754	-336.756	1.5
5-NitroTz	-462.525	-462.528	2.0
5-AminoTz	-313.479	-313.483	2.7
5- CarboxyTz	-446.629	-446.629	0.0
5-PhenylTz	-489.148	-489.152	2.4
Isomers	B3lyp/6-31+G*		
Tetrazole	-258.263	-258.267	2.9
5-HydroxyTz	-333.487	-333.491	1.9
5-MethylTz	-297.589	-297.592	2.4
5-EthylTz	-336.903	-336.907	2.6
5-NitroTz	-462.751	-462.756	2.8
5-AminoTz	-313.625	-313.631	3.6
5- CarboxyTz	-446.836	-446.839	2.1
5-PhenylTz	-489.334	-489.338	2.9

optimized geometrical parameters fall within the same range to normal tetrazole ring. In case of phenyl substitution, 1H-isomers have longer bond lengths within the ring and a shorter N-H bond in comparison to the 2H-isomers. According to K.Geetha et al., this abnormality is caused by the pseudo -electron participation from the phenyl ring[16]. This reflect that the C-atom of the 1H-tetrazole ring experienced more induced electronegative character from the phenyl ring system, which slightly increased the tetrazole ring current resulting bond elongation, i.e., 1H-tautomer is experiencing more extensive delocalization within the ring system.

obtained very low values under B3lyp/6-31G level for 5-Hydroxy-2H-tetrazole and 5-Carboxy-2H-tetrazole (Table.1). However, on applying polarization function, a reasonably good result of 1.9 and 2.1kcal mol^{-1} were predicted for these two isomers respectively (Table.2). Still, trends in the relative energies depend highly on the electronic properties of the substituents, showing that substitution deeply influence the stability of the tetrazole tautomers. For example, with the electron donating amide group, we obtain a comparable value as high as 2.7 kcal

mol^{-1} and 3.6 kcal mol^{-1}.

Table 2: Total energies (in Hartrees) and relative energies $E_{1H–2H}$ (in kcal/mol) of ground state isomers.

Isomers	B3lyp/6-311++G**		
	1H	2H	*E*1*H*–2*H*
Tetrazole	-258.324	-258.329	2.92
5-HydroxyTz	-333.576	-333.579	1.99
5-MethylTz	-297.659	-297.663	2.52
5-EthylTz	-336.983	-336.987	2.61
5-NitroTz	-462.866	-462.870	2.99
5-AminoTz	-313.705	-313.711	3.01
5- CarboxyTz	-446.952	-446.955	1.98
5-PhenylTz	-489.442	-489.447	2.99
Isomers		B3lyp/cc-pVTZ	
Tetrazole	-258.345	-258.349	2.47
5-HydroxyTz	-333.602	-333.604	1.81
5-MethylTz	-297.683	-297.687	2.11
5-EthylTz	-337.011	-337.014	2.21
5-NitroTz	-462.903	-462.907	2.27
5-AminoTz	-313.730	-313.734	2.46
5- CarboxyTz	-446.986	-446.988	1.62
5-PhenylTz	-489.485	-489.489	2.68

Tautomeric preference

The possibilities and existence of tautomerism between 1H- and 2H-tetrazole provide reasonable data concerning the influence of those selected substituents to the activation barrier on tetrazole isomers. The intramolecular 1,2-prototropic shift is a plausible tautomerisation for neighboring N-atoms[21]. In the crystalline phase, tetrazole exists exclusively as its 1H-tautomer[22], and, on the other hand, in solution, 1H- and 2H-tautomer co-exist, and the relative proportion of the more polar 1H-form increases with increasing solvent polarity and, in the gas phase, the existence of 1H-tetrazole has been suggested by microwave spectroscopy[19,25]. We investigated the possibility for 1H-and 2H-tetrazole to co-exist under the influence of suitable substituents even in the gas phase. As a rule, 2-substituted isomers are more stable than 1-substituted tetrazoles in the gas phase, and the stability of 1-substituted tetrazoles relative to the corresponding 2-substituted isomers increase in going to condensed state[23-25]. Tautomeric equilibrium in 5-substituted tetrazoles is strongly dependent on the phase, nature of the substituents and its position[25]. We expect the introduction of substituents to the ring Nitrogen atom stabilizes the corresponding 1H- or 2H-isomers. Transition states species were fully optimized and the geometries do not show any appreciable change in bond

Table 3 : Total energies(hartrees) and activation energies($kcalmol^{-1}$) of the transition state species.

	B3LYP/6-31G		B3LYP/6-31+G*	
Isomers	Total	AE	Total	AE
	Energy		Energy	
Tetrazole	-258.035	61.49	-258.174	55.44
5-HydroxyTz	-333.223	63.37	-333.397	58.35
5-MethylTz	-297.353	60.86	-297.501	55.22
5-EthylTz	-336.657	60.86	-336.815	54.59

5-NitroTz	-462.421	64.63	-462.658	58.35
5-AminoTz	-313.389	55.84	-313.541	52.08
5- CarboxyTz	-446.525	64.63	-446.743	57.73
5-PhenylTz	-489.054	58.98	-489.247	53.96
Isomers	B3LYP/6-311++G**		B3LYP/cc-pVTZ	
Tetrazole	-258.238	53.97	-258.260	55.85
5-HydroxyTz	-333.489	55.85	-333.517	54.86
5-MethylTz	-297.574	65.17	-297.599	55.37
5-EthylTz	-336.898	56.06	-336.927	55.33
5-NitroTz	-462.775	59.67	-462.814	58.69
5-AminoTz	-313.625	53.71	-313.650	52.66
5- CarboxyTz	-446.862	58.20	-446.897	57.39
5-PhenylTz	-489.358	55.68	-489.402	55.15

lengths in the cyclic moiety for all the species. However, very small bond elongation between N_1 and N_2 (~0.1 Å) could be found in all the transition state structures. We considered this slight elongation in N_1-N_2 to be the result from the formation of hydrogen bonded complexes of the tetrazole tautomers because X-ray diffraction studies of the crystalline structure of tetrazole revealed that the 1H-tetrazole molecules are linked by N-H···N and C-H···N bridges[26,27]. The predictions of activation barrier for all the tetrazole isomers were 60.0±6.0 kcal mol^{-1} (Table 3). Concerning the results of B3lyp/6-31G and B3lyp/6-31+G* levels, isomers with electron withdrawing hydroxy, nitro and carboxy groups are found to predict higher activation barrier than those of the other species. The difference in activation energy from unsubstituted tetrazole is~3.01kcal mol^{-1}(Table 3). The cc-pVTZ level predicts 55.85 kcal mol^{-1} energy barrier for the unsubstituted tetrazole; while nitro substituted isomer predict 58.69 kcal mol^{-1} (Table 3). Although we obtained almost the same trends in activation energy, we considered basis set with polarization function, i.e., B3lyp/6-311++G** is highly suitable, where unsubstituted transition state species predicted 53.97 kcal mol^{-1} energy barrier. The overall results show that electron donating group lower activation energy to a small extent for the existence of equilibrium condition between the two tautomers.

Geometry based index of aromaticity

The optimized geometries of the tetrazole and its substituted isomers were analyzed and their structural indices are summarized in Table 4. Harmonic Oscillator Model of Aromaticity (HOMA) was used in this study as a criterion for the estimation of the characteristic degree of aromaticity.

Krygowski and Cyranski, the overall aromaticity in the hydrocarbon and heterocycles tends to decreases with bond elongation above the optimal bond length[28]. We used to define the aromaticity index HOMA and its components EN and GEO to analyze the aromatic properties of the tetrazole. The index is defined by Krygowski in the following expression[29]:

$$HOMA = 1 - \sum_{=1}(\quad -)^2 = - \quad -$$ where n is the number of bonds, a is an empirical

constant (for C–C and C–N bonds 257.7 and 93.5, respectively), R_{opt} is a bond length in the fully aromatic system and R_i is a bond length obtained in calculation or crystallographic data. HOMA = 0 describes model non-aromatic system while HOMA = 1 stands for model aromatic system like benzene. The EN and GEO terms describe decrease of aromaticity due to a lengthening of the mean bond lengths and increase in bond lengths alternation, respectively. Both terms are independent on each other[30,31]. The HOMA model has been successful in describing the aromatic character of many diverse π-electronsystems.

Reliable theoretically obtained molecular geometries may be applied for the evaluation of HOMA index of Aromaticity [32,33].The optimized bond lengths obtained so far at different basis sets are used to evaluate the degree of aromaticity of tetrazole and its substituted isomers. Here in our 5-membered heterocycles, the HOMA index of aromaticity was evaluated, starting from the bond length (l_i), according to the formula[34]:-

Table 4. HOMA at B3LYP/6-31G, B3LYP/6-31+G*, B3LYP/6-311++G** and B3LYP/cc-pVTZ levels of theory.

			HOMA values		

Isomers	B3LYP/6-31G			B3LYP/6-31+G*		
	1H	2H	Ts	1H	2H	Ts
Tetrazole	67.78	84.84	-8.68	89.12	97.58	65.15
5-HydroxyTz	65.84	85.04	-52.9	86.03	97.27	49.72
5-MethylTz	68.76	87.86	-9.14	89.06	92.89	63.99
5-EthylTz	68.33	83.92	-7.30	89.14	96.87	62.95
5-NitroTz	75.26	86.06	35.18	92.68	95.20	74.43
5-AminoTz	62.38	81.79	-99.0	86.07	96.43	42.29
5- CarboxyTz	76.83	84.38	33.38	93.59	96.99	73.85
5-PhenylTz	72.39	83.62	-5.30	90.89	98.76	64.17
Isomers	B3LYP/ 6-311++G**			B3LYP/cc-pVTZ		
Tetrazole	88.98	98.03	65.55	89.43	98.4	63.11
5-HydroxyTz	85.69	97.62	54.74	85.83	98.06	52.01
5-MethylTz	88.74	97.31	63.73	89.38	97.93	61.59
5-EthylTz	88.70	97.18	62.89	69.14	97.97	61.01
5-NitroTz	91.97	97.89	74.21	92.39	98.35	72.59
5-AminoTz	85.24	96.56	43.23	85.98	96.93	38.82
5- CarboxyTz	93.46	97.31	74.72	93.80	97.81	73.66
5-PhenylTz	90.68	96.98	64.19	91.58	97.69	62.97

HOMA = 100-(100/n) $\sum \alpha (l_{opt} - l_i)^2$ **n** = No. of bonds in the ring, □ = Normalizing factor,
□ = 93.52 for both C-N and N-N bonds, $\mathbf{l_{opt}}$ = optimal bond length in angstrom
$\mathbf{l_{opt}}$ = 1.334 for C-N bond, $\mathbf{l_{opt}}$ = 1.309 for N-N bond, $\mathbf{l_i}$ = calculated individual bond length

The calculated HOMA indices of all the isomers predict certain degree of aromaticity except for the transition state geometries from B3lyp/6-31G level of theory. In this case, the calculated HOMA values predict non-aromatic properties with the exception of nitro- and carboxy-substituted species having 35.18 and 33.38 HOMA values (Table 4). Calculations with 6-31G basis set on HOMA index predict non-aromatic property and the values are exceptionally lower as compare to fully aromatic benzene and other five membered heterocycles [34-38]. We are deeply convinced that this basis set does not fit well for the calculation of HOMA index for the titled compounds and other five-membered heterocycles. Except for this case, our calculated HOMA values correspond to the presence of certain degree of aromaticity.

According to Ivashkevitch et al., 2H-tautomer with HOMA values 98 is considered more stable isomer than the 1H-tautomer with HOMA values 92[34]. The same pattern where 2H-tautomers have higher HOMA values for all tetrazole isomers from the B3lyp/6-31+G*, B3lyp/6-31++G** and B3lyp/cc-pVTZ levels were seen from Table 4. These results support higher aromatic character of 2H-tautomer over 1H-tautomer in C-substituted Tetrazole isomers.

III. Conclusions

1. Optimised geometries of substituted tetrazoles predict bond lengths very close to unsubstituted tetrazole. The electron donating and withdrawing properties of the selected substituents influence the tetrazole only to a small extent. We are convinced that the nature of the ring have a strong resistance to substituents effect.
2. Ease of tautomeric transformation is not much improved by the electronic effect of our substituents as expected. Activation barrier of substituted isomers does not deviate much from the unsubstituted compound for both the tautomers. Also the 2H-tautomer is not affected as expected by substitution under normal condition in the gas phase. This implies that chances for the co-existence of 1H-and 2-H Isomers in the gas phase is very low. .

3. HOMA calculation predict 2H-tautomer is more aromatic than 1H-tautomer and these results support any previous study showing the predominance property of 2H-tautomer over 1H-tautomer. It is a known fact that lack of aromaticity results in less favored tautomer. Strong electronic resistance to substituents results in small change in the degree of aromaticity with respect to the unsubstituted tetrazole.

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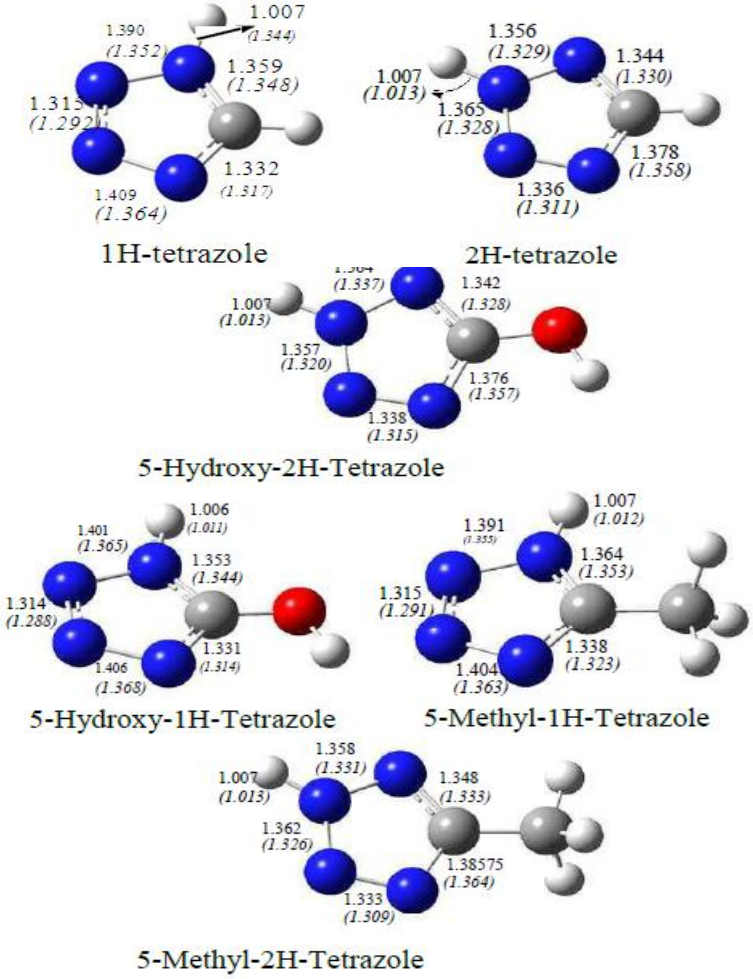
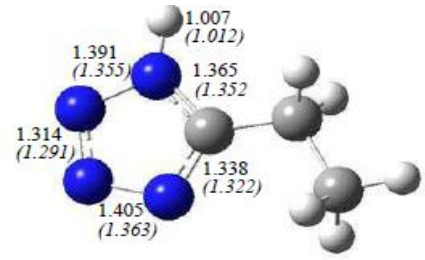
Supporting Information:

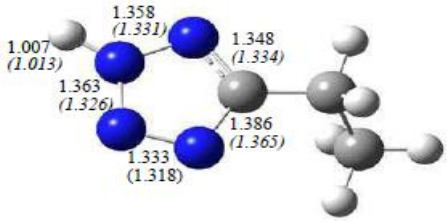
Gas Phase Computational Studies Of Substituted Tetrazoles

Figure 1: Bond lengths (in Å) for the optimized structures of uns ubstituted and 5-substituted 1H-and 2H-tetrazole at B3LYP/6-31G level of theory. The values in parentheses are at B3LYP/6-31+G (d).





5-Ethyl-1H-Tetrazole



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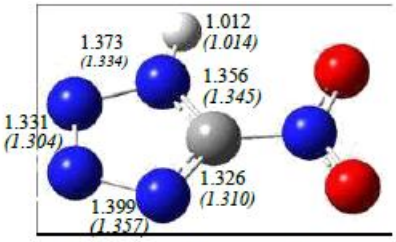

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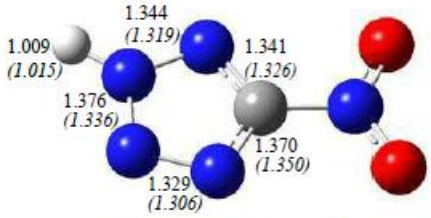

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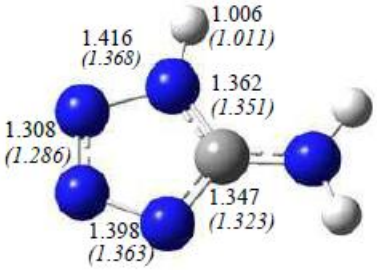
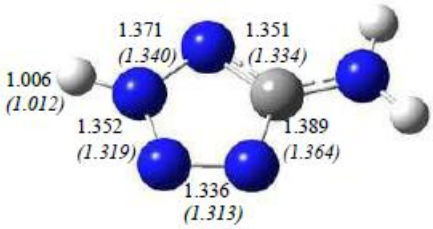


5-Amino-1H-Tetrazole



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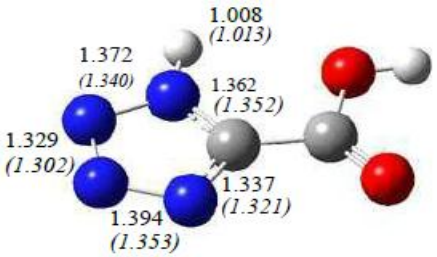
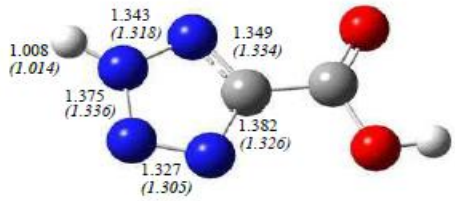


5-Carboxy-1H-Tetrazole



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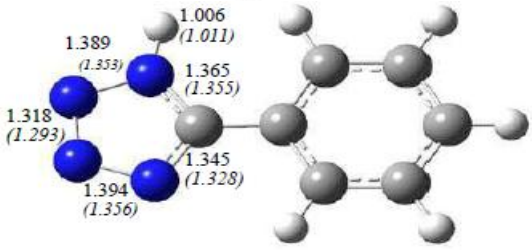
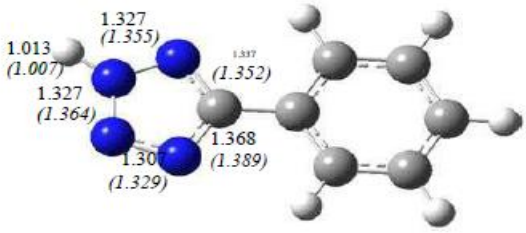


5-Phenyl-1H-Tetrazole



5-Phenyl-2H-Tetrazole

Figure 2: Optimized geometries of the transition state [(bond lengths are given in Å and the values in parentheses are at B3LYP/6-31+G (d)] with the total energies in hartrees and activation energies in kcal/mol at the B3LYP/6-31G and B3LYP/6-31+G* levels of theory.

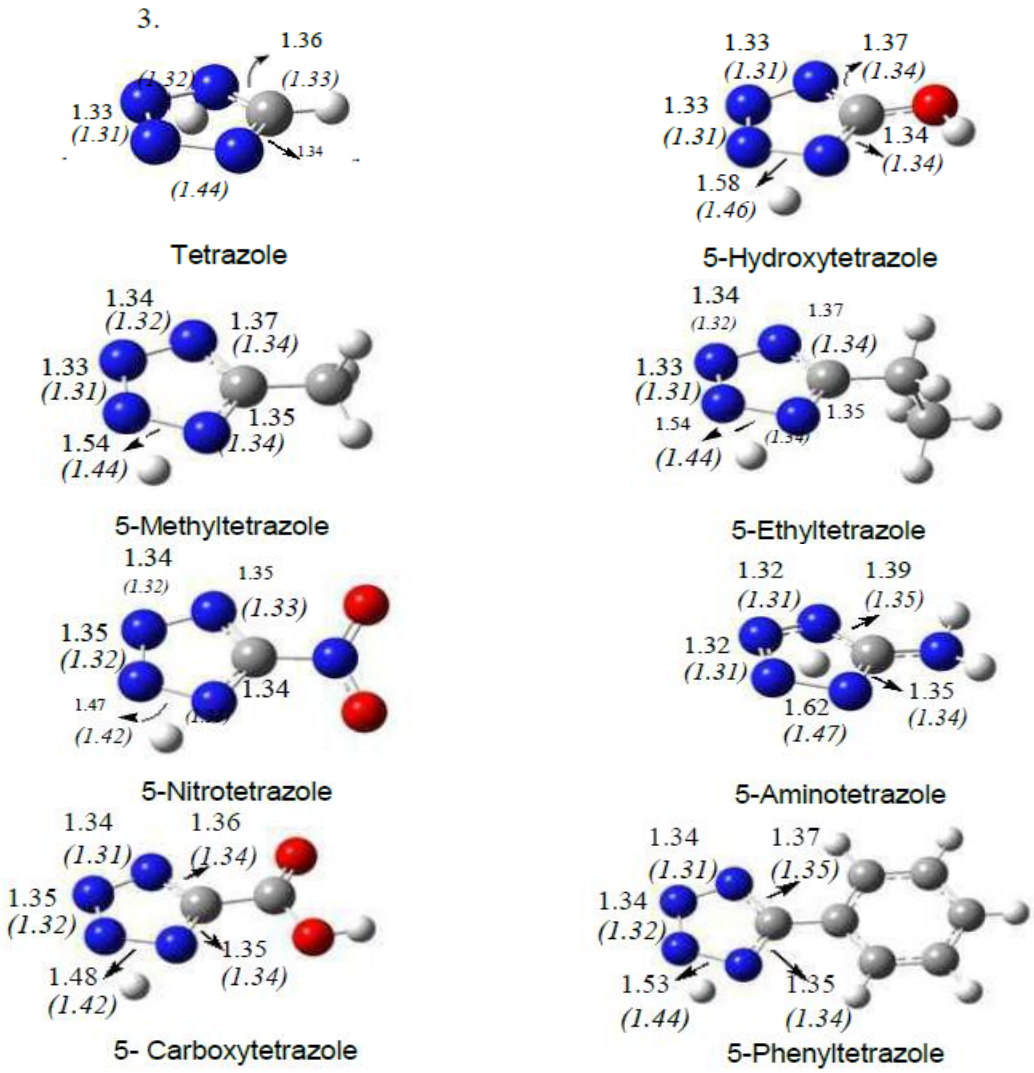
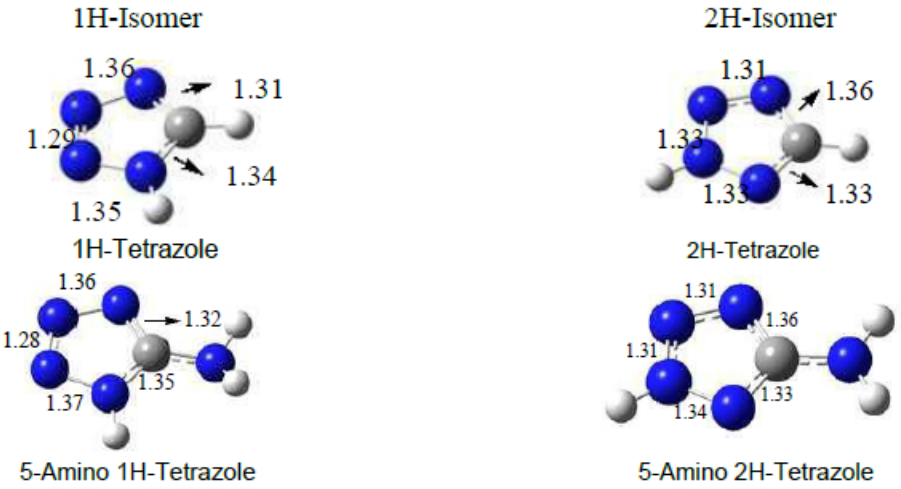
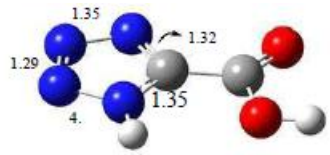
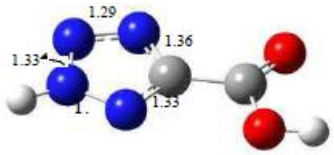


Figure 3: Optimized geometries of Tetrazoles and its substituted isomers (bond lengths are given in Å) with relative energies and activation en ergies in kcal/mol at the B3LYP/6-311++G** level of theory

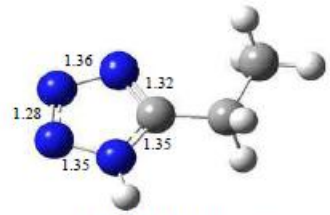




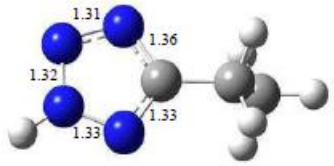
5-Carboxy 1H-Tetrazole



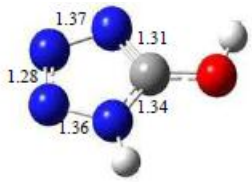
5-Carboxy 2H-Tetrazole



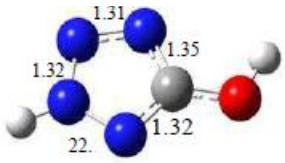
5-Ethyl 1H-Tetrazole



5-Ethyl 2H-Tetrazole



5-Hydroxy 1H-Tetrazole



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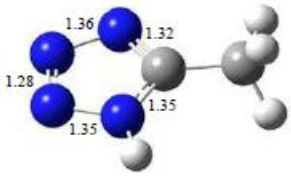
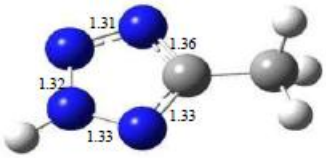


5-Methyl 1H-Tetrazole



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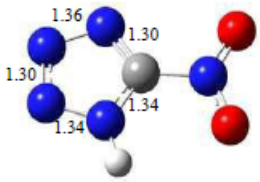
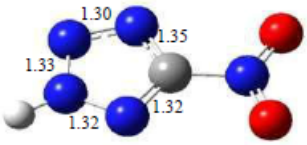
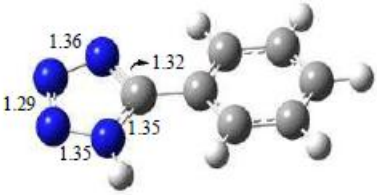


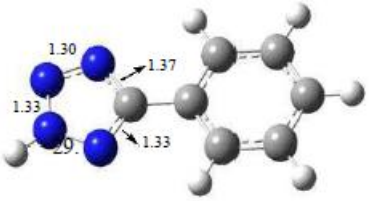
5-Nitro 1H-Tetrazole



5-Nitro 2H-Tetrazole



5-Phenyl 1H-Tetrazole



5-Phenyl 2H-Tetrazole

Figure 4 : Optimised Transition state structures at B3lyp/6-311++G** level (bond length in Å).

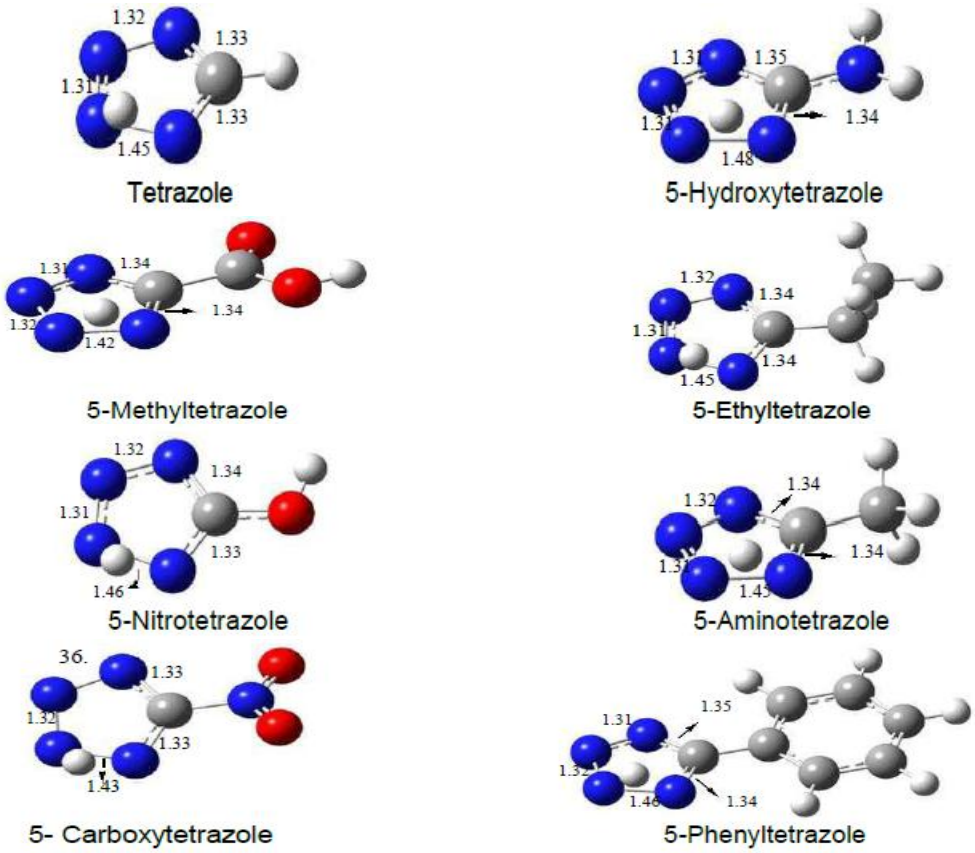
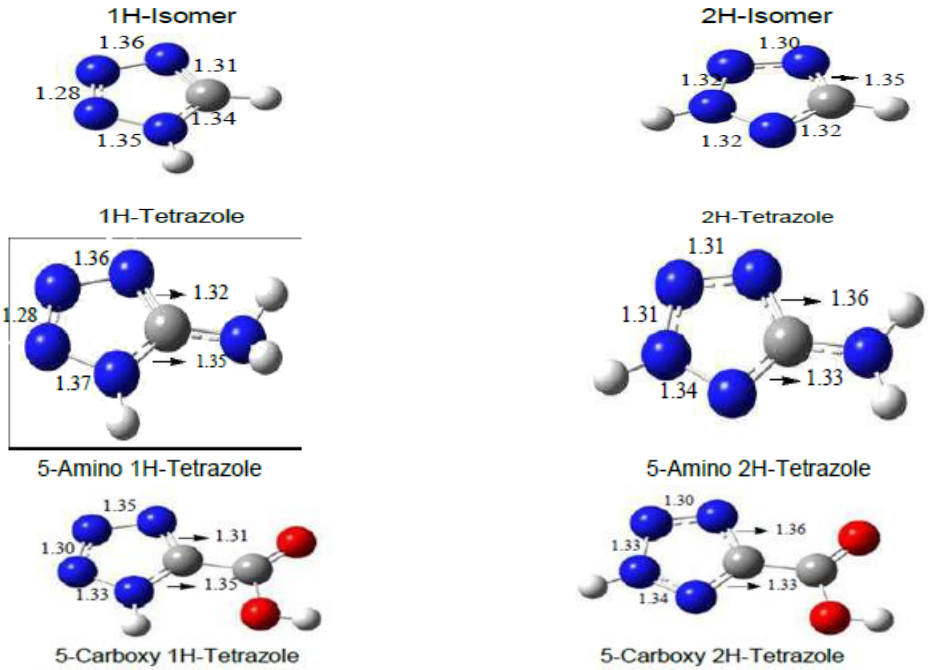


Figure 5 : Optimized geometries of tetrazole and its substituted isomers (bond lengths are given in Å) at the B3LYP/cc-pVTZ level of theory.



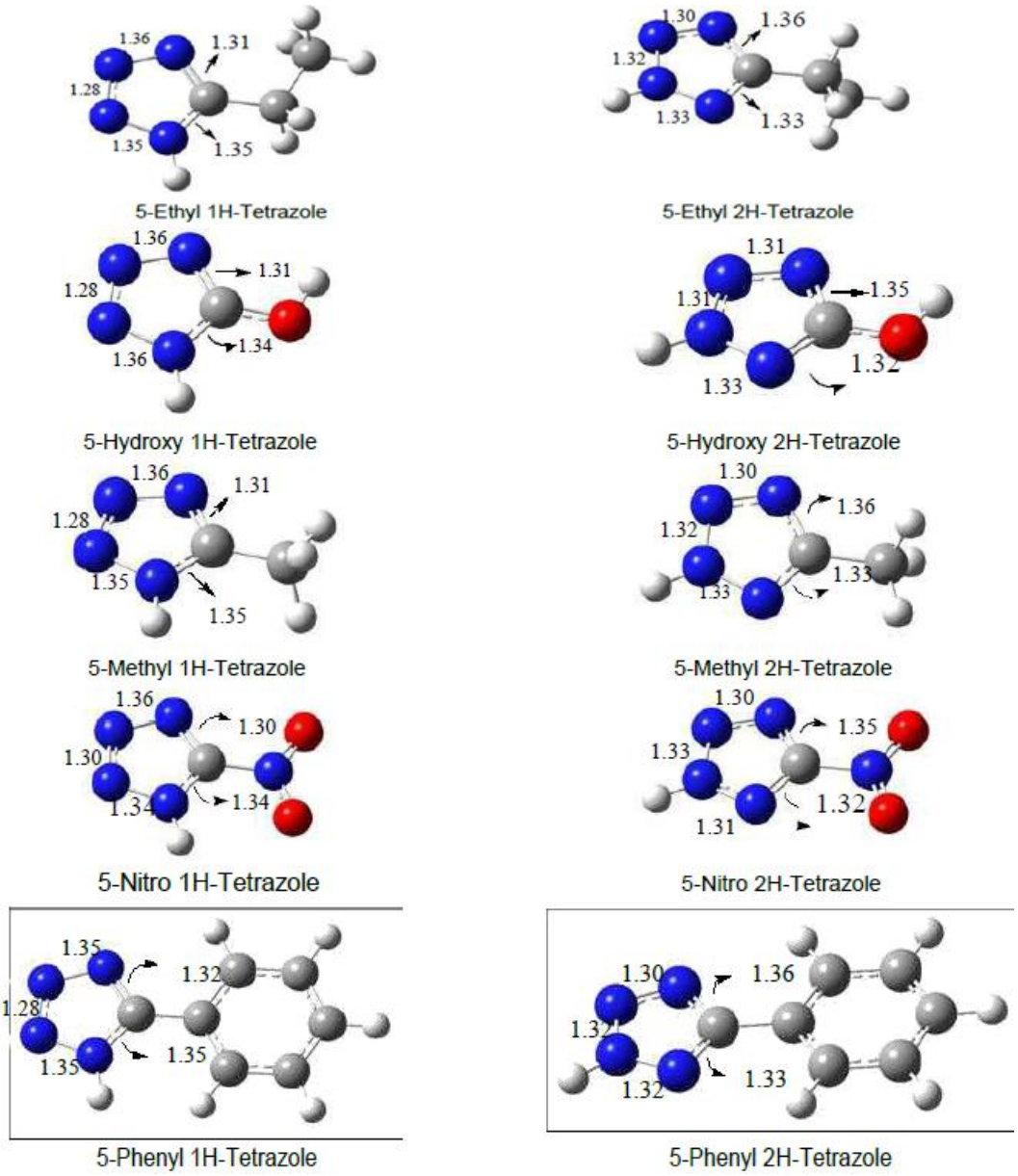
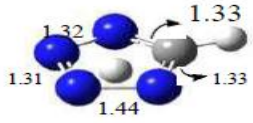
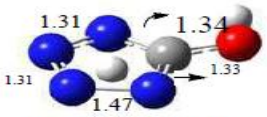


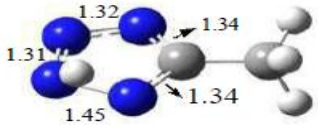
Figure 6: Optimised transition states geometries at b3lyp/cc-pVTZ level.



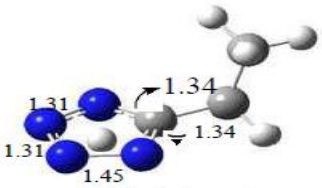
Tetrazole



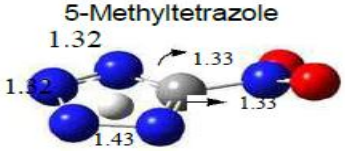
5-Hydroxytetrazole



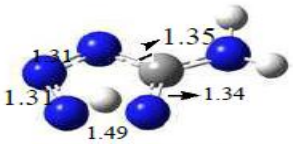
5-Methyltetrazole



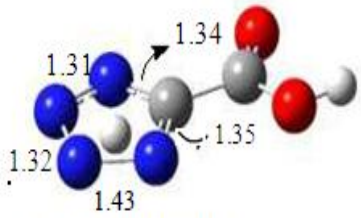
5-Ethyltetrazole



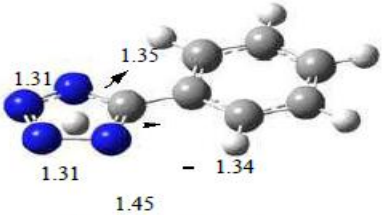
5-Nitrotetrazole



5-Aminotetrazole



5- Carboxytetrazole



5-Phenyltetrazole

A DFT (B3LYP) with basis sets 6-31G, 6-31+G*, 6-311++G** and cc-pVTZ were interrogated to study tetrazole and its substituted tautomers. The results predict 2H-tautomer to be more energetic over 1H-tautomer. $E_{1H\text{-}2H}$ between unsubstituted tautomers compares fairly well with experimental value; 6.95 ± 1.50 kJ mol^{-1}. Activation barrier for all the species were predicted as 60.0±6.0kcal mol^{-1}.

Gas Phase Computational Studies of C-Substituted Tetrazole

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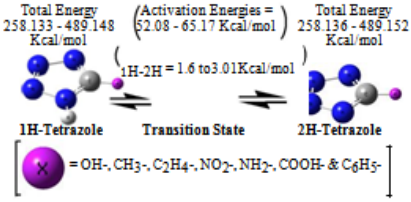
Graphical Information



Substitutions did not impart large changes. Predictions on the difference of activation barrier between substituted and unsubstituted isomers were very small.