



Theoretical investigation of the effect of substituent on the cyclic-open tautomerism in 5-phenyl-1,2,3,4-oxatriazole: Molecular orbital treatment, DFT calculation

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Received: 4th January, 2012 ; Accepted: 31st January, 2012

ABSTRACT

The effect of substituents R= H, Cl, OH, CH₃, NO₂ and CN in 5-phenyl-1,2,3,4-oxatriazole, on the oxatriazole ↔ azide tautomerism, was investigated at B3LYP/6-311G** level of (DFT) method. The structural and energetic parameters were calculated at optimized geometry. For all substituents the p-substituent of benzoyl azide forms are largely favored. There is no large difference in dipole moment between two conformers c oxatriazole and aroyl azide. The reaction is spontaneous and the rate of reaction in case of CH₃ group is lower than others, with higher energy barrier ΔE= 2.71Kcal/mol, while the rate of reaction is faster than others in case of CN group, with lower energy barrier 2.4Kcal/mol. The reaction of cyclic-open conversion of 5-phenyl-1,2,3,4-oxatriazole to corresponding aroyl azide is exothermic reaction. © 2012 Trade Science Inc. - INDIA

INTRODUCTION

The reviews by Evans et al.^[1] and by Gray^[2] give very valuable surveys on physical properties and thermodynamic and decomposition processes of inorganic azides. Bonding in nitrogen compounds^[3] and in inorganic azides^[4] was discussed. The electronic structures as well as molecular orbital (MO) calculations were performed on some benzoyl azides^[5]. Most of the reported studies are not up to date and properties of azides is still missing.

As for carbonyl azide the situation is less satisfactory in fact, the first ultraviolet (UV) spectrum of benzoyl azide is reported in 1966 by Bhaskar^[6]. Attachment of a C=O group to an azide group –N₃ will affect the geometry, reactivity and structure of the azide group and hence the acyl azide molecule. This is clear when

comparing the dipole moment of C₆H₅N₃ which is 1.44D^[7], using the benzene as a solvent, with that of C₆H₅CON₃ which is 2.60D^[7] in the same solvent.

The attachment of an azide group to a carbonyl group in acyl azides plays a unique and significant role in the structure, geometry, stability and reactivity of these compounds. The cyclic conformers of formoyl, acetyl and thioformoyl azides are 1,2,3,4-oxatriazole. MO calculations used both HF and MP methods have shown that formoyl and acetyl azides are more stable than the corresponding oxatriazole^[8].

Two types of nuclei with an oxygen and three N-atoms are possible namely 1,2,3,4-oxatriazoles and 1,2,3,5-oxatriazoles. The neutral aromatic species have not yet been reported^[9] but 1,2,3,4-oxatriazolium salt and mesoionic species are known.

The synthesis of oxatriazoles was reported as early

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as 1896^[10], but the first proved in 1994^[11]. The neutral 1,2,3,4-oxatriazoles still await synthesis but some of their properties have been predicted by theoretical calculation^[12].

In this work we have examined the influence of various substituents R=H, Cl, CH₃, OH, NO₂ and CN in 5-phenyl-1,2,3,4-oxatriazole as shown in Figure (1) on stabilities of the cyclic structure of phenyl oxatriazole and corresponding open conformer of benzoyl azide by ab-initio calculations using DFT method combine with B3LYP/6-311G** level. In addition, the effect of these groups on geometrical parameters of transition state, the transition state is detected by presence of only one imaginary frequency. The cyclic-open conversion reaction of 5-phenyl-1,2,3,4-oxatriazoles have been investigated by varying the N10-O11 distance and optimizing the remaining structural parameters for each choice of the N10-O11 distance.

COMPUTATIONAL METHODS

The hybrid DFT method based on Becke's Threfunctional^[13] with non-local correlation provide by the Lee, Yang and Parr functional (LYP)^[14] designated B3LYP, is used throughout. All calculations were performed with GAMESS^[15] program package at 6-311G** basis set. Assuming C1 symmetry, the geometry of ground state, transition state and products of studied molecules was fully optimized. The ring opening reaction of 5-phenyl-1,2,3,4-oxatriazoles being with the molecule in it's geometry optimized ground state and is simulated by stepwise elongation of r(N10-O11) the bond Figure (1). The nature of stationary point is characterized by calculating the corresponding vibrational frequency and transition states are located and confirmed by having one imaginary frequency of vibration.

RESULT AND DISCUSSION

15-phenyl-1,2,3,4-oxatriazole

MO calculations were carried out using Density Functional Theory DFT method combine with B3LYP/6-311G** as basis set on cyclic conformer of benzoyl azide, i.e on 5-phenyl-1,2,3,4-oxatriazole. Results are

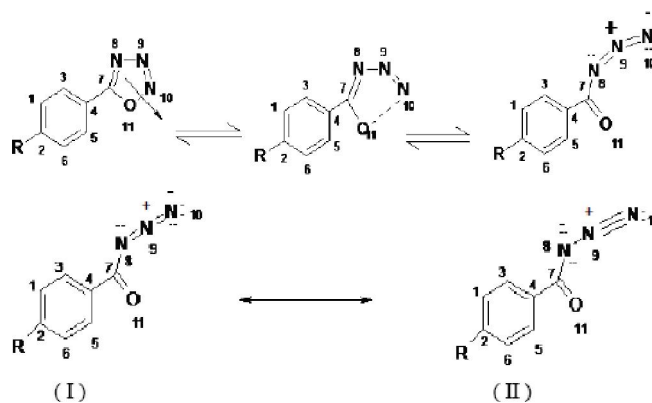


Figure 1 : The structure of oxatriazoles, transition states and final product of benzoyl azides, the resonating structure of benzoyl azides (I) and (II) at R=H, CH₃, OH, Cl, NO₂ and CN as substituents.

TABLE 1 : Total energy, dipole moment and equilibrium geometrical parameters, bond length Å, bond order (), bond angles ° and charges for 5-phenyl-1,2,3,4-oxatriazole, transition state and benzoyl azide at R= H as obtained from B3LYP/6-311G** procedure.

Parameter	5-phenyl-1,2,3,4-oxatriazole	TS	Benzoyl azide
E/au	-509.2879 81096	-509.2836 954417	-411.982 5027
Dipole moment/D	4.773	3.515	3.213
Bond length,(bond order)			
N10-O11	1.448 (0.889)	1.813 (0.547)	-
N9-N10	1.245 (1.650)	1.181 (1.907)	1.125 (2.229)
N8-N9	1.369 (1.148)	1.337 (1.182)	1.241 (1.320)
C7-N8	1.310 (1.576)	1.361 (1.350)	1.436 (0.984)
C7-O11	1.327 (1.161)	1.264 (1.504)	1.208 (2.048)
Bond angle,°			
O11C7N8	112.34	118.43	122.78
C7N8N9	104.38	103.22	114.84
N8N9N10	113.19	124.28	174.84
C4C7N8	127.01	119.52	112.39
Charge density			
C7	0.432	0.455	0.045
N8	-0.275	-0.289	-0.351
N9	-0.037	0.053	0.319
N10	0.037	0.038	-0.104
O11	-0.254	-0.336	-0.334
Imaginary frequency/ I	-	308.84	-

given in TABLE (1). The potential energy diagram for the cyclic-open conversion involved transition state is shown in Figure (1). In TABLE (1), shows how the values of energy, bond length, bond order, bond angle and charges vary as a function of $r(\text{N10-O11})$ distance through the cyclic-open conversion process. Elongation of the distance $r(\text{N10-O11})$ puts a strain on the molecule and total energy increases. Maximum strain is obtained at $r(\text{N10-O11})=1.813\text{\AA}$ which represents the transition state, this state is detected by presence of only one imaginary frequency $\nu=321.12\text{cm}^{-1}$. The geometric parameters of transition state are given in TABLE (1) where one finds $r(\text{N10-O11})=1.813\text{\AA}$, the $r(\text{C7-O11})$ bond is 1.264\AA (approaching the $\text{C}=\text{O}$ bond and shorter than equilibrium bond length in 5-phenyl-1,2,3,4-oxatriazoles, 1.327\AA); the $r(\text{C7-N8})$ bond is 1.361\AA approaching a $\text{C}-\text{N}$ single bond and longer than equilibrium bond length in 5-phenyl-1,2,3,4-oxatriazoles, 1.31\AA . Both $\text{N}-\text{N}$ bond lengths are shorter at the transition state compared to the equilibrium bond length in 5-phenyl-1,2,3,4-oxatriazole.

At $r(\text{N10-O11})=3.354\text{\AA}$, the equilibrium geometry of the open conformer is obtained where by results in TABLE (1) are typical for the open conformer of benzoyl azide^[16]. A value of 1.208\AA , with bond order 2.048 between C7-O11 indicates an almost pure $\text{C}=\text{O}$ group, whereas a value of 1.12\AA with bond order 2.229 between N9-N10 indicates a bond resonating between double and triple ones as shown in Figure (1) and values of 1.436\AA with bond order 0.984 and 1.24\AA with

TABLE 2 : Thermodynamic parameters of the Oxatriazole \leftrightarrow benzoyl azide process of studied compounds with $\text{R}=\text{H}, \text{Cl}, \text{OH}, \text{CH}_3, \text{NO}_2$ and CN as substituent in para position of 5-phenyl-1,2,3,4-oxatriazole as obtained from B3LYP/6-311G procedure.**

Substituents	E_r	ΔH	ΔE	ΔE^*	ΔS
H	-18.51	-19.71	2.69	-0.176	3.59
CH_3	-6.43	-8.12	2.71	-0.167	2.94
OH	-18.56	-19.93	2.56	-0.289	2.75
Cl	-18.96	-16.32	2.48	-0.338	3.87
NO_2	-13.37	-14.70	2.40	-0.377	2.94
CN	-19.30	-20.48	2.40	-0.392	2.94

E_r : Reaction energy is given by $E_{\text{product}} - E_{\text{reactant}}$; ΔH : Heat of reaction is given by $E_r + d(\text{ZPE}) + d(\text{TC})$; ΔE : Energy barrier is given by $E_{\text{TS}} - E_{\text{ST}}$; ΔE^* : Activation energy is given by $dE + d(\text{ZPE}) + d(\text{TC}) + RT$; ΔS : Enthalpy of reaction. Ref:^[16]

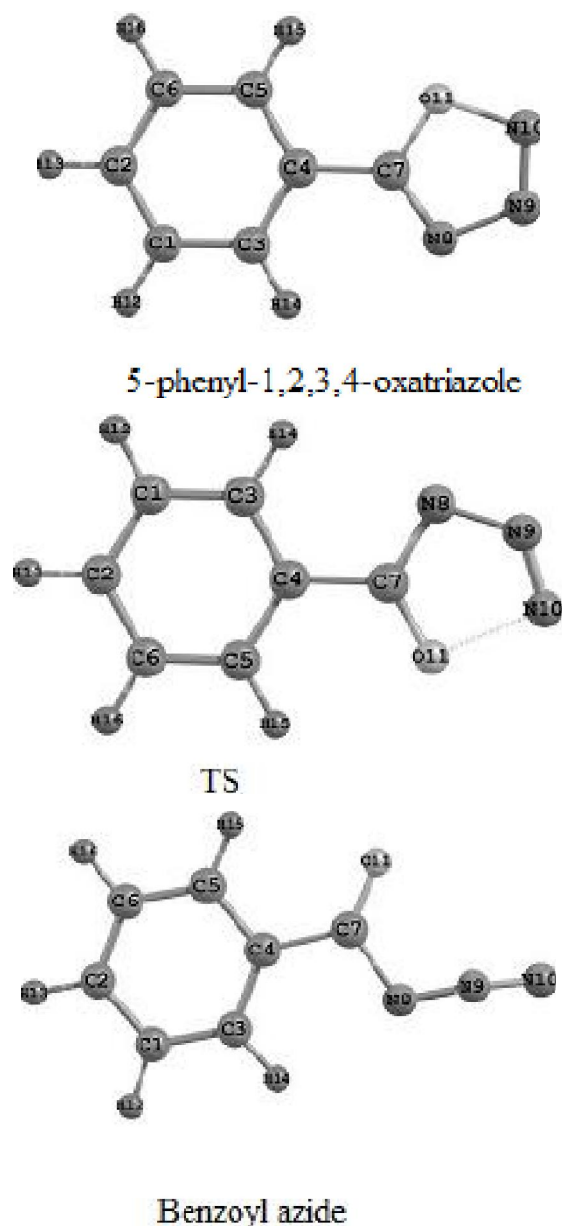


Figure 2 : The conversion of 5-phenyl-1,2,3,4-oxatriazole to benzoyl azide involving the optimized geometric structure of reactant, product and transition state by using DFT-B3LYP/6-311G level of calculation.**

bond order 1.32 between the C7-N8 and N8-N9 indicates almost pure single bonds. One clearly sees how bond angles vary: $\theta(\text{O11C7N8})$ from 112.34° to 122.78° , $\theta(\text{C7N8N9})$ from 104.38° to 114.84° and $\theta(\text{N8N9N10})$ from 113.19° to 174.84° , as one goes from 5-phenyl-1,2,3,4-oxatriazoles to benzoyl azide. It is important to find that $\theta(\text{N8N9N10})=174.84^\circ$, i.e. the azide group is not completely linear. The $\theta(\text{C4C7N8})$ is 112.78° , indicating a distorted sp^2 hybridization for the C-atom.

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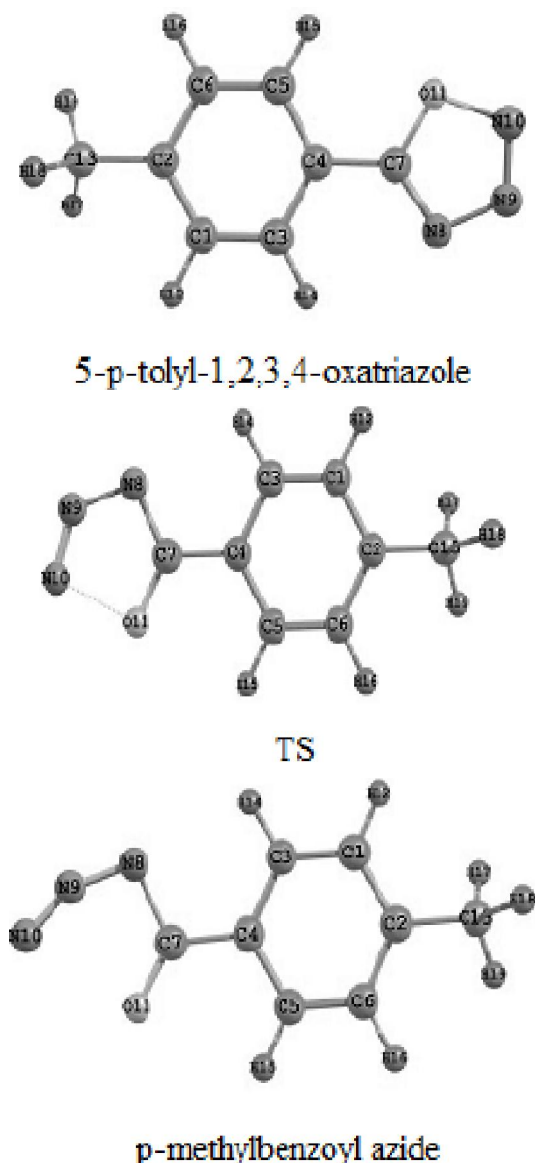


Figure 3 : The conversion of 5-p-tolyl-1,2,3,4-oxatriazole to p-methylbenzoyl azide involving the optimized geometric structure of reactant, product and transition state by using DFT-B3LYP/6-311G** level of calculation.

The diagram for the conversion of 5-phenyl-1,2,3,4-oxatriazole to open conformer of benzoyl azide is shown in Figure (2). Thermodynamic parameters for the conversion cyclic structure of 5-phenyl-1,2,3,4-oxatriazole to open structure of benzoyl azide given in TABLE (2), one finding activation energy for this process is only -0.176 Kcal/mol, so the reaction of the ring opening of 5-phenyl-1,2,3,4-oxatriazole to benzoyl azide is spontaneous and value of energy barrier is 2.689 Kcal/mol. Such a result means that 5-phenyl-1,2,3,4-oxatriazole, mostly, can not be formed

TABLE 3 : Total energy, dipole moment and equilibrium geometrical parameters, bond length Å, bond order (), bond angles ° and charges for 5-p-tolyl-1,2,3,4-oxatriazole, transition state and p-methylbenzoyl azide at R= CH₃ as obtained from B3LYP/6-311G** procedure.

Parameter	5-p-tolyl-1,2,3,4-oxatriazole	TS	Benzoyl azide
E/au	-548.6172 566737	-548.6129 391157	-548.6275 008897
Dipole moment/D	5.46	4.19	3.70
Bond length,(bond order)			
N10-O11	1.449 (0.888)	1.815 (0.545)	-
N9-N10	1.245 (1.649)	1.181 (1.905)	1.130 (2.189)
N8-N9	1.368 (1.150)	1.336 (1.186)	1.256 (1.390)
C7-N8	1.311 (1.572)	1.362 (1.343)	1.459 (0.995)
C7-O11	1.328 (1.160)	1.264 (1.505)	1.210 (1.987)
Bond angle, °			
O11C7N8	112.29	118.36	119.55
C7N8N9	104.39	103.24	101.94
N8N9N10	113.24	124.39	173.70
C4C7N8	127.04	119.50	113.99
Charge density			
C7	0.430	0.453	0.430
N8	-0.277	-0.291	-0.314
N9	-0.039	0.052	0.185
N10	0.035	0.035	-0.159
O11	-0.256	-0.338	-0.343
Imaginary frequency/ I	-	378.27	-

and, it formed changes immediately to open tautomer. On the other hand the process is exothermic, the value of reaction energy is -18.51 Kcal/mol and heat of reaction is -19.71 Kcal/mol.

There is no large difference between two isomers in dipole moment between the two conformers cyclic oxatriazole and open benzoyl azide. The total energy of the 5-phenyl-1,2,3,4-oxatriazole is -509.288 H compared to -509.3175 H for benzoyl azide, a difference is -18.51 Kcal/mol between two isomers with benzoyl azide of lower energy. The results indicate that the open conformer, benzoyl azide is more stable than the cyclic conformer of 5-phenyl-1,2,3,4-oxatriazole.

5-p-tolyl-1,2,3,4-oxatriazole

The conversion of 5-p-tolyl-1,2,3,4-oxatriazole to p-methyl benzoyl azide has been investigated theoretically. Starting with optimized geometry which has the parameters, $r(\text{N10-O11}) = 1.449\text{\AA}$, $r(\text{C7-O11}) = 1.338\text{\AA}$ and $\theta(\text{O11C7N8}) = 112.29^\circ$. One increases the $r(\text{N10-O11})$ distance, freezes and calculates of results are given in TABLE (3).

As the $r(\text{N10-O11})$ bond length increased, the total energy increases, N10-O11 bond order decreases and N9-N10 bond order increases. In addition, $\theta(\text{N8C7O11})$ increases, the total energy has maximum value of -548.61294H at $r(\text{N10-O11}) = 1.815\text{\AA}$, the transition state is produced and detected by presence of only one imaginary frequency $\nu=378.27\text{cm}^{-1}$, giving an activation energy -0.167Kcal/mol . Hence, the cyclic conformer of 5-p-tolyl-1,2,3,4-oxatriazole is easily opened and produced p-methyl benzoyl azide. A diagram for the cyclic-open conversion of 5-p-tolyl-1,2,3,4-oxatriazole is shown in Figure (3).

The $r(\text{C7-O11})$ bond is 1.328\AA with bond order 1.16 in equilibrium cyclic conformer and shortness gradually to 1.21\AA with bond order 1.987 in equilibrium conformer of open p-methyl benzoyl azide. On the other hand, the $r(\text{C7-N8})$ bond is 1.311\AA (almost a double bond $\text{C}=\text{N}$ bond) in 5-p-tolyl-1,2,3,4-oxatriazole and elongates gradually to 1.459\AA (almost single $\text{C}-\text{N}$ bond) in equilibrium azide. Other variations are equally important; the variation of $r(\text{N8-N9})$ from 1.368\AA with bond order 1.15 (single bond) in equilibrium cyclic conformer to 1.256\AA with bond order 1.39 indicates a bond resonating between double and triple ones. These results mean that N9 should carry a positive charge whereas N8 should carry a negative charge. Calculations give 0.185 and -0.314 as the charges on N9 and N8, respectively.

From thermodynamic parameters, the reaction of conversion of 5-p-tolyl-1,2,3,4-oxatriazole to corresponding open conformer of azide reaction is exothermic with heat of reaction -8.12Kcal/mol and reaction energy is -6.43Kcal/mol . There is no difference in dipole moment between two conformers and the open conformer of p-methyl benzoyl azide is lower energy than corresponding cyclic oxatriazole with energy difference is 2.71Kcal/mol . The results indicate that open

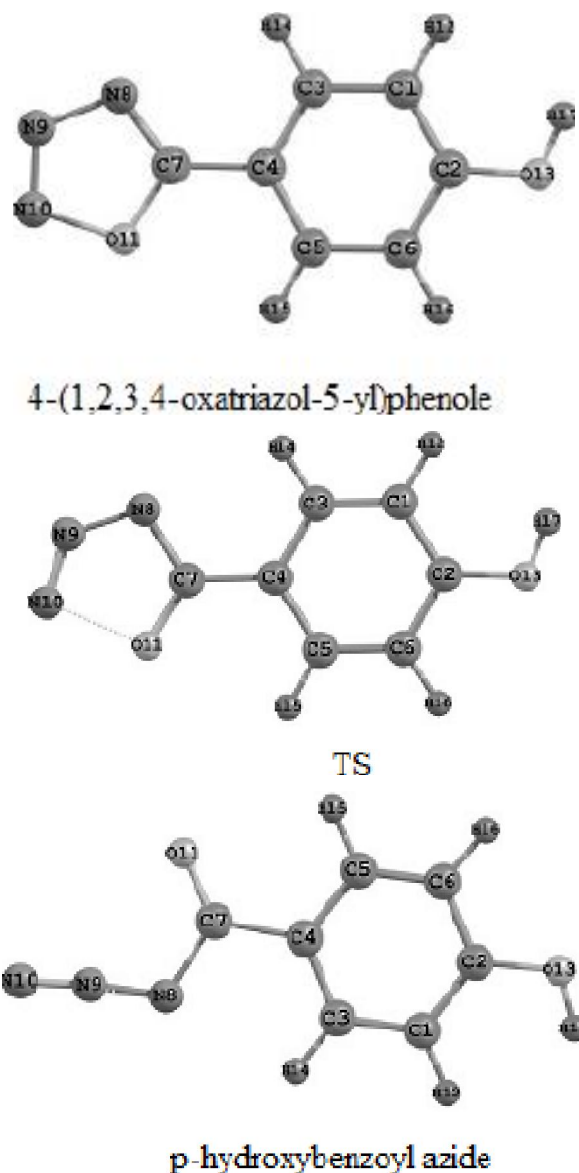


Figure 4 : The conversion of 4-(1,2,3,4-oxatriazol-5-yl)phenole to p-hydroxybenzoyl azide involving the optimized geometric structure of reactant, product and transition state by using DFT-B3LYP/6-311G** level of calculation.

conformer of p-methyl benzoyl azide is more stable than 5-p-tolyl-1,2,3,4-oxatriazole and the reaction is spontaneous.

4-(1,2,3,4-oxatriazol-5-yl)phenole

The conversion of 4-(1,2,3,4-oxatriazol-5-yl)phenole to p-hydroxy benzoyl azide has been investigated theoretically. Starting with optimized geometry of 4-(1,2,3,4-oxatriazol-5-yl)phenole which has parameters $r(\text{N10-O11}) = 1.452\text{\AA}$, $r(\text{C7-O11}) = 1.327\text{\AA}$ and $\theta(\text{O11C7N8}) = 112.29^\circ$, one in increases the $r(\text{N10-O11})$

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TABLE 4 : Total energy, dipole moment and equilibrium geometrical parameters, bond length Å, bond order (), bond angles ° and charges for 4-(1,2,3,4-oxatriazol-5-yl)phenole, transition state and p-hydroxybenzoyl azide at R= OH as obtained from B3LYP/6-311G procedure.**

Parameter	4-(1,2,3,4-oxatriazol-5-yl) phenole	TS	p-hydroxybenzoyl azide
E/au	-584.5345065364	-584.5304218412	-584.560769626
Dipole moment/D	5.42	4.36	4.22
Bond length,(bond order)			
N10-O11	1.452 (0.883)	1.811 (0.547)	-
N9-N10	1.245 (1.650)	1.182 (1.900)	1.126 (2.226)
N8-N9	1.367 (1.153)	1.335 (1.190)	1.240 (1.328)
C7-N8	1.313 (1.564)	1.364 (1.338)	1.440 (0.973)
C7-O11	1.327 (1.161)	1.265 (1.499)	1.209 (2.044)
Bond angle, °			
O11C7N8	112.30	118.20	122.55
C7N8N9	104.38	103.27	114.79
N8N9N10	113.37	124.31	174.99
C4C7N8	126.98	121.17	112.339
Charge density			
C7	0.432	0.454	0.446
N8	-0.282	-0.296	-0.356
N9	-0.039	0.049	0.318
N10	0.033	0.033	-0.109
O11	-0.260	-0.340	-0.340
Imaginary frequency/I	-	321.12	-

O11) distance step by step till transition state at $r(\text{N10-O11}) = 1.811 \text{ \AA}$, the transition state is characteristic by presence of one imaginary frequency $\nu = 321.12 \text{ cm}^{-1}$. all geometrical parameters are given in TABLE (4).

The $r(\text{C7-O11})$ bond is 1.327 \AA with bond order 1.161 in equilibrium cyclic conformer of 4-(1,2,3,4-oxatriazol-5-yl)phenole and shortness gradually to 1.209 \AA with bond order 2.044 in equilibrium conformer of p-hydroxy benzoyl azide. On the other hand, the $r(\text{C7-N8})$ is 1.313 \AA (almost a double bond $\text{C}=\text{N}$) in 4-(1,2,3,4-oxatriazol-5-yl)phenole and elongates gradually to 1.44 \AA (almost single bond $\text{C}-\text{N}$) in equilibrium azide. The variation of $r(\text{N8-N9})$ from 1.367 \AA with

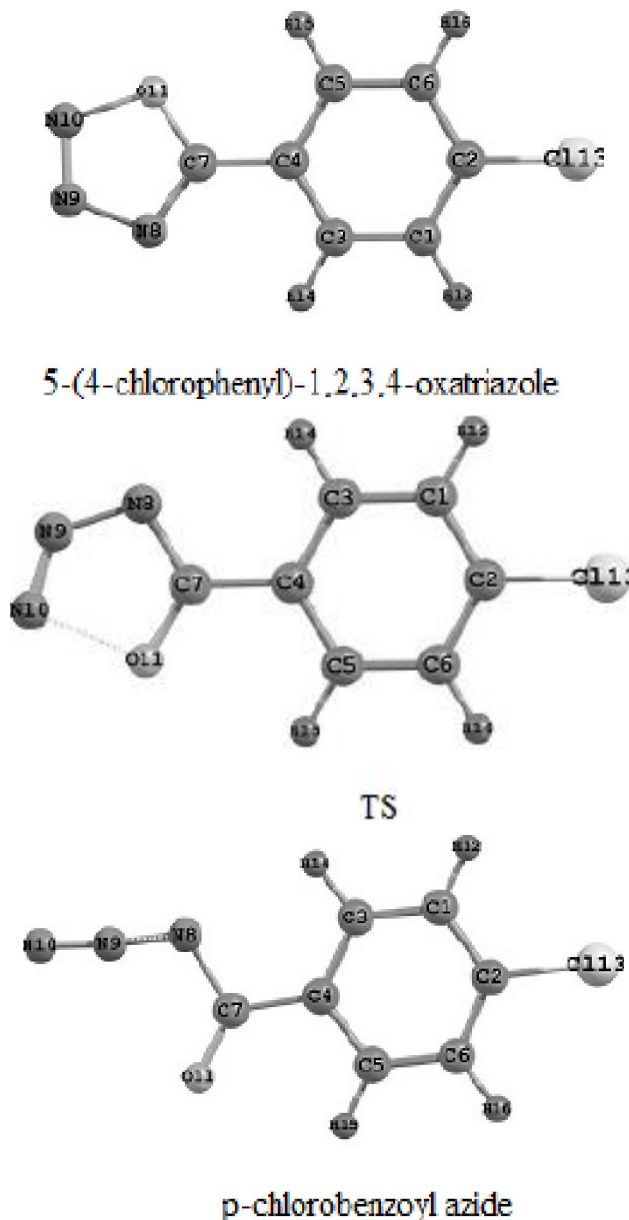


Figure 5 : The conversion of 5-(4-chlorophenyl)-1,2,3,4-oxatriazole to p-chlorobenzoyl azide involving the optimized geometric structure of reactant, product and transition state by using DFT-B3LYP/6-311G level of calculation.**

bond order 1.153 (single bond) in equilibrium cyclic conformer to 1.24 \AA with bond order 1.328 indicates a bond resonating between double and triple ones.

Charges on N8 and N9 are -0.356 and 0.318 respectively these results corresponding with the resonating structure of azide group. A diagram for ring opening of oxatriazole ring in 4-(1,2,3,4-oxatriazol-5-yl)phenole is shown in Figure (4), with activation energy -0.289 Kcal/mol which agree with energy barrier 2.56 Kcal/mol and reaction energy is -18.56 Kcal/mol

TABLE 5 : Total energy, dipole moment and equilibrium geometrical parameters, bond length Å, bond order (), bond angles ° and charges for 5-(4-chlorophenyl)-1,2,3,4-oxatriazole, transition state and p-chlorobenzoyl azide at R= Cl as obtained from B3LYP/6-311G procedure.**

Parameter	5-(4-chlorophenyl)-1,2,3,4-oxatriazole	TS	p-chlorobenzoyl azide
E/au	-968.9103 380218	-968.906 3857723	-968.9405 578293
Dipole moment/D	3.12	1.81	1.49
Bond length,(bond order)		1.810 (0.547)	
N10-O11	1.451 (0.886)	1.181 (1.908)	-
N9-N10	1.244 (1.653)	1.338	1.125 (2.232)
N8-N9	1.369 (1.148)	(1.181)	1.242 (1.317)
C7-N8	1.310 (1.575)	1.359	1.434 (0.989)
C7-O11	1.326 (1.163)	(1.353)	1.208 (2.048)
		1.264 (1.502)	
Bond angle, ?			
O11C7N8	112.47	118.49	120.28
C7N8N9	104.32	103.18	114.81
N8N9N10	113.25	124.16	174.79
C4C7N8	126.88	119.48	112.32
Charge density			
C7	0.435	0.458	0.452
N8	-0.275	-0.289	-0.352
N9	-0.034	0.054	0.320
N10	0.041	0.042	-0.098
O11	-0.255	-0.336	-0.333
Imaginary frequency/I	-	382.60	-

so the reaction is exothermic and spontaneous. There is no difference in dipole moment between two conformers and the total energy of open conformer is lower than cyclic conformer, so p-hydroxy benzoyl azide is more stable.

5-(4-chlorophenyl)-1,2,3,4-oxatriazole

The conversion of 5-(4-chlorophenyl)-1,2,3,4-oxatriazole to p-chloro benzoyl azide has been investigated theoretically. Starting with optimized geometry of 5-(4-chlorophenyl)-1,2,3,4-oxatriazole which has parameters $r(\text{N10-O11}) = 1.451 \text{ \AA}$, one increases the $r(\text{N10-O11})$ distance step by step till transition state at

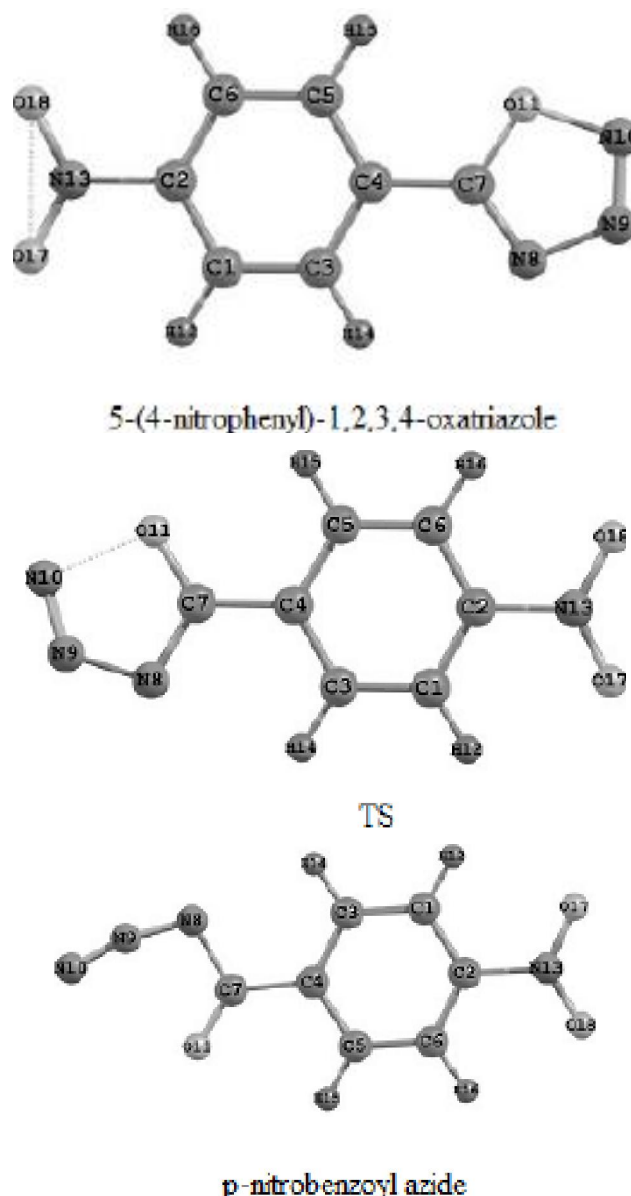


Figure 6 : The conversion of 5-(4-nitrophenyl)-1,2,3,4-oxatriazole to p-nitrobenzoyl azide involving the optimized geometric structure of reactant, product and transition state by using DFT-B3LYP/6-311G level of calculation.**

$r(\text{N10-O11}) = 1.807 \text{ \AA}$, the transition state is characteristic by presence of one imaginary frequency $\nu = 382.6 \text{ cm}^{-1}$. all geometrical parameters are given in TABLE (5).

The $r(\text{C7-O11})$ bond is 1.326 \AA with bond order 1.163 in equilibrium cyclic conformer of 5-(4-chlorophenyl)-1,2,3,4-oxatriazole and shortness gradually to 1.208 \AA with bond order 2.048 in equilibrium conformer of p-chloro benzoyl azide. On the other hand, the $r(\text{C7-N8})$ is 1.310 \AA (almost a double bond $\text{C}=\text{N}$)

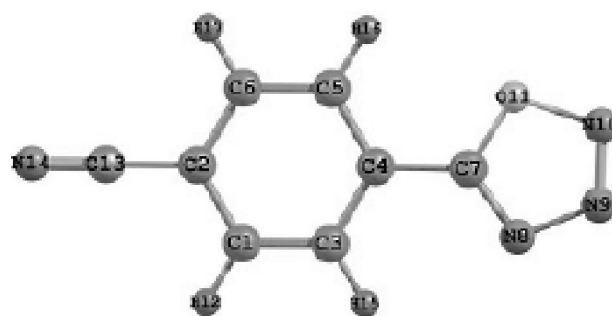
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TABLE 6 : Total energy, dipole moment and equilibrium geometrical parameters, bond length Å, bond order (), bond angles ° and charges for 5-(4-nitrophenyl)-1,2,3,4-oxatriazole, transition state and p-nitrobenzoyl azide at R=NO₂ as obtained from B3LYP/6-311G procedure.**

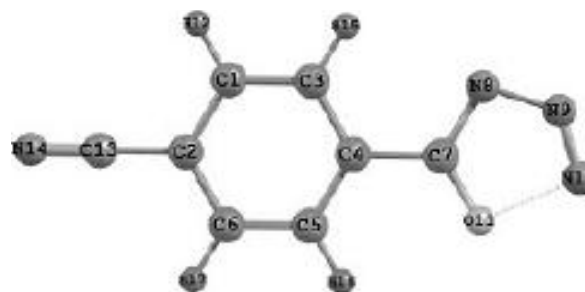
Parameter	5-(4-nitrophenyl)-1,2,3,4-oxatriazole	TS	P-chlorobenzoyl azide
E/au	-713.8417 584071	-713.8379 307757	-713.8630 664413
Dipole moment/D	0.72	1.34	2.37
Bond length,(bond order)		1.797 (0.560)	
N10-O11	1.449 (0.889)	1.182 (1.906)	-
N9-N10	1.244 (1.654)	1.342 (1.169)	1.121 (2.236)
N8-N9	1.370 (1.144)	1.354 (1.374)	1.249 (1.377)
C7-N8	1.308 (1.583)	1.265 (1.492)	1.446 (1.002)
C7-O11	1.325 (1.164)		1.207 (2.033)
Bond angle, ?			
O11C7N8	112.62	118.61	120.45
C7N8N9	104.27	103.14	104.22
N8N9N10	113.14	123.54	166.12
C4C7N8	126.74	119.58	113.72
Charge density			
C7	0.443	0.465	0.441
N8	-0.268	-0.284	-0.324
N9	-0.029	0.056	0.249
N10	0.049	0.052	-0.033
O11	-0.251	-0.331	-0.334
Imaginary frequency/I	-	392.20	-

in 5-(4-chlorophenyl)-1,2,3,4-oxatriazole and elongates gradually to 1.434Å (almost single bond C-N) in equilibrium azide. The variation of r(N8-N9) from 1.369Å with bond order 1.148 (single bond) in equilibrium cyclic conformer to 1.242Å with bond order 1.317 indicates a bond resonating between double and triple ones.

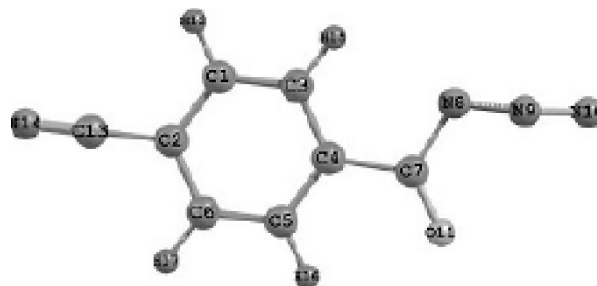
Charges on N8 and N9 are -0.352 and 0.320 respectively these results corresponding with the resonating structure of azide group. A diagram for ring opening of oxatriazole ring in 5-(4-chlorophenyl)-1,2,3,4-oxatriazole is shown in Figure (5), with activation energy -0.338Kcal/mol which agree with energy barrier 2.48Kcal/mol and reaction energy is -18.96Kcal/mol



4-(1,2,3,4-oxatriazol-5-yl)benzotrile



TS



p-cyanobenzoyl azide

Figure 7 : The conversion of 4-(1,2,3,4-oxatriazol-5-yl)benzotrile to p-cyanobenzoyl azide involving the optimized geometric structure of reactant, product and transition state by using DFT-B3LYP/6-311G level of calculation.**

so the reaction is exothermic and spontaneous. There is no difference in dipole moment between two conformers and the total energy of open conformer is lower than cyclic conformer, so p-chloro benzoyl azide is more stable.

5-(4-nitrophenyl)-1,2,3,4-oxatriazole

The conversion of 5-(4-nitrophenyl)-1,2,3,4-oxatriazole to p-nitro benzoyl azide has been investigated theoretically as an example for withdrawing group. At r(N10-O11)= 1.797Å, this transition state is ap-

peared at shorter distance less than other donating groups, the transition state is characteristic by presence of one imaginary frequency $\nu=392.2\text{cm}^{-1}$. all geometrical parameters are given in TABLE (6).

The r(C7-O11) bond is 1.325\AA with bond order 1.164 in equilibrium cyclic conformer of 5-(4-nitrophenyl)-1,2,3,4-oxatriazole and shortness gradually to 1.207\AA with bond order 2.033 in equilibrium conformer of p-nitro benzoyl azide. On the other hand, the r(C7-N8) is 1.308\AA (almost a double bond C=N) in 5-(4-nitrophenyl)-1,2,3,4-oxatriazole and elongates gradually to 1.446\AA (almost single bond C-N) in equilibrium azide. The variation of r(N8-N9) from 1.37\AA with bond order 1.144 (single bond) in equilibrium cyclic conformer to 1.249\AA with bond order 1.377 indicates a bond resonating between double and triple ones.

Charges on N8 and N9 are -0.324 and 0.249 respectively these results corresponding with the resonating structure of azide group. A diagram for ring opening of oxatriazole ring in 5-(4-nitrophenyl)-1,2,3,4-oxatriazole is shown in Figure (6), with activation energy -0.377Kcal/mol which agree with energy barrier 2.4Kcal/mol and reaction energy is -13.37Kcal/mol so the reaction is exothermic and spontaneous. The dipole moment of azide greater slightly than cyclic oxatriazole and the total energy of open conformer is lower than cyclic conformer, so p-nitro benzoyl azide is more stable.

4-(1,2,3,4-oxatriazol-5-yl)benzotrile

The conversion of 4-(1,2,3,4-oxatriazol-5-yl)benzotrile to p-cyano benzoyl azide has been investigated theoretically as another example for withdrawing group. At r(N10-O11)= 1.798\AA , this transition state is appeared at shorter distance less than other donating groups, the transition state is characteristic by presence of one imaginary frequency $\nu=388.28\text{cm}^{-1}$. all geometrical parameters are given in TABLE (7).

The r(C7-O11) bond is 1.326\AA with bond order 1.164 in equilibrium cyclic conformer of 4-(1,2,3,4-oxatriazol-5-yl)benzotrile and shortness gradually to 1.208\AA with bond order 2.05 in equilibrium conformer of p-cyano benzoyl azide. On the other hand, the r(C7-N8) is 1.308\AA (almost a double bond C=N) in 4-(1,2,3,4-oxatriazol-5-yl)benzotrile and elongates gradually to 1.429\AA (almost single bond C-N) in equi-

TABLE 7 : Total energy, dipole moment and equilibrium geometrical parameters, bond length \AA , bond order (), bond angles $^\circ$ and charges for 4-(1,2,3,4-oxatriazol-5-yl)benzotrile, transition state and p-cyanobenzoyl azide at R= CN as obtained from B3LYP/6-311G** procedure.

Parameter	4-(1,2,3,4-oxatriazol-5-yl)benzotrile	TS	p-cyanobenzoyl azide
E/au	-601.5499 493288 0.71	-601.5461 202068 1.22	-601.5807 124343 2.43
Dipole moment/D	0.71	1.22	2.43
Bond length,(bond order)			
N10-O11	1.450 (0.888)	1.798 (0.559)	-
N9-N10	1.244 (1.654)	1.182 (1.905)	1.124 (2.237)
N8-N9	1.370 (1.145)	1.341 (1.172)	1.244 (1.309)
C7-N8	1.308 (1.580)	1.355 (1.370)	1.429 (1.000)
C7-O11	1.326 (1.164)	1.265 (1.492)	1.208 (2.050)
Bond angle, ?			
O11C7N8	112.59	119.16	123.43
C7N8N9	104.28	102.93	114.80
N8N9N10	113.17	125.71	174.66
C4C7N8	126.76	119.59	112.29
Charge density			
C7	0.436	0.461	0.454
N8	-0.270	-0.286	-0.349
N9	-0.030	0.055	0.322
N10	0.047	0.049	-0.089
O11	-0.252	-0.332	-0.327
Imaginary frequency/ I	-	388.28	-

librium azide. The variation of r(N8-N9) from 1.37\AA with bond order 1.145 (single bond) in equilibrium cyclic conformer to 1.244\AA with bond order 1.3097 indicates a bond resonating between double and triple ones.

Charges on N8 and N9 are -0.349 and 0.322 respectively these results corresponding with the resonating structure of azide group. A diagram for ring opening of oxatriazole ring in 4-(1,2,3,4-oxatriazol-5-yl)benzotrile is shown in Figure (7), with activation energy -0.392Kcal/mol which agree with energy barrier 2.4Kcal/mol and reaction energy is -19.3Kcal/mol

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so the reaction is exothermic and spontaneous. The dipole moment of azide greater slightly than cyclic oxatriazole and the total energy of open conformer is lower than cyclic conformer, so p-cyano benzoyl azide is more stable.

CONCLUSION

The attachment of an azide group to a carbonyl group in aroyl azides plays a unique and significant role in the structure, geometry, stability and reactivity of these compounds. The structures of some members of this series of compounds have been investigated theoretically. The results obtained in this work show that benzoyl azide and other substituted benzoyl azides in para position at R=Cl, OH, CH₃, NO₂ and CN, have a pure covalent C=O group with no ionic resonating structures in addition to approximate linear azide group. In all studied compounds there is a positive charge accumulates on N8 and other negative charge on N9, these results corresponding with the resonating structure of azide group.

The cyclic conformers of benzoyl azide, p-methylbenzoyl azide, p-hydroxybenzoyl azide, p-chlorobenzoyl azide, p-nitrobenzoyl azide and p-cyanobenzoyl azide are 5-phenyl-1,2,3,4-oxatriazole, 5-p-tolyl-1,2,3,4-oxatriazole, 4-(1,2,3,4-oxatriazol-5-yl)phenol, 5-(4-chlorophenyl)-1,2,3,4-oxatriazole, 5-(4-nitrophenyl)-1,2,3,4-oxatriazole and 4-(1,2,3,4-oxatriazol-5-yl)benzotrile. MO calculations using density functional theory method (DFT) combine with B3LYP/6-311G** as basis set have shown that open conformer of aroyl azides are more stable than the corresponding oxatriazoles and the activation energy of cyclic-open conversion has a negative value for all studied compounds so the reaction of conversion is spontaneous whereas the energy barrier is higher for R=CH₃ (2.71 Kcal/mol and lower for R= NO₂ and CN (2.4 Kcal/mol). There is no difference in dipole moment between two conformers cyclic oxatriazoles and corresponding open azides and open conformer of azides lower in energy less than cyclic oxatriazoles so open conformer of azides more stable than cyclic conformer of oxatriazoles and reaction of cyclic-open conversion is proceeds in exothermic process.

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