

APPENDIX

Investigations of hydroxy group migration on 1,2,3- and 1,2,4-triazoles

Figure 1. N-hydroxy-1,2,3-triazoles.

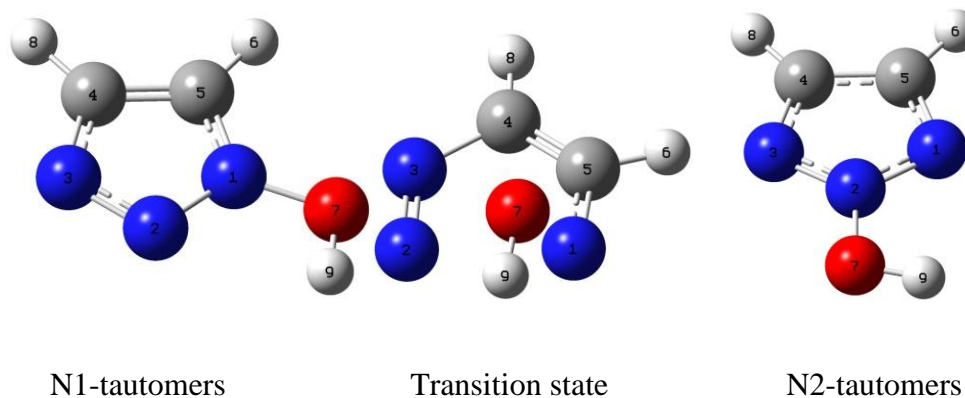
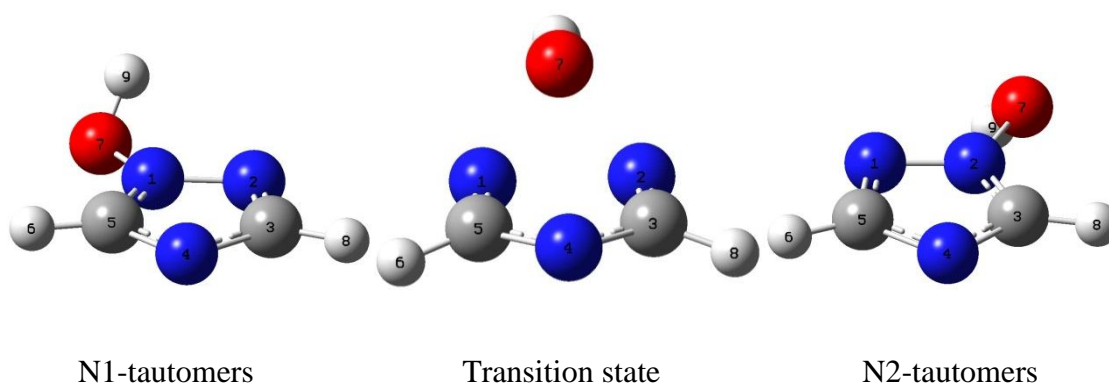


Figure 2. N-hydroxy-1,2,4-triazoles.



Study of –OH group migration and effect of –OH group on the energetic properties of triazole isomers was carried out using the same method applied to the parent isomer. Substitution on ground state isomer was done by replacing proton with hydroxy group at N1 position of 1,2,3- and 1,2,4-isomers, and all the structures were fully optimized at the HF and DFT level of theories with the same selected basis sets.

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Table 1. Ground state total energies*of N-hydroxy triazole isomers at HF level (*hartrees).

<i>Basis Sets</i>	<i>1,2,3-Isomers</i>		<i>1,2,4-Isomers</i>	
	N1-OH	N2-OH	N1-OH	N2-OH
6-31G(d)	-315.55960562	-315.56622226	-315.59501581	-315.59501581
6-311G(d)	-315.63083489	-315.63818693	-315.66651243	-315.66651243
6-311++G(d,p)	-315.64931168	-315.65602722	-315.68463000	-315.68462998
cc-pVDZ	-315.59305810	-315.60075987	-315.62815387	-315.62815387
cc-pVTZ	-315.68143755	-315.68855836	-315.71595461	-315.71595461
Aug-cc-pVDZ	-315.61548461	-315.62191091	-315.64977752	-315.64977752
Aug-cc-pVTZ	-315.68582214	-315.69257800	-315.72038285	-315.72038285

As seen in Table 1, HF method predicted ground state total energies of 1,2,3-isomers from -315.55960562 hartrees to -315.68582214 hartrees for N1-hydroxy tautomer, and from -315.69257800 hartrees to -315.56622226 hartrees for N2-hydroxy tautomer. Predicted total energies of 1,2,4-isomers started from -315.62815387 hartrees to -315.72038285 hartrees for N1-hydroxy tautomer and from -315.62815387 hartrees to -315.72038258 hartrees for N2-hydroxy tautomer respectively.

Table 2. Ground state total energies*of N-hydroxy triazole isomers at DFT level (*hartrees).

<i>Basis Sets</i>	<i>1,2,3-Isomers</i>		<i>1,2,4-Isomers</i>	
	N1- OH	N2- OH	N1- OH	N2-OH
6-31G(d)	-317.38004885	-317.38657222	-317.40636438	-317.40636438
6-311G(d)	-317.45750881	-317.46474869	-317.48456491	-317.48456491
6-311++G(d,p)	-317.47770818	-317.48454385	-317.50489885	-317.50489943
cc-pVDZ	-317.40839492	-317.41572153	-317.43395627	-317.43395627
cc-pVTZ	-317.50353650	-317.51045193	-317.52963012	-317.52963012
Aug-cc-pVDZ	-317.43683369	-317.44342666	-317.46229777	-317.46229777
Aug-cc-pVTZ	-317.50948369	-317.51611948	-317.53560253	-317.53560253

Predictions of ground state total energies in DFT method ranged from -317.38004885 hartrees to -317.50948369 hartrees for N1-hydroxy tautomer and from -317.38657222 hartrees to -317.51611948 hartrees for N2-hydroxy tautomer of 1,2,3-isomers.

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Results obtained from various basis sets are in between -317.38 and -317.53 hartrees. Predicted total energy in the case of 1,2,4-isomers ranged between -317.40636438 hartrees to -317.53560253 hartrees for both the N1- and N2-hydroxy tautomers as shown in Table 2.

Table 3. Energy*difference between ground state tautomers (*kcal mol⁻¹).

<i>Basis Sets</i>	HF		DFT	
	<i>1,2,3-Isomers</i>	<i>1,2,4-Isomers</i>	<i>1,2,3-Isomers</i>	<i>1,2,4-Isomers</i>
6-31G(d)	4.15	0.0	4.09	0.0
6-311G(d)	4.61	0.0	4.54	0.0
6-311++G(d,p)	4.21	0.0	4.29	0.0
cc-pVDZ	4.83	0.0	4.59	0.0
cc-pVTZ	4.47	0.0	4.34	0.0
aug-cc-pVDZ	4.03	0.0	4.14	0.0
aug-cc-pVTZ	4.24	0.0	4.16	0.0

The difference in energies between the two tautomers are shown at **Table 4.32**. Interesting results were obtained for 1,2,4-isomer where all the basis sets predicted zero relative energies with both the HF and DFT methods, while 1,2,3-isomer predicted 4.03 kcal mol⁻¹ to 4.83 kcal mol⁻¹ ground state relative energies. N-substituted-1,2,4-triazole's tautomers were, therefore, theoretically equivalent systems according to the obtained results in Table 3.

Transition state total energies are shown at Table 3 where HF predicted ranges from -315.44180811 hartrees to -315.56798845 hartrees for 1,2,3-isomer and from -315.42761513 hartrees to -315.55208269 hartrees for 1,2,4-isomer. DFT method predicted transition state total energies from -317.29414432 hartrees to -317.42516630 hartrees for 1,2,3-isomer and from -317.27574212 hartrees to -317.37621296 hartrees for 1,2,4-isomer respectively.

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Table 4. Transition state total energies*of N-hydroxy triazole isomers (*hartrees).

Basis sets	1,2,3-isomers		1,2,4-isomers	
	HF	DFT	HF	DFT
6-31G(d)	-315.44180811	-317.29414432	-315.42761513	-317.25047495
6-311G(d)	-315.51351972	-317.37445489	-315.49808715	-317.32655360
6-311++G(d,p)	-315.53196679	-317.39477528	-315.51613740	-317.34387595
cc-pVDZ	-315.47502832	-317.32122000	-315.45987032	-317.27574212
cc-pVTZ	-315.56277998	-317.41858592	-315.54682746	-317.37067264
aug-cc-pVDZ	-315.49815330	-317.35093849	-315.48406955	-317.30371105
aug-cc-pVTZ	-315.56798845	-317.42516630	-315.55208269	-317.37621296

Calculated activation energies at Table 4 show high energy barriers for the migration of hydroxy group in triazoles. Predicted activation energies for 1,2,3-isomer was $\sim 74.0 \pm 1.0$ kcal mol⁻¹ at HF level of calculations and $\sim 53.0 \pm 1.0$ kcal mol⁻¹ at DFT level of calculations. Predicted activations energies for 1,2,4-isomer was higher in comparison to 1,2,3-isomers where HF predicted $\sim 105.0 \pm 1.0$ kcal mol⁻¹ and DFT predicted 99.0 ± 2.0 kcal mol⁻¹.

Table 5. Activation energies*of N-hydroxy triazole isomers (*kcal mol⁻¹).

Basis sets	1,2,3-Isomers		1,2,4-Isomers	
	HF	DFT	HF	DFT
6-31G(d)	73.919	53.906	105.045	97.822
6-311G(d)	73.616	52.117	105.688	99.154
6-311++G(d,p)	73.635	52.041	105.731	101.043
cc-pVDZ	74.065	54.703	105.599	99.281
cc-pVTZ	74.459	53.307	106.129	99.747
aug-cc-pVDZ	73.626	53.900	103.983	99.515
aug-cc-pVTZ	73.942	52.910	105.609	100.018

Table 5 show HOMO-LUMO energy gaps where predicted values from 0.21409 hartrees to 0.35252 hartrees were obtained for 1,2,3-isomers, and from 0.2826 hartrees to 0.36266 hartrees were obtained for 1,2,4-isomers in both the applied methods.

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Table 6. HOMO-LUMO energy gap $\Delta E_{HOMO-LUMO}$ (in hartrees) of ground state N-hydroxy substituted triazole isomers at the HF and DFT levels.

Basis sets	HF				DFT			
	1,2,3		1,2,4		1,2,3		1,2,4	
	N1-OH	N2-OH	N1-OH	N2-OH	N1-OH	N2-OH	N1-OH	N2-OH
6-31G(d)	0.21409	0.19729	0.21826	0.21827	0.26271	0.24863	0.26804	0.26811
6-311G(d)	0.24115	0.20903	0.24879	0.24880	0.26187	0.24863	0.26663	0.26657
6-311 ++G(d,p)	0.34359	0.32743	0.35276	0.35272	0.25561	0.24435	0.25648	0.25642
cc-pvdz	0.21996	0.19593	0.22327	0.22328	0.26194	0.24912	0.25696	0.25695
cc-pvtz	0.24711	0.21526	0.25572	0.25572	0.26161	0.24943	0.2662	0.26617
aug-cc-pvdz	0.3463	0.3297	0.35624	0.35624	0.25375	0.24252	0.25196	0.25193
aug-cc-pvtz	0.35252	0.33694	0.36266	0.36264	0.2561	0.24516	0.25338	0.25351

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Table 7. HOMO-LUMO energy gap of N-hydroxy substituted transition state species at the HF and DFT levels (*hartrees).

Basis sets	HF		DFT	
	1,2,3	1,2,4	1,2,3	1,2,4
6-31G(d)	0.24457	0.34047	0.10741	0.14849
6-311G(d)	0.24960	0.34471	0.10723	0.14448
6-311++G(d,p)	0.27867	0.36074	0.10634	0.1421
cc-pvdz	0.24467	0.33529	0.10723	0.14872
cc-pvtz	0.24930	0.34445	0.10862	0.14813
aug-cc-pvdz	0.28293	0.35611	0.10614	0.14470
aug-cc-pvtz	0.28757	0.35526	0.10799	0.14607

Calculated HOMO-LUMO energy gaps for transition state species started from 0.10614 hartrees to 0.28757 hartrees for 1,2,3-isomer and from 0.1421 hartrees to 0.36074 hartrees for 1,2,4-isomer within HF and DFT method of calculations as seen in Table 7. B3lyp/aug-cc-pVDZ predicted 0.10614 hartrees (66.60 kcal mol⁻¹) for 1,2,3-isomer, which was the smallest gap, and the largest gap was predicted at HF/6-311++g(d,p) as 0.36074 hartrees (226.37 kcal mol⁻¹) for 1,2,4-isomer.