A THEORETICAL STUDY OF THE 1,2,3-TRIAZOLO-IMINODIAZOMETHANE ISOMERISM IN THE GAS PHASE

Rostislav E. Trifonov,[1,*] Ibon Alkorta,[2] Vladimir A. Ostrovskii,[1] and José Elguero[2]

[1]*St.-Petersburg Institute of Technology, Moskovskii 26, 198013, St-Petersburg, Russia*
[2]*Instituto de Química Médica, CSIC, Juan de la Cierva 3, E-28006, Madrid, Spain*

Abstract- The ring opening reactions of the 1,2,3-triazolate anion, of the three tautomers of N*H*-1,2,3-triazole, and of different 1,2,3-triazolium cations, to give the corresponding iminodiazomethanes, have been studied by means of *ab initio* calculations at the HF/6-31G** level. The 1,5-electrocyclization reactions of 1,2,3-triazolate and 1*H*-1,2,3-triazole proceed through planar transition states with high and medium energy barriers, respectively. In both cases the cyclic forms are thermodynamically more stable than the open-ring ones. In contrast, the decomposition of the 1,2-*H*-1,2,3-triazolium cation into protonated iminodiazomethane is an exothermic process. In the last case, the preferable way of the reaction proceeds *via* non-aromatic intermediates (1,4H_2- and 1,1H_2-1,2,3-triazolium ions) which have a very low activation energy towards the ring opening. It has been found that there is a high $\pi\pi$-conjugation between diazomethyl and imine fragments in the chain forms.

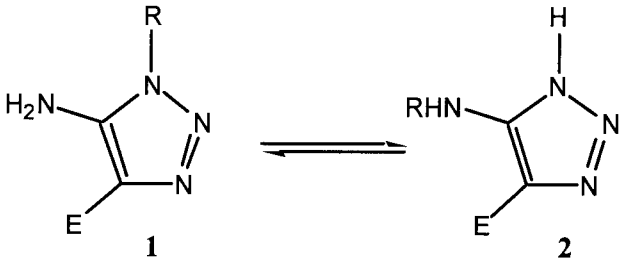
INTRODUCTION

An important property of many heterocycles is their capability of ring-chain isomerism.[1] This process is often the first step of various chemical and physico-chemical transformations of these compounds and it is related to several fundamental properties of the heterocyclic systems, such as aromaticity, electron structure and nature of the heteroatoms.[2]

Among azoles, 1,2,3-triazoles are probably those which show the higher lability of the cycle. Different isomeric forms of C_2H_3N, CH_2N_2 as well as some other unstable molecules, formed after a primary cleavage, were detected as products of photochemical, thermal, and electron-impact fragmentation of 1,2,3-triazoles.[3-5] The mechanism of the decomposition of 1,2,3-triazoles and the thermodynamic stability of the cycle are governed precisely by the first stage, the breaking of one cyclic bond. There are two main ways of opening the triazole ring by breaking one of the C-N bonds or one of the N-N bonds. Experimentally, the primary products of the C-N bond cleavage are the vinyl azides.[6] These compounds are widely used as substrates in synthesis of 1,2,3-triazoles.[7] According to known data, the isomerization of 1,2,3-triazoles to vinyl azides proceeds *via* intermediate 4*H*-1,2,3-triazoles.[7,8] The second way of the

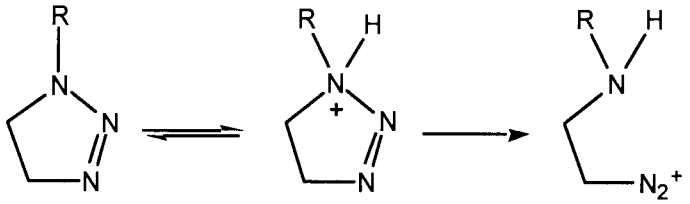
Dedicated to Professor Teruaki Mukaiyama on the occasion of his 73rd anniversary.

1,2,3-triazole ring opening, *i.e.* the cleavage of N-N bond, leads to the corresponding intermediate α-diazoimines.[9] This kind of reversible ring transformation is very well known, for instance, the Dimroth rearrangement (**1** ⇌ **2**) which proceeds through analogous ring-opened structures.[10]



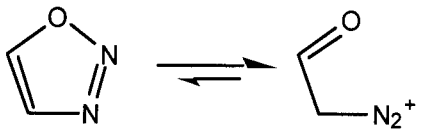
1 **2**

The same type of ring opening is also observed in the cases of benzotriazoles and of 1,2,3-triazolines (**3** ⇌ **4** → **5** path).[1,4,11]



3 **4** **5**

The 1,2,3-oxadiazole/α-diazoketone isomerization (**6** ⇌ **7**) has a close analogy with the previously discussed 1,2,3-triazole/α-diazoimine one since in both cases the open-ring forms are quite similar.[12,13]



6 **7**

The isomerism of 1,2,3-triazoles to the corresponding α-diazoimines has been the subject of various both experimental[14-16] and theoretical studies.[17,18] Recently Fabian, Bakulev and Kappe using *ab initio* methods showed that the 1,5-electrocyclization of iminodiazomethane (*E*) to 1*H*-1,2,3-triazole proceeds *via* a planar pseudopericyclic nonrotatory transition state.[18] However, they have not examined the possibility of the isomerism between the different prototropic forms of 1,2,3-triazoles.[18]

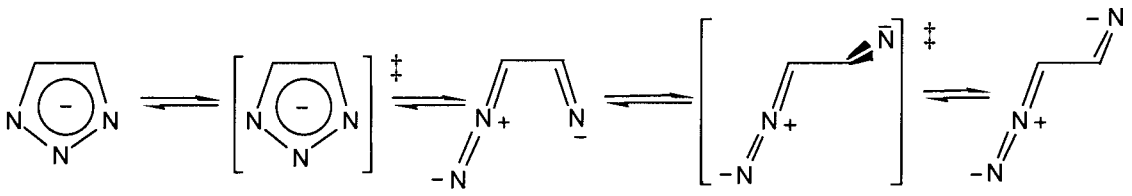
In the present work we have studied the ring-opening by N-N bond cleavage, in the gas phase, of all known tautomeric forms of unsubstituted 1,2,3-triazole by means of *ab initio* calculations at the HF/6-31G** level.

CALCULATIONS

All calculations were performed using GAMESS[19] and Gaussian-94[20] program packages. Geometries of all structures as well as transition states were fully optimized at HF/6-31G** basis set,[21] which has given satisfactory results in similar calculations. [22-24] All stationary points were proved to be minima or transition states by frequency calculations carried out at the same computational level. IRC calculations have been performed to confirm the connecting structures of each transition state. The ZPE correction has not been used to calculate the relative energies of the structures.

1,2,3-TRIAZOLATE ISOMERISM

1,2,3-Triazole is a weak N-H acid (pK_a 9.26, PA_{exp} 346.9 kcal/mol)[25,26] which in the presence of bases loses a proton to give the triazolate anion (**8**). Therefore, the presence of this anion as an intermediate in various chemical transformations can be postulated. In this case, only one form for the initial heterocycle (**8**) and for the open-ring forms (**10**) and (**12**) are possible (Scheme 1).



8 **9** **10** **11** **12**

Scheme 1

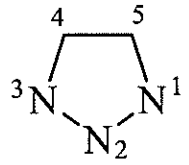
The ring expansion of triazolate (**8**) is a high endothermic process: open-ring forms (**10**) and (**12**) are 68 and 65 kcal mol^{-1} respectively less stable than initial form (**8**) (Table 1). The relative energy of the ring opening transition state (**9**) is very high (75 kcal mol^{-1}).

Table 1. Total and relative energies of different forms and transition states of the 1,5-electrocyclization reaction of 1,2,3-triazolate-iminodiazomethane transformation calculated at HF/6-31G** level.

Form	E, a.u.	ΔE, kcal mol^{-1}
8	-240. 197 593	0.00
9	-240. 077 760	75.20
10	-240. 089 158	68.04
11	-240. 082 434	72.26
12	-240. 093 679	65.21

As it can be seen from Table 2, the initial aromatic anion (**8**), transition state (**9**), as well as the products (**10, 12**) of the ring expansion have planar geometry (C_{2v}, C_s symmetries). The similar bond distances in structure (**8**) corresponds to its aromatic character while the open ring forms have clearly localized double (N2-N3, N3-N4 and C5-N1) and single (C4-C5) bonds.

The rotational barrier around the C-C bond in the imine anion (**10**) [through transition state (**11**)] is small, indicating a weak $\pi\pi$-interaction between the imine and diazomethyl groups in the chain forms (**10**) and (**12**) which agrees with the long C-C distance encountered in these systems.



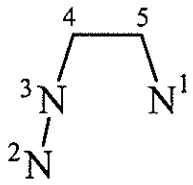


Table 2. Geometry of different forms and transition states of the 1,5-electrocyclization reaction of 1,2,3-triazolate-iminodiazomethane transformation calculated at HF/6-31G** level.

Form	Bonds lengths, Å					Angles					Torsion angles	
	1-2	2-3	3-4	4-5	5-1	1-2-3	2-3-4	3-4-5	4-5-1	5-1-2	3-4-5-1	2-3-4-5
8	1.309	1.309	1.334	1.377	1.334	111.4	107.1	107.1	107.1	107.1	0.0	0.0
9	(2.575)	1.150	1.278	1.562	1.225	(79.7)	142.1	109.0	121.6	87.5	-0.1	0.1
10	-	1.133	1.269	1.545	1.226	-	176.7	122.3	126.4	-	0.0	0.0
11	-	1.137	1.264	1.565	1.227	-	177.7	122.8	125.0	-	90.0	0.0
12	-	1.142	1.265	1.537	1.228	-	175.9	123.6	123.4	-	0.0	180.0

Table 4. Geometry of different forms and transition states of NH-1,2,3-triazole diazoiminomethane 1,5-electrocyclization reaction calculated at HF/6-31G** level.

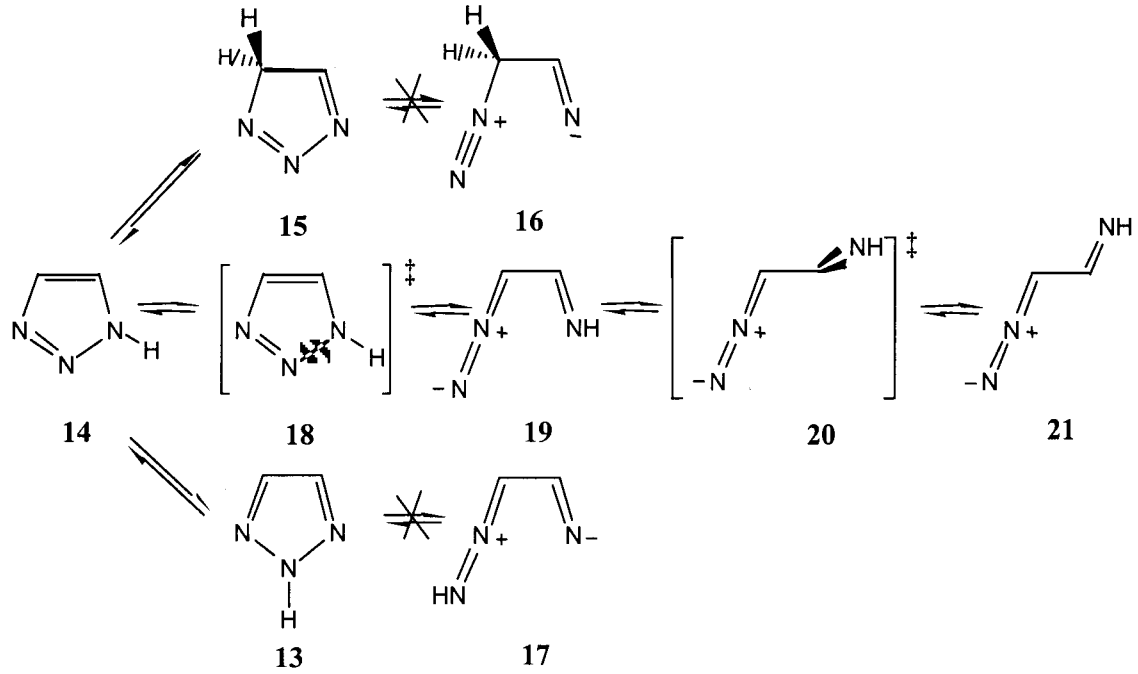
Form	Bonds lengths, Å					Angles					Torsion angles		
	1-2	2-3	3-4	4-5	5-1	1-2-3	2-3-4	3-4-5	4-5-1	5-1-2	3-4-5-1	2-3-4-5	H-1-5-4
13	1.286	1.286	1.274	1.400	1.274	117.3	103.1	108.2	108.2	103.1	0.0	0.0	180.0 (H-2-1-5)
14	1.318	1.266	1.356	1.356	1.343	108.0	109.3	108.0	103.6	111.2	0.0	0.0	180.0
15	1.429	1.215	1.450	1.486	1.257	112.5	109.9	100.5	110.4	106.7	0.0	0.0	-120.4 (H-4-3-2)
18	1.998	1.155	1.328	1.419	1.274	92.5	128.0	107.4	114.8	97.3	0.0	0.0	180.0
19	-	1.103	1.303	1.449	1.259	-	178.1	118.3	123.1	-	0.0	0.1	180.0
20	-	1.117	1.280	1.491	1.251	-	179.7	120.0	121.3	-	90.0	0.9	179.5
21	-	1.111	1.293	1.452	1.256	-	179.9	119.2	121.1	-	180.0	0.0	180.0

Considering the structures of the transition states as well as those of the products (**10**, **12**) and the initial cyclic form (**8**) the process shown on Scheme 1 should be interpreted as a typical pseudopericyclic 1,5-electrocyclization.[18]

It may be concluded that the ring opening of the cyclic anion (**8**) *via* the cleavage of the N-N bond is extremely improbable. So adverse conditions for breaking the cyclic N-N bond in the case of 1,2,3-triazolate anion (**8**) can be ascribed to: i) the small delocalization of the negative charge in the chain forms (**10**) and (**12**) and ii) to the high aromaticity of the initial anion (**8**), which considerable stabilizes it.[27]

N*H*-1,2,3-TRIAZOLE ISOMERISM

Unsubstituted 1,2,3-triazole exists as a mixture of aromatic 1*H*- (**14**) and 2*H*- tautomers (**13**) (Scheme 2). According to previous theoretical calculations the latter is thermodynamically more stable than the former by 3-4 kcal mol^{-1}.[22] In solution, the relative amounts of both tautomers are quite comparable: 1,2,3-triazole in solution contains from 55 to 85% of 2*H*-form (**13**) depending on the medium nature.[28] In gas phase the 2*H*-1,2,3-triazole (**13**) is predominant with a presence of about 99%.[22,29] These differences between gas phase and solution are related to the differences between dipole moments ((**13**), 0.2 D, (**14**), 4.4 D).[22] Besides the stable aromatic forms (**13**, **14**), theoretically 1,2,3-triazole could exist also in the non-aromatic 4*H*-form (**15**). Although the latter is extremely energetically unfavourable (25 kcal mol^{-1}), it can be considered as intermediate in some chemical transformations of 1,2,3-triazoles.[8]



Scheme 2

According to our calculations, the N-N ring-opening of tautomers 2*H* (**13**) and 4*H* (**15**) does not lead to the open ring products (**16**) and (**17**), but to other systems with additional broken bonds. For example, the

energy minimization of **16** leads to the hydrogen-bonded complex of diazomethane with hydrocyanic acid (Figure 1).

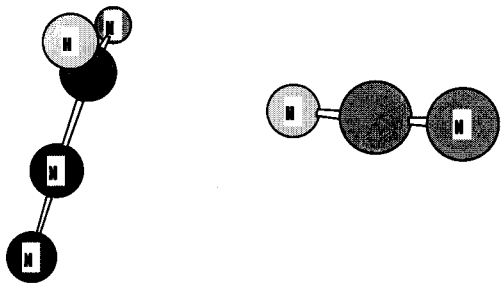


Figure 1. Hydrogen bonded products of the ring expansion of non-aromatic 4*H*-1,2,3-triazole (**15**). The distance between hydrogen atom of hydrocyanic acid and carbon atom of diazomethane consists 2.687 Å.

In the case of 1*H*-1,2,3-triazole (**14**), the ring opening process (**14** → **19**) as well as the subsequent rotation about the C-C bond in the corresponding open-ring form (path **19** → **20** → **21**) were investigated. The activation energy for the ring-opening of **14** through the transition state (**18**) is much lower than in the case of the 1,2,3-triazolate anion (**8**), but nevertheless is still high (40 kcal mol^{-1}, Table 3). It is worth mentioning that activation barriers calculated at the HF level are about 1.5 time higher than at the B3LYP, MP2, and MP4 levels of theory.[18] The process is still endothermic, the initial cyclic form (**14**) being more stable compared with open ring ones (**19**, **21**) by about 20 kcal mol^{-1}. For compounds (**19**) and (**21**) we have only calculated the *E* configuration (about the C=NH bond), for (**19**), the *Z* one lies 2.2 kcal mol^{-1} higher in energy according to MP4 calculations.[18]

Table 3. Total and relative energies of different forms and transition states of the 1,5-electrocyclization reaction of 1,2,3-triazole-iminodiazomethane transformation calculated at HF/6-31G** level.

Form	*E*, a.u.	Δ*E*, kcal mol^{-1}
13	-240.784754	0.00
14	-240.776976	4.88
15	-240.743595	25.83
18	-240.712533	45.32
19	-240.743352	25.98
20	-240.724746	37.66
21	-240.742339	26.62

All stable open-ring forms (**19**, **21**) as well as the transition state (**18**) have planar structures (Table 4). According to Fabian, Bakulev and Kappe,[18] this process must be described as a pseudopericyclic 1,5-electrocyclization. The C-C bond rotation, which transforms **19** into **21** (only 0.6 kcal mol^{-1} more stable), through the transition state (**20**), shows a high barrier (11.7 kcal mol^{-1}) due to the partial double bond character of the bond. This is apparent when comparing the C-C bond length of the minima [(**19**) 1.449; (**21**) 1.452 Å] with the C-C bond length in the TS ((**20**) 1.491 Å). This process is related to that of α-diazo-ketones (**7**).[12,13,18]

ISOMERISM OF 1,2,3-TRIAZOLIUM IONS

1,2,3-Triazole is a weak heterocyclic base, both in solution and in the gas phase, pK_{BH+} -0.16,[30] PA_{exp} 209.3.[26] Under the protonation of neutral 1,2,3-triazole, two different tautomeric forms of the aromatic 1,2,3-triazolium cation (**22**, **23**) can be obtained which are very different regarding their thermodynamic stability (Scheme 3). The most stable one by 13 kcal mol^{-1} is the so-called imidazole-like cation (**22**) (because the NH protons are in 1,3-positions like in imidazolium cation).[30,31] As in the case of the ring-chain isomerization of neutral 1,2,3-triazole, here also the non-aromatic unstable forms of 1,2,3-triazolium cation (**24**) and (**25**) have been considered.

The complete picture of the ring-opening routes are shown in Scheme 3. The pathways involving the pyrazole-like aromatic cation (**23**) (the NH protons in 1,2-positions) and the two non-aromatic 1,1H_2- and 1,4H_2-triazolium ions (**24**) and (**25**) have been considered.[32]

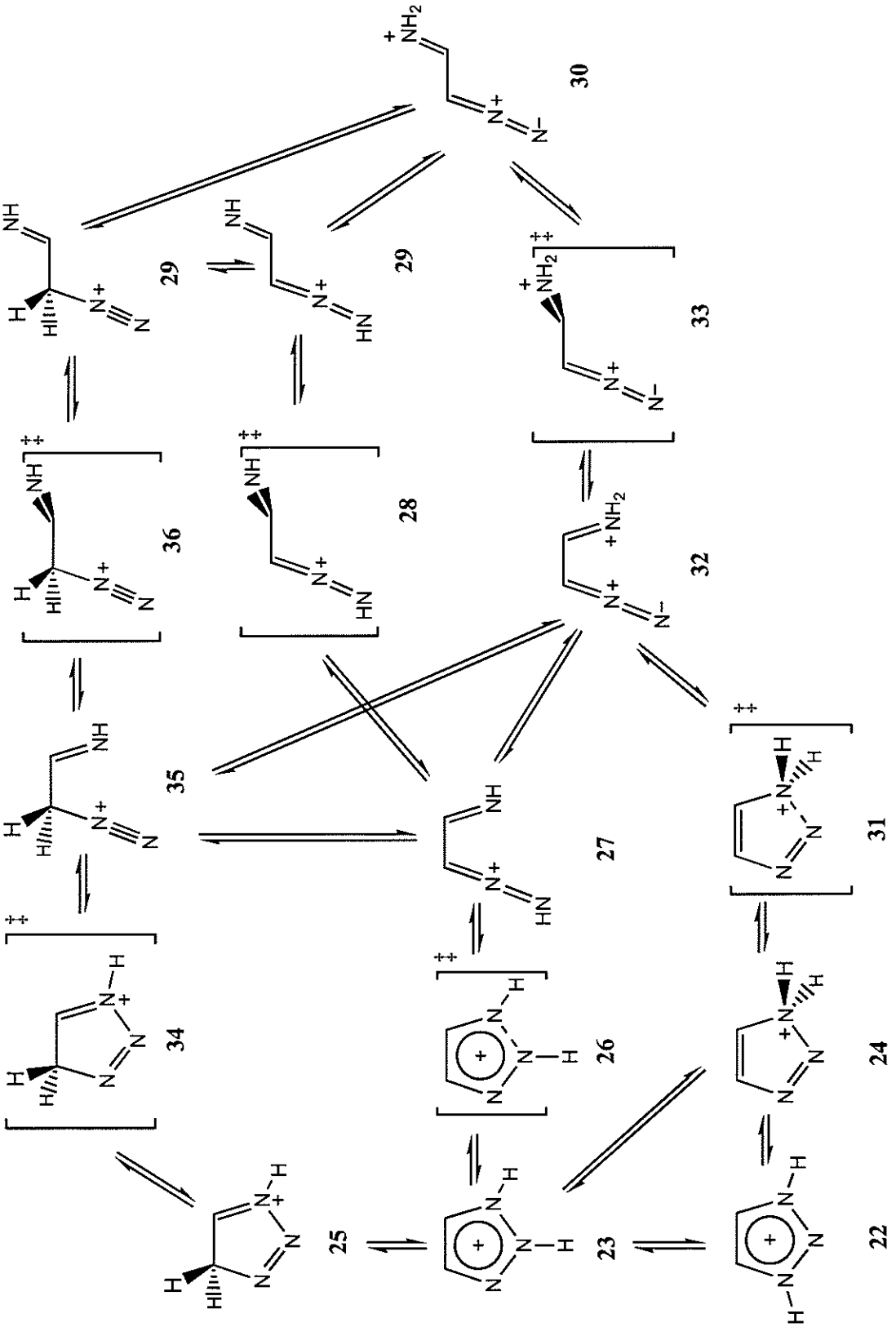
The first route is the ring-chain isomerization of cation (**23**) through transition state (**26**). The activation energy of the direct reaction (**23** → **26** → **27**) is very high (56.2 kcal mol^{-1}), a value which is higher than in the case of 1*H*-1,2,3-triazole (**14**) (Table 5). The final product (**27**) is only 10.5 kcal mol^{-1} below the transition state.

Table 5. Total and relative energies of different forms and transition of the 1,5-electrocyclization reaction of 1,2,3-triazole-iminodiazomethane transformation calculated at HF/6-31G** level.

Form	*E*, a.u.	Δ*E*, kcal mol^{-1}	Form	*E*, a.u.	Δ*E*, kcal mol^{-1}
22	-241.140347	0.00	**30**	-241.136838	2.20
23	-241.119125	13.32	**31**	-241.058985	51.06
24	-241.061773	49.31	**32**	-241.133948	4.02
25	-241.086537	33.77	**33**	-241.090846	31.06
26	-241.029572	69.51	**34**	-241.076617	39.99
27	-241.046305	59.01	**35**	-241.111266	18.25
28	-241.036658	65.07	**36**	-241.104566	22.45
29	-241.045521	59.50	**37**	-241.104846	22.28

The elongation of the N-N bond in the initial form (**23**) produces a slightly non-planar transition state (**26**) to yield a clearly non-planar final product (**27**) (Table 6). Considering the non-planarity of **26** and **27**, this process differs from the ones considered above and can be described as to a monorotatory pericyclic reaction.

The rotation around the C-C bond which transforms the *cis*-chain form (**27**) to the *trans*-form (**29**) though the transition state (**28**) shows a small barrier due to the C-C single bond character as indicated by its long intermolecular distance (around 1.5 Å in all the process). The protonated open-ring forms on the nitrogen atom of the diazogroup (**27**) and (**29**) are thermodynamically very unstable compared with (**23**) (Table 5). An alternative route for the interconversion of **27** and **29** is the prototropic tautomerization to **32** and **30** which are about 55 kcal mol^{-1} more stable. It should be noted that open-ring cations (**30**) and (**32**) are even more stable than the initial cyclic 1,2*H*-1,2,3-triazolium ion (**23**).



Scheme 3

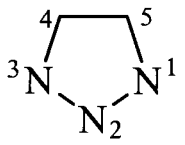
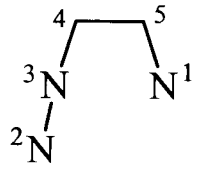



Table 6. Geometry of different forms and transition states of the 1,5-electrocyclization reaction of 1,2,3-triazolium-iminodiazomethane transformation calculated at HF/6-31G** level.

Form	Bond length, Å					Angles					Torsion angles			
	1-2	2-3	3-4	4-5	5-1	1-2-3	2-3-4	3-4-5	4-5-1	5-1-2	H-1-5-4	H-2-3-4	1-5-4-3	2-3-4-5
22	1.277	1.277	1.353	1.353	1.353	104.9	113.2	104.3	104.3	113.2	180.0	-	0.0	0.0
23	1.320	1.273	1.320	1.389	1.317	111.8	107.0	108.3	105.2	107.7	180.0	180.0	0.0	0.0
24	1.514	1.198	1.425	1.315	1.444	106.8	113.4	109.3	106.1	104.5	-117.3 117.4	-	0.0	0.0
25	1.445	1.202	1.449	1.486	1.263	107.8	112.5	102.0	105.9	111.8	180.0	-	0.0	0.0
26	(2.192)	1.213	1.246	1.510	1.242	(86.7)	131.5	110.3	113.7	(96.1)	175.7	108.8	-3.5	-10.3
27	-	1.170	1.240	1.501	1.243	-	170.6	119.5	116.9	-	179.6	155.3	-7.1	-66.6
28	-	1.174	1.238	1.516	1.238	-	170.3	121.2	115.4	-	178.6	175.7	90.1	-85.3
29	-	1.175	1.244	1.487	1.245	-	169.8	122.9	114.1	-	-179.2	179.6	-178.1	-90.1
30	-	1.084	1.363	1.372	1.305	-	177.8	117.0	124.7	-	0.0 180.0	-	180.0	180.0
31	1.760	1.158	1.429	1.319	1.422	102.0	118.5	109.6	110.7	99.3	-116.1 116.1	-	0.0	0.0
32	-	1.084	1.367	1.371	1.309	-	178.4	120.1	129.3	-	180.0 0.0	-	0.0	-179.9
33	-	1.094	1.329	1.466	1.272	-	176.4	116.5	121.6	-	-178.9 1.5	-	90.0	-147.5
34	1.810	1.141	1.462	1.512	1.240	100.3	121.3	102.4	112.0	104.1	179.7	-	0.0	0.0
35	-	1.072	1.511	1.518	1.240	-	178.7	107.0	118.9	-	180.0	-	0.0	0.0
36	-	1.073	1.548	1.521	1.242	-	178.4	107.6	116.1	-	179.0	-	80.1	-49.6
37	-	1.073	1.562	1.513	1.243	-	178.8	108.1	115.6	-	177.0	-	107.7	-52.0

The rotational isomerism (**32** → **33** → **30**) has an activation energy of 27.0 kcal mol^{-1}. This high energy of the transition state (**33**) as well as the planarity and short C-C distances of both rotamers (**32**) and (**30**) correspond to an unusual strong ππ-conjugation between the protonated imine and the diazomethyl fragments.

The non-aromatic form (**24**) can be obtained through a hydrogen rearrangement from **23** or **22**. Energetically **24** is 49 kcal mol^{-1} less stable than **23**. The instability of (**24**) is patent with the small energetic difference with the transition state (**31**) that provides as a final product (**32**) which is 44 kcal mol^{-1} more stable than **24**. In principle, the isomerism (**24** → **31** → **32**) is similar to the cyclization of vinyldiazomethane in 3*H*-pyrazole,[18] however, the (**24** → **31**) activation is achieved only by elongation of cyclic N-N bond and not by a synchronous rotation of the imine fragment. The 90° rotation occurs during the (**31** → **32**) transformation. Although the cyclic form (**24**) is much less stable compared to aromatic form (**23**) the proposed path (**23** → **24** → **31** → **32**) is much better than the first one (**23** → **26** → **27** → **32**). The transition states corresponding to prototropic steps (**23** → **24** and **27** → **32**) have not been calculated because these proton migrations require very high activation energies in the gas phase but very low in solution were the process described in Scheme 3 occurs.[23,24,34,35]

The last studied reaction pathway starts with the non-aromatic form (**25**) which lies 20 kcal mol^{-1} above **23**. As in the previous case, the transition state (**34**) is very close energetically to the starting structure (**25**) (only 6 kcal mol^{-1} above). The calculated open ring forms (**35**) and (**37**) are more stable by 15 and 11 kcal mol^{-1} than the initial cyclic structure (**25**) (Table 5).

In addition, open-form (**35**) by prototropic tautomerization can lead to the more stable form (**32**) or, *via* low energetic transition states (**36**) and (**37**), to the most stable form (**30**). Let us note that rotation process of the open-ring form (**32**) to the *trans*-form (**30**) is energetically preferable by the path (**32** → **35** → **36** → **37** → **30**) than through transition state (**33**). Here also the prototropic processes (**32** → **35** and **37** → **30**) have not been calculated for the reason discussed previously.

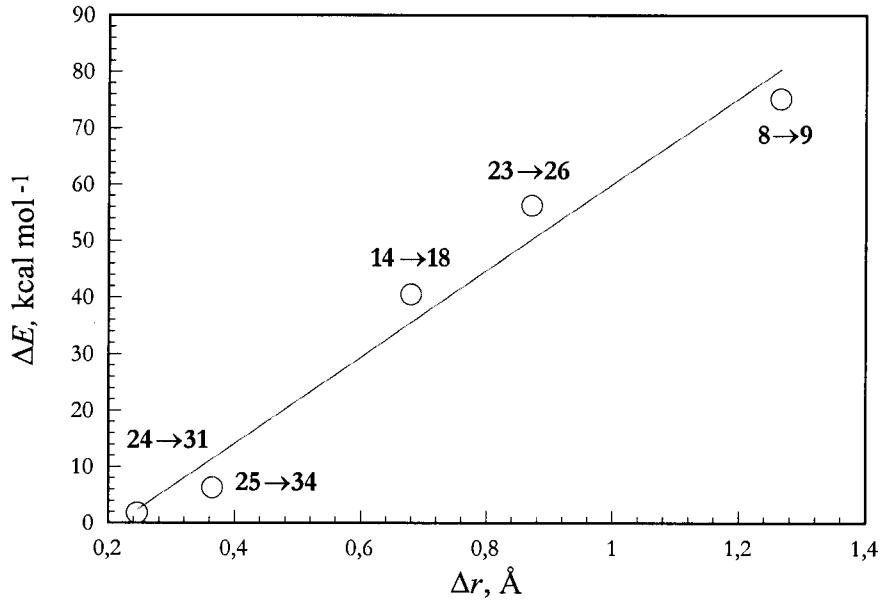


Figure 2. Relation of activation energy of cyclic forms (**8**, **14**, **23**, **24**, **25**) to their corresponding transition states (**9**, **18**, **26**, **31**, **34**) against the relative elongation of the N^1-N^2 bond.
$\Delta E = (77 \pm 7)\,\Delta r - (16 \pm 6)$, R 0.986, s 6.16, n 5.

Using the activation energy data of the ring-chain isomerism of all possible cyclic forms of 1,2,3-triazole including the triazolate anion and the triazolium ions (**8**, **14**, **23**, **24**, **25**) to their respective transition states (**9**, **18**, **26**, **31**, **34**) a good correlation can be found with the relative elongation of the N1-N2 bond (calculated as the difference of N1-N2 bond length between the corresponding transition states and initial cyclic forms) (Fig. 2). According to this observation and taking into account the Hammond postulate,[36] it can be concluded that the ring expansion mechanism of the processes studied is the same in all cases, in spite of the significant differences in activation energies and geometries of the transition states.

CONCLUSIONS AND OUTLOOKS

In the present work, the 1,2,3-triazole–iminodiazomethane isomerism of all possible prototropic forms has been examined using an unified point of view. The probability of the process increases from 1,2,3-triazolate anion through the neutral *NH*-1,2,3-triazole to 1,2,3-triazolium cations. In conclusion, the acid-catalyzed mechanism for the cleavage of N-N bond of the 1,2,3-triazole is the most probable. In the case of the isomerism of the protonated 1,2,3-triazole ring to most stable open-chain forms (**30**) and (**32**) (due to their high $\pi\pi$-conjugation between imine and diazomethyl fragments), the non-aromatic 1,1*H*- and 1,4*H*- cations are the key intermediates of the process. From the data obtained, it is possible to predict that the formation of diazoiminomethanes from 1,2,3-triazoles would occur experimentally only in acidic or strong acidic media.

ACKNOWLEDGMENTS

All calculations were performed at Instituto de Química Médica, Madrid. This work was supported by the Spanish DGCYT (Project No. SAF 97-0044-C02).

REFERENCES AND NOTES

1. H. C. van der Plas, *Ring Transformation of Heterocycles,* Academic Press, London, 1973. R. E. Valters and W. Fleitsch, *Ring-chain Tautomerism,* Plenum Press, New York, 1985.
2. K. N. Zelenin and V. V. Alekseev, *Khim. Geterotsikl. Soedin.*, 1988, 3. K. N. Zelenin and V. V. Alekseev, *Khim. Geterotsikl. Soedin.,* 1992, 851.
3. G. Maier, C. Schmidt, H. P. Reisenauer, E. Endlein, D. Becker, J. Eckwert, A. Hess, and L. J. Schaad, *Chem. Ber.,* 1993, **126**, 2337. G. Maier, J. Eckwert, A. Bothur, H. P. Reisenauer, and C. Schmidt, *Liebigs Ann.,* 1996, 1041.
4. H. Wamhoff, 1,2,3-Triazoles and Their Benzo Derivatives, in *Comprehensive Heterocyclic Chemistry,* ed. by A. R. Katritzky and C. W. Rees, Pergamon Press, Oxford, 1984, Vol. 5, p. 686, p. 691. W.-Q. Fan and A. R. Katritzky, 1,2,3-Triazoles, in *Comprehensive Heterocyclic Chemistry II*; ed. by R. C. Storr, Elsevier, Oxford, 1996, Vol. 4, pp. 1-126.
5. E. M. Burgess, R. Carithers, and L. McCullagh, *J. Am. Chem. Soc.,* 1968, **90**, 1923.
6. L. L. Lohr, Jr., M. Hanamura, and K. Morokuma, *J. Am. Chem. Soc.*, 1983, **105**, 5541.
7. R. W. Saalfrank, U. Wirth, and C.-J. Lurz, *J. Org. Chem.,* 1989, **54**, 4356.
8. L. A. Burke, G. Leroy, M. T. Nguyen, and M. Sana, *J. Am. Chem. Soc.,* 1978, **100**, 3668.
9. M. Regitz, B. Arnold, D. Danion, H. Schubert, and G. Fusser, *Bull. Soc. Chim. Belg.,* 1981, **90**, 615.
10. D. J. Brown, *Mechanisms of Molecular Migration,* ed. by B. S. Thyagarajan, Wiley-Interscience, New York, 1968. Vol.1, pp. 209-245. G. L'abbé, P. Van Stappen, and S. Toppet, *Tetrahedron*, 1985, **41**, 4621.
11. P. Scheiner, *Triazole Decomposition in: Selective Organic Transformations* Vol. 1, ed. by B. S. Thyagarajan, Wiley-Interscience, New York, 1970.

12. G. B. Gill, The Wolf rearrangement in: *Comprehensive Organic Synthesis: Selectivity Strategy Efficiency in Modern Organic Chemistry,* ed. by B. M. Trost and I. Fleming, Vol. 3, G. Pattenden (Ed), Pergamon Press, Oxford, 1984, p. 887.
13. F. Kaplan and G. K. Meloy, *J. Am. Chem. Soc.*, 1966, **88**, 950. H. Hope and K. T. Black, *Acta Crystallogr.*, 1972, **B28**, 3632.
14. R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 947. A. R. Katritzky, D. L. Ostercamp, and T. I. Yousaf, *Tetrahedron*, 1987, **43**, 5171.
15. D. Moderhack, *Liebigs Ann. Chem.*, 1989, 1271.
16. R. W. Saalfrank, B. Weiss, U. Wirth, K. Peters, and H. G. Von Schnering, *Z. Naturforsch.,* 1989, **44b**, 587.
17. V. A. Bakulev and I. P. Gloriozov, *Khim. Geterotsikl. Soedin.*, 1989, 504 .
18. W. M. F. Fabian, V. A. Bakulev, and C. O. Kappe, *J. Org. Chem.,* 1998, **63**, 5801.
19. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem.,* 1993, **14**, 1347.
20. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J.A. Pople, *Gaussian 94*,. Gaussian Inc., Pittsburgh, PA, 1995.
21. R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724.
22. J. Catalán, M. Sánchez-Cabezudo, J. L. G. de Paz, J. Elguero, R. W. Taft, and F. Anvia, *J. Comput. Chem.,* 1989, **10**, 426. E. Fos, J. Vilarrasa, and J. Fernández, *J. Org. Chem.,* 1985, **50**, 4894. J. R. Cox, S. Woodcock, I. H. Hiller, and M. A. Vincent, *J. Phys. Chem.*, 1990, **94**, 5499.
23. J. Catalán, J. L. G. de Paz, M. Sánchez-Cabezudo, and J. Elguero, *Bull. Soc. Chim. Fr.*, 1986, 429.
24. I. Alkorta, I. Rozas, and J. Elguero, *J. Chem. Soc., Perkin Trans. 2*, 1998, 2671.
25. L. D. Hansen, B. D. West, E. J. Baca, and C. L. Blank, *J. Am. Chem. Soc.,* 1968, **90**, 6588. J. Catalán, J. L. M. Abboud, and J. Elguero, *Adv. Heterocycl. Chem.,* 1987, **41**, 187.
26. J. Catalán, R. M. Claramunt, J. Elguero, J. Laynez, M. Menéndez, F. Anvia, J. H. Quian, M. Taagepera, and R. W. Taft, *J. Am. Chem. Soc.*, 1988, **110**, 4105.
27. A. R. Katritzky, M. Karelson, and N. Malhotra, *Heterocycles,* 1991, **32**, 127. V. A. Ostrovskii, G. B Erysalimskii, and M. B. Shcherbinin, *Zh. Org. Khim.*, 1995, **31**, 1422. B. Ya. Simkin and M. N. Gluhovtsev, *Khim. Geterotsikl. Soedin.*, 1989, 1587.
28. A. Albert and P. J. Taylor, *J. Chem. Soc,. Perkin Trans. 2,* 1989, 1903. E. Bojarska-Olejnik, L. Stefaniak, M. Witanowski, B. T. Hamdi, and G. A. Webb, *Magn. Res. Chem.*, 1985, **23**, 166. E. Bojarska-Olejnik, L. Stefaniak, M. Witanowski, and G. A. Webb, *Bull. Pol. Acad. Sci. Chem.*, 1987, **35**, 85. J. Elguero, C. Marzin, A. R. Katritzky, and P. Linda, *The Tautomerism of Heterocycles,* Academic Press, New York, 1976.
29. M. H. Palmer, I. Simpson, and J. R. Wheeler, *Z. Naturforsch.,* 1981, **36a**, 1246.
30. R. E. Trifonov, V. A. Ostrovskii, L. I. Vereshchagin, M. B. Shcherbinin, N. P. Shirokova, and A. O. Koren, *Zh. Org. Khim.*, 1995, **31,** 928.
31. O. Mó, J. L. G. de Paz, and M. Yáñez, *J. Phys. Chem.*, 1986, **90**, 5597. K. Nielsen, I. Sotøfte, and H. Johansen, *Acta Chem. Scand.,* 1993, **47**, 943.
32. It has been established experimentally that the solvent assisted intermolecular proton transfer between the different tautomers of N*H*-1,2,3-triazoles is more favorable than the intramolecular one.[33] Theoretical calculations support this conclusion.[23,24,33,34]
33. L. Lunazzi, F. Parisi, and D. Macciantelli, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1025.
34. M. W. Wong, R. Leung-Toung, and C. Wentrup, *J. Am. Chem. Soc.*, 1993, **115**, 2465.
35. I. Alkorta and J. Elguero, *J. Chem. Soc., Perkin Trans. 2*, 1998, 2497.
36. J. March, *Advanced Organic Chemistry*, Fourth Edition, Wiley-Interscience, New York, 1992, pp. 215-216.

Received, 23rd March, 1999

12. G. B. Gill, The Wolf rearrangement in: *Comprehensive Organic Synthesis: Selectivity Strategy Efficiency in Modern Organic Chemistry,* ed. by B. M. Trost and I. Fleming, Vol. 3, G. Pattenden (Ed), Pergamon Press, Oxford, 1984, p. 887.
13. F. Kaplan and G. K. Meloy, *J. Am. Chem. Soc.*, 1966, **88**, 950. H. Hope and K. T. Black, *Acta Crystallogr.*, 1972, **B28**, 3632.
14. R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 947. A. R. Katritzky, D. L. Ostercamp, and T. I. Yousaf, *Tetrahedron*, 1987, **43**, 5171.
15. D. Moderhack, *Liebigs Ann. Chem.*, 1989, 1271.
16. R. W. Saalfrank, B. Weiss, U. Wirth, K. Peters, and H. G. Von Schnering, *Z. Naturforsch.,* 1989, **44b**, 587.
17. V. A. Bakulev and I. P. Gloriozov, *Khim. Geterotsikl. Soedin.*, 1989, 504 .
18. W. M. F. Fabian, V. A. Bakulev, and C. O. Kappe, *J. Org. Chem.,* 1998, **63**, 5801.
19. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem.,* 1993, **14**, 1347.
20. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J.A. Pople, *Gaussian 94*,. Gaussian Inc., Pittsburgh, PA, 1995.
21. R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724.
22. J. Catalán, M. Sánchez-Cabezudo, J. L. G. de Paz, J. Elguero, R. W. Taft, and F. Anvia, *J. Comput. Chem.,* 1989, **10**, 426. E. Fos, J. Vilarrasa, and J. Fernández, *J. Org. Chem.,* 1985, **50**, 4894. J. R. Cox, S. Woodcock, I. H. Hiller, and M. A. Vincent, *J. Phys. Chem.*, 1990, **94**, 5499.
23. J. Catalán, J. L. G. de Paz, M. Sánchez-Cabezudo, and J. Elguero, *Bull. Soc. Chim. Fr.*, 1986, 429.
24. I. Alkorta, I. Rozas, and J. Elguero, *J. Chem. Soc., Perkin Trans. 2*, 1998, 2671.
25. L. D. Hansen, B. D. West, E. J. Baca, and C. L. Blank, *J. Am. Chem. Soc.,* 1968, **90**, 6588. J. Catalán, J. L. M. Abboud, and J. Elguero, *Adv. Heterocycl. Chem.,* 1987, **41**, 187.
26. J. Catalán, R. M. Claramunt, J. Elguero, J. Laynez, M. Menéndez, F. Anvia, J. H. Quian, M. Taagepera, and R. W. Taft, *J. Am. Chem. Soc.*, 1988, **110**, 4105.
27. A. R. Katritzky, M. Karelson, and N. Malhotra, *Heterocycles,* 1991, **32**, 127. V. A. Ostrovskii, G. B Erysalimskii, and M. B. Shcherbinin, *Zh. Org. Khim.*, 1995, **31**, 1422. B. Ya. Simkin and M. N. Gluhovtsev, *Khim. Geterotsikl. Soedin.*, 1989, 1587.
28. A. Albert and P. J. Taylor, *J. Chem. Soc,. Perkin Trans. 2,* 1989, 1903. E. Bojarska-Olejnik, L. Stefaniak, M. Witanowski, B. T. Hamdi, and G. A. Webb, *Magn. Res. Chem.*, 1985, **23**, 166. E. Bojarska-Olejnik, L. Stefaniak, M. Witanowski, and G. A. Webb, *Bull. Pol. Acad. Sci. Chem.*, 1987, **35**, 85. J. Elguero, C. Marzin, A. R. Katritzky, and P. Linda, *The Tautomerism of Heterocycles,* Academic Press, New York, 1976.
29. M. H. Palmer, I. Simpson, and J. R. Wheeler, *Z. Naturforsch.,* 1981, **36a**, 1246.
30. R. E. Trifonov, V. A. Ostrovskii, L. I. Vereshchagin, M. B. Shcherbinin, N. P. Shirokova, and A. O. Koren, *Zh. Org. Khim.*, 1995, **31,** 928.
31. O. Mó, J. L. G. de Paz, and M. Yáñez, *J. Phys. Chem.*, 1986, **90**, 5597. K. Nielsen, I. Sotøfte, and H. Johansen, *Acta Chem. Scand.,* 1993, **47**, 943.
32. It has been established experimentally that the solvent assisted intermolecular proton transfer between the different tautomers of N*H*-1,2,3-triazoles is more favorable than the intramolecular one.[33] Theoretical calculations support this conclusion.[23,24,33,34]
33. L. Lunazzi, F. Parisi, and D. Macciantelli, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1025.
34. M. W. Wong, R. Leung-Toung, and C. Wentrup, *J. Am. Chem. Soc.*, 1993, **115**, 2465.
35. I. Alkorta and J. Elguero, *J. Chem. Soc., Perkin Trans. 2*, 1998, 2497.
36. J. March, *Advanced Organic Chemistry*, Fourth Edition, Wiley-Interscience, New York, 1992, pp. 215-216.

Received, 23rd March, 1999