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Theoretical study of photoinduced ring-isomerization in the 1,2,4-oxadiazole series

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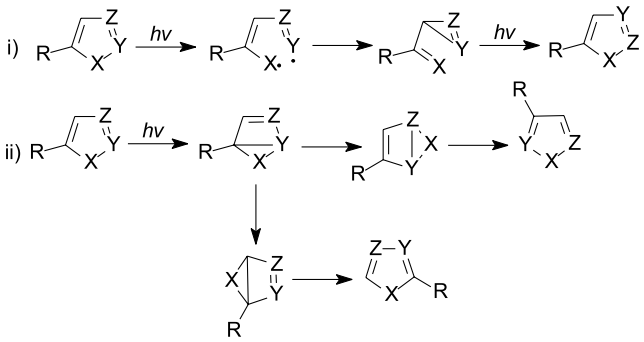
Abstract—A theoretical study of photoinduced ring-isomerization of 3-amino-5-methyl- and 3-amino-5-phenyl-1,2,4-oxadiazoles is reported. The results well agree with the reported experimental data: in particular, they explain the ring-photoisomerization into the corresponding 2-amino-1,3,4-oxadiazoles through a ring contraction-ring expansion route; moreover, the occurrence of competing pathways involving both the ring contraction and the internal cyclization–isomerization mechanism during irradiation of the 5-alkyl substituted substrates in the presence of a base has been also substantiated.

1. Introduction

Photoinduced ring rearrangements of five-membered heterocycles represent a wide class of reactions that received a lot of attention both for the development of synthetic procedure and the description of their mechanisms.[1–3] Among these, two generally observed pathways are represented by (i) the ring contraction-ring expansion mechanism, which explains the interchange of two adjacent ring atoms and involves a three-membered ring intermediate, and (ii) the internal cyclization–isomerization route (also named 'electrocyclic ring closure-heteroatom migration' route), which involves an initial bicyclic isomer (the Dewar isomer) through the formation of a bond between positions 2 and 5 of the starting ring, followed by a sigmatropic shift to form the rearranged ring (Scheme 1). A general scheme which is a combination of the two pathways above has also been proposed; furthermore, a 'zwitterion-tricyclic' route in sulfur containing heterocycles, and a 'fragmentation–addition' route have been also recognized.[2]

For a given heterocycle, competing pathways involving both ring contraction and internal cyclization have been documented, and they have been shown to depend on the structure of the starting ring and on the photoreaction medium.[4,5] In some cases, e.g. in the isothiazole series the occurrence of the above competing pathways was also affected by the presence of a base such as triethylamine (TEA) in the irradiation medium.[5]



Scheme 1. The photoisomerization of five-membered heterocyckes.

A theoretical approach has been used to rationalize many of these photochemical isomerizations. In this respect, we recently proposed a unified description by using semi-empirical calculations,[6–9] in some case also confirmed by ab initio studies.[10–13] By this description, a singlet excited state of a heterocyclic molecule will decay into the corresponding triplet state or into the corresponding Dewar isomer, depending on energetic factors. The Dewar isomer will develop into the internal cyclization–isomerization route; in turn, the triplet state will develop through cleavage of the weakest bond of the ring (generally, the $X-C_\alpha$ bond, where X is a heteroatom of the ring) giving open-chain products or ring contraction products, and then the corresponding ring expansion isomer.

In the frame-work of our general project on the

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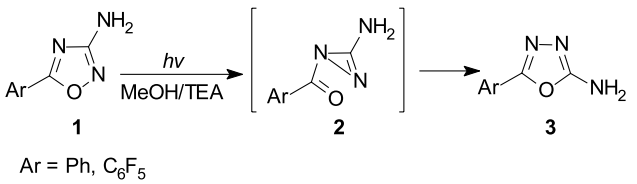
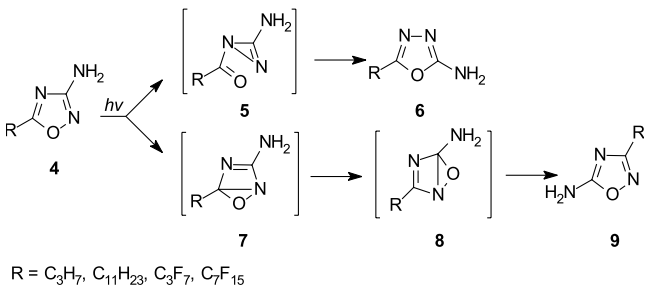
photoreactivity of O–N bond containing azoles, we previously described[14] the occurrence of ring photorearrangement of 1,2,4-oxadiazoles into 1,3,4-oxadiazoles which was found to be restricted to oxadiazoles containing an XH group at C(3) of the ring in one hand, and favored by the presence of a base in the irradiation medium, in the other.[15] On this basis, tautomeric or acid–base equilibria in the starting oxadiazole or in the intermediates are supposed to be involved during the transformation, which was framed in the ring contraction-ring expansion pattern. Experimental observations on 3-amino-5-phenyl-1,2,4-oxadiazole showed that the yield of photorearranged 2-amino-1,3,4-oxadiazole was enhanced when irradiation was carried out in the presence of a base (Scheme 2).[15]



Scheme 2. Photoisomerization of 5-aryl-3-amino-1,2,4-oxadiazoles.s.

By contrast, during the irradiations of some 3-amino-5-alkyl-1,2,4-oxadiazoles, the occurrence of two competing photorearrangements has been recently revealed (see Scheme 3):[16] in methanol, the ring contraction-ring expansion was the only process involved, whereas, in the presence of triethylamine (TEA) as a base, both ring contraction-ring expansion and internal cyclization–isomerization routes were observed (the latter reported for the first time in the oxadiazole series leads to a ring-degenerate photoisomerization).



Scheme 3. Photoisomerization of 5-alkyl-3-amino-1,2,4-oxadiazoles.

Irradiations performed on the corresponding fluorinated analogues showed the same trend of photoreactivity: 3-amino-5-perfluoroalkyl- and 3-amino-5-pentafluorophenyl-1,2,4-oxadiazoles behaved differently towards the ring-phototransformation process.[17]

To gain some information on the substituent effect and to test the validity of the above-described hypothesis for more complex heterocycles, we have now performed a computational survey on the 3-amino-5-methyl-1,2,4-oxadiazole (model compound for 5-alkyl derivatives) and on 3-amino-5-phenyl-1,2,4-oxadiazole (model compound for 5-aryl derivatives) considering all the possible species that could be involved in the very first steps of the photoreaction. Taking into account previous results using this theoretical approach, we investigated the ground and the lowest triplet state of the substrate, the triplet biradicals that result from the homolytic cleavage of O(1)–N(5) and O(1)–C(5) bonds (the former being the species supposed to occur in the isomerization process leading to the formation of diazirine intermediates and therefore of the 1,3,4-oxadiazoles).[†] Moreover, the Dewar isomers of 3-amino-5-methyl-(phenyl)-1,2,4-oxadiazoles (precursors of the ring-degenerate isomers) in their singlet state have been also considered. To simulate irradiations in the presence of TEA, all the above mentioned species have been also treated in their deprotonated forms.

2. Results and discussion

2.1. General methodology

We performed ab initio calculations using 6-31G** basis set on Gaussian 98, using UHF method.[18] The calculations were usually done using Møller-Plesset perturbations (MP2). The Polak–Ribiere algorithm with gradient calculations was adopted for geometry optimizations. The open-shell states were treated at the same level of accuracy as the closed state states. We verified that the obtained structures

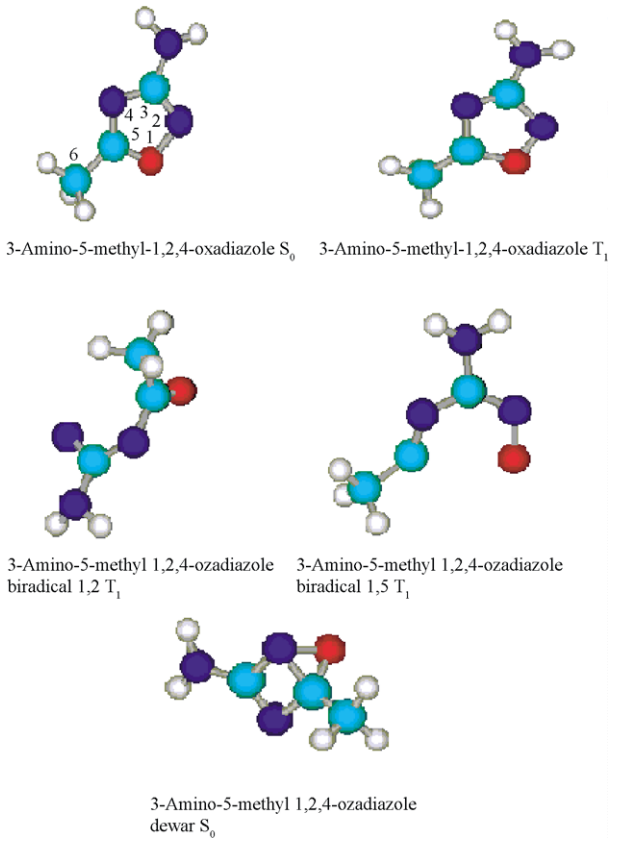


Figure 1. Structures of possible intermediates in the photochemical isomerization of 3-amino-5-methyl-1,2,4-oxadiazole.

[†] The O(1)–N(2) bond cleavage has been recognized in several phorotransformation of O–N bond containing heterocycles such as 1,2,4-oxadiazoles or isoxazoles, however, we choose to include 1,5-biradical [from O(1)–C(5) bond cleavage] in our calculations for a complete comparison of potential species involved.

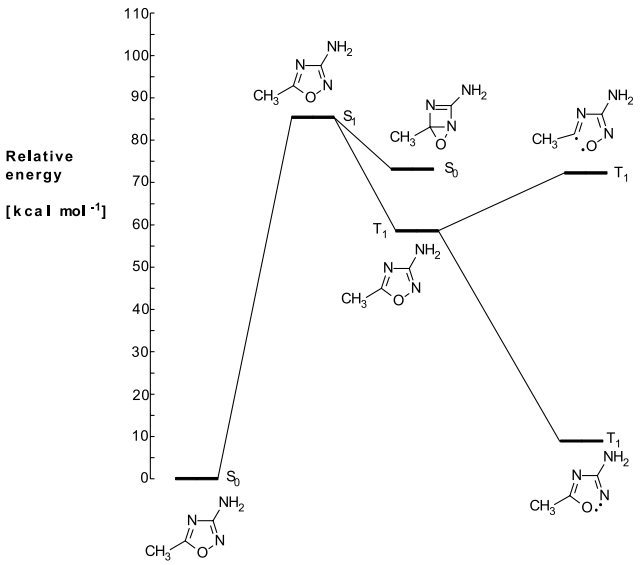


Figure 2. Relative energies of the species involved in the photoisomerization of 3-amino-5-methyl-1,2,4-oxadiazole.

were minima on the potential energy surfaces calculating the frequencies of the optimized structures.

2.2. 3-Amino-5-methyl-1,2,4-oxadiazole

Structures referring to the 3-amino-5-methyl-1,2,4-oxadiazole are illustrated in Figure 1; the relative energy profile referring to these structures is reported in Figure 2; energy values and geometrical data (bond distances and angles) are reported in Tables 1 and 2. In the ground state the substrate shows bond lengths in agreement with the aromatic character of the molecule: N_2-C_3 and N_4-C_5 resemble double bonds, C_5-O_1 as well as O_1-N_2 shows an intermediate length between a single and a double bond, C_3-N_4 resembles a single bond. In the triplet state N_2-C_3, N_4-C_5, and C_5-O_1 appear to be single bonds while C_3-N_5 has the length of a double bond. The triplet state of 3-amino-5-methyl-1,2,4-oxadiazole showed a $\pi,\pi)^*$ character with the LSOMO at -6.32 eV and the HSOMO at -3.86 eV. The 1,2 biradical is a π,π^* triplet with the LSOMO at -6.68 eV and the HSOMO at -6.50 eV. Furthermore, the 1,5 biradical is a π,π^* triplet with the LSOMO at -5.24 eV and the HSOMO at -4.71 eV. It is clear from the energy diagram (Fig. 2) that the formation of the triplet species is significantly favored over the formation of the Dewar isomer; furthermore the formation of the 1,2-biradical is strongly favored with respect to the formation of the 1,5-biradical, and this drives the reaction towards the formation of the 1,3,4-oxadiazole product.

2.3. Deprotonated 3-amino-5-methyl-1,2,4-oxadiazole

The same kind of calculations were performed on the conjugated bases of the species described above. In the presence of a base, in fact, we could observe the formation of the corresponding conjugated bases of all the possible intermediates in the photochemical reaction. However it is not possible to exclude that the base is involved in the acid–base equilibria of one of the intermediates or of the excited states of the substrate rather than on the deprotonation of the substrate in its ground state. The structural properties of this compound are collected in Figure 3 and in Tables 1 and 2.

It is noteworthy that the structure of the triplet state strictly resembles that of the ground state. The triplet state of the conjugated base of 3-amino-5-methyl-1,2,4-oxadiazole showed a π,π^* character with the LSOMO at -5.82 eV

Table 1. Structural properties and energies of possible intermediates and their corresponding conjugated bases (c.b.) in the photochemical isomerization of 1,2,4-oxadiazole derivatives

Compound[a]	Electr. state	Structural element						Relative energy (kcal mol^{-1})
		O_1-N_2 (Å)	N_2-C_3 (Å)	C_3-N_4 (Å)	N_4-C_5 (Å)	C_5-O_1 (Å)	N_2-C_5 (Å)	
3-Amino-5-methyl-1,2,4-oxadiazole	S_0	1.394	1.286	1.369	1.281	1.305		0
3-Amino-5-methyl-1,2,4-oxadiazole	S_1							86
3-Amino-5-methyl-1,2,4-oxadiazole	T_1	1.336	1.438	1.260	1.398	1.431		58
3-Amino-5-methyl-1,2,4-oxadiazole 1,2-biradical	T_1	–	1.352	1.305	1.410	1.186		9
3-Amino-5-methyl-1,2,4-oxadiazole 1,5-biradical	T_1	1.287	1.309	1.388	1.244	–		71
3-Amino-5-methyl-1,2,4-oxadiazole dewar	T_1	1.472	1.456	1.273	1.458	1.361	1.438	73
3-Amino-5-methyl-1,2,4-oxadiazole c.b.	S_0	1.352	1.404	1.334	1.357	1.441		0
3-Amino-5-methyl-1,2,4-oxadiazole c.b.	S_1							57
3-Amino-5-methyl-1,2,4-oxadiazole c.b.	T_1	1.352	1.406	1.334	1.357	1.442		64
3-Amino-5-methyl-1,2,4-oxadiazole c.b. 1,2-biradical	T_1	–	1.355	1.364	1.323	1.229		33
3-Amino-5-methyl-1,2,4-axadiazole c.b. 1,5-biradical	T_1	1.278	1.373	1.419	1.229	–		79
3-Amino-5-methyl-1,2,4-oxadiazole c.b. dewar	S_0	1.480	1.496	1.343	1.415	1.390	1.423	44
3-Amino-5-phenyl-1,2,4-oxadiazole	S_0	1.428	1.338	1.422	1.336	1.365		0
3-Amino-5-phenyl-1,2,4-oxadiazole	T_1	1.341	1.471	1.355	1.386	1.433		32
3-Amino-5-phenyl-1,2,4-oxadiazole 1,2-biradical	T_1	–	1.339	1.361	1.438	1.216		12
3-Amino-5-phenyl-1,2,4-oxadiazole 1,5-biradical	T_1	1.182	1.445	1.386	1.278	–		41
3-Amino-5-phenyl-1,2,4-oxadiazole dewar	S_0	1.628	1.484	1.331	1.538	1.379	1.545	61
3-Amino-5-phenyl-1,2,4-oxadiazole c.b.	S_0	1.428	1.338	1.422	1.336	1.365		0
3-Amino-5-phenyl-1,2,4-oxadiazole c.b.	S_1							98
3-Amino-5-phenyl-1,2,4-oxadiazole c.b.	T_1	2.008	1.360	1.413	1.370	1.260		56
3-Amino-5-phenyl-1,2,4-oxadiazole c.b. 1,2-biradical	T_1	–	1.367	1.387	1.408	1.226		7
3-Amino-5-phenyl-1,2,4-oxadiazole c.b. 1,5-biradical	T_1	1.234	1.404	1.434	1.212	–		70
3-Amino-5-phenyl-1,2,4-oxadiazole c.b. dewar	S_0	1.621	1.516	1.398	1.492	1.401	1.520	57

[a] c.b.=conjugated base.

Table 2. Other structural properties of possible intermediates and their corresponding conjugated bases (c.b.) in the photochemical isomerization of 1,2,4-oxadiazole derivatives

Compound[a]	Angle (°)									
	1–2–3	2–3–4	3–4–5	4–5–1	5–1–2	2–5–4	3–2–5	5–2–1	1–5–2	2–5–6
3-Amino-5-methyl-1,2,4-oxadiazole S_0	102.45	114.9	101.67	113.85	107.13					
3-Amino-5-methyl-1,2,4-oxadiazole T_1	102.78	115.52	105.33	107.56	108.78					
3-Amino-5-methyl-1,2,4-oxadiazole 1,2-diradical	71.65	121.72	121.31	121.6	58.94					
3-Amino-5-methyl-1,2,4-oxadiazole 1,5-diradical	114.52	128.44	122.24	78.57	88.40					
3-Amino-5-methyl-1,2,4-oxadiazole dewar	99.04	101.57	84.98	109.99	60.87	93.94	79.45	55.74	63.39	127.33
3-Amino-5-methyl-1,2,4-oxadiazole c.b. S_0	104.05	113.58	105.54	108.28	108.05					
3-Amino-5-methyl-1,2,4-oxadiazole c.b. T_1	104.08	113.49	105.61	108.26	108.06					
3-Amino-5-methyl-1,2,4-oxadiazole c.b. 1,2-biradical	80.03	127.31	118.76	129.86	84.05					
3-Amino-5-methyl-1,2,4-oxadiazole c.b. 1,5-biradical	115.53	120.45	122.21	79.00	89.86					
3-Amino-5-methyl-1,2,4-oxadiazole c.b. dewar	100.42	96.9	85.80	112.92	59.34	97.08	80.07	57.19	63.47	126.18
3-Amino-5-phenyl-1,2,4-oxadiazole S_0	107.28	108.74	106.89	110.47	106.61					
3-Amino-5-phenyl-1,2,4-oxadiazole T_1	107.50	108.32	107.50	109.36	107.33					
3-Amino-5-phenyl-1,2,4-oxadiazole 1,2-biradical	66.72	123.17	125.57	115.61	56.03					
3-Amino-5-phenyl-1,2,4-oxadiazole 1,5-biradical	122.70	128.96	126.97	77.42	83.78					
3-Amino-5-phenyl-1,2,4-oxadiazole dewar	101.98	95.82	92.27	107.28	61.16	85.64	86.18	51.54	67.42	130.09
3-Amino-5-phenyl-1,2,4-oxadiazole c.b. S_0	107.28	108.74	106.89	110.47	106.61					
3-Amino-5-phenyl-1,2,4-oxadiazole c.b. T_1	93.22	117.55	111.50	117.96	99.77					
3-Amino-5-phenyl-1,2,4-oxadiazole c.b. 1,2-biradical	69.67	118.02	124.58	120.14	47.31					
3-Amino-5-phenyl-1,2,4-oxadiazole c.b. 1,5-biradical	121.51	123.40	139.01	50.95	76.63					
3-Amino-5-phenyl-1,2,4-oxadiazole c.b dewar	103.27	92.83	91.68	110.64	59.88	89.09	86.22	52.86	67.26	128.74

[a] c.b.=conjugated base.

and the HSOMO at −1.67 eV. The 1,2 biradical is a n,π* triplet with the LSOMO at −5.35 eV and the HSOMO at −1.62 eV. Furthermore, the 1,5 biradical is a n,π* triplet with the LSOMO at −3.59 eV and the HSOMO at −3.12 eV. The relative energies for the five above-mentioned structures are shown in Figure 4 and Table 1. It is evident that the excitation of the oxadiazole anion to its singlet state is favored compared to the excitation of the neutral form. The more interesting data, however, come from the possible evolution pattern of the first formed S_1 excited state. In facts, the intersystem crossing $S_1 \rightarrow T_1$ has a small barrier (~7 kcal/mol) and the formation of the 1,3,4-oxadiazole through the more stable 1,2-biradical is slowed down. On the other hand, the formation of the Dewar isomer is favored over the intersystem crossing (i.s.c.) to the T_1 state and, as confirmed by experimental results, the ring-degenerate isomerization through the internal cyclization–isomerization route starts competing with the ring contraction-ring expansion pathway.

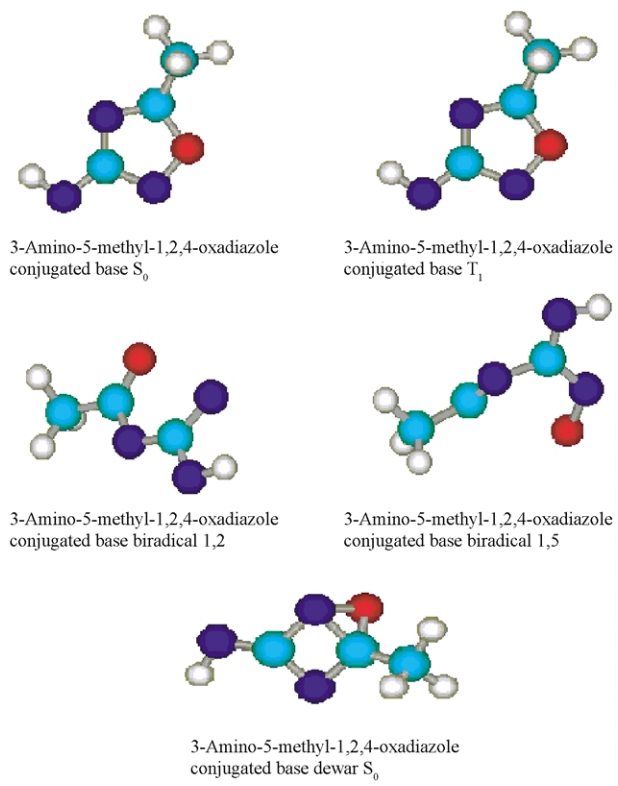


Figure 3. Structures of possible intermediates in the photochemical isomerization of the conjugated base of 3-amino-5-methyl-1,2,4-oxadiazole.

2.4. 3-Amino-5-phenyl-1,2,4-oxadiazole

To justify the absence of the above competing pathways in the reactivity of 5-aryl derivatives, similar calculations have

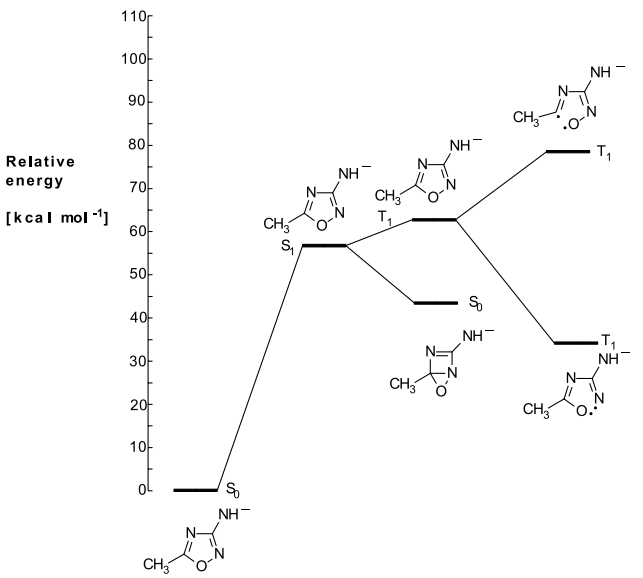


Figure 4. Relative energies of the species involved in the photoisomerization of the conjugated base of 3-amino-5-methyl-1,2,4-oxadiazole.

been considered for the 3-amino-5-phenyl-1,2,4-oxadiazole. At the ground state, this compound already showed some different properties with respect to the corresponding 5-methyl derivative, its structure presenting a highly dienic character (see Fig. 5 and Tables 1 and 2). In fact the N_2-C_3 and N_4-C_5 distances are intermediate between a single and a double C–N bond, the C_3-N_4 and C_5-O_1 bonds show typical distances for single bonds. In the triplet state the structure is clearly deformed with some inverted distances: in fact, the N_2-C_3 distance is similar to that of a single C–N bond while C_3-N_4 showed an intermediate distance between single and double C–N bond. Both S_0 and T_1 states of 3-amino-5-phenyl-1,2,4-oxadiazole are planar.

The triplet state of 3-amino-5-phenyl-1,2,4-oxadiazole showed a π,π^* character with the LSOMO at −6.47 eV and the HSOMO at −3.72 eV. The 1,2 biradical is a π,π^* triplet with the LSOMO at −6.57 eV and the HSOMO at −6.39 eV. On the contrary, the 1,5 biradical is a π,σ^* triplet with the LSOMO at −4.70 eV and the HSOMO at −4.31 eV. The relative energies for the five above-mentioned structures are shown in Figure 6 and Table 1. Interestingly, the data are in strong agreement with the experimental results: the singlet state (whose energy of 92 kcal/mol was obtained from the fluorescence spectrum)

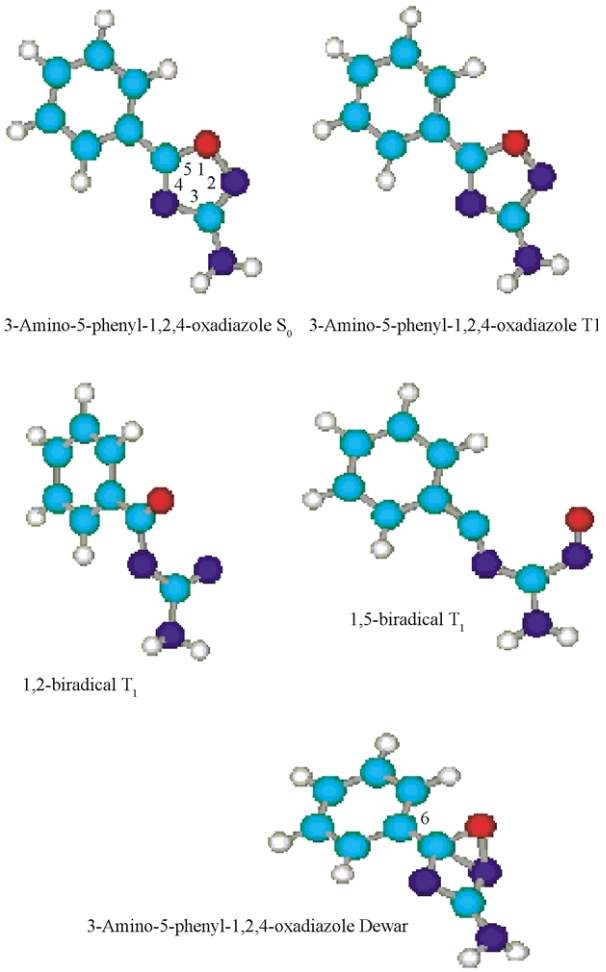


Figure 5. Structures of possible intermediates in the photochemical isomerization of 3-amino-5-phenyl-1,2,4-oxadiazole.

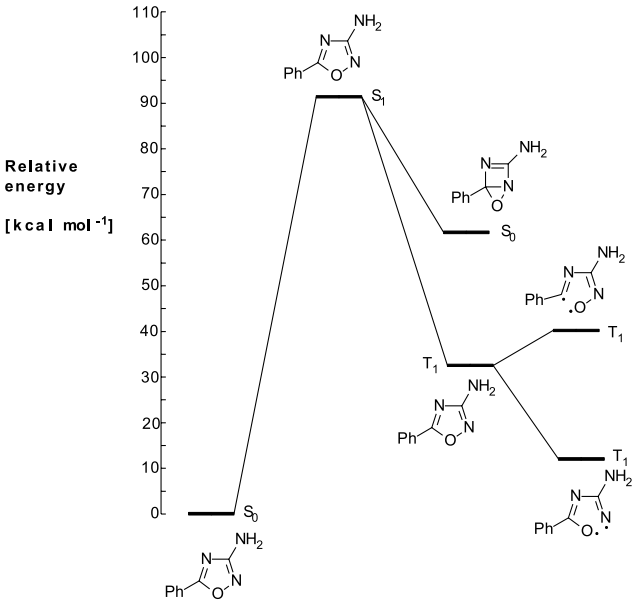


Figure 6. Relative energies of the species involved in the photoisomerization of 3-amino-5-phenyl-1,2,4-oxadiazole.

could evolve to give both the Dewar isomer and the corresponding triplet state; however, the formation of the triplet state is strongly favored and the ring-degenerate isomerization from the Dewar species is not observed.

2.5. Deprotonated 3-amino-5-phenyl-1,2,4-oxadiazole

The structural properties of the conjugated bases of all the possible intermediates in the irradiation of 3-amino-5-phenyl-1,2,4-oxadiazole are collected in Figure 7 and in Tables 1 and 2. We can see that the triplet state is deformed with the O_1-N_2 bond almost broken (and this will play a significant role driving the reaction towards the formation of the 1,2-biradical) and the C_5-O_1 bond similar to a double C–O bond. The triplet state of the conjugated base of 3-amino-5-phenyl-1,2,4-oxadiazole showed π,σ^* character with the LSOMO at −1.00 eV and the HSOMO at −0.11 eV. The 1,2 biradical is a π,π^* triplet with the LSOMO at −1.54 eV and the HSOMO at −0.50 eV. Furthermore, the 1,5 biradical is a π,π^* triplet with the LSOMO at −0.38 eV and the HSOMO at 0.69 eV. The relative energies for the five above-mentioned structures are shown in Figure 8 and Table 1. These data also agree with the experimental findings: the Dewar isomer and the triplet state of the anion have almost the same energy, however, the geometry of the triplet state (see above) and the significant stability of the triplet 1,2-biradical, will drive the reaction towards the formation of the 1,3,4-oxadiazole as the only product.

3. Conclusion

Although the reactions have all been carried out in methanol, which as a protic solvent will favor acid–base equilibria and could stabilize the intermediates involved, calculations performed on the model compounds in the gas phase are in agreement with the experimental results previously reported. For the 5-phenyl derivative, the

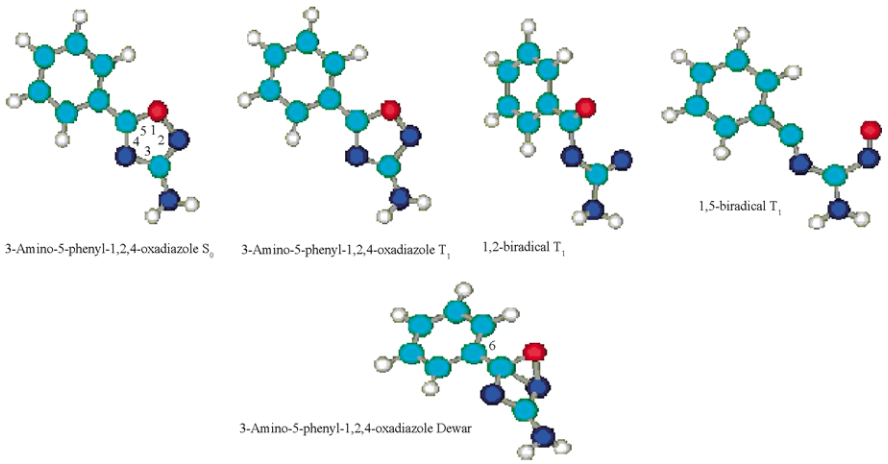


Figure 7. Structures of possible intermediates in the photochemical isomerization of the conjugated base of 3-amino-5-phenyl-1,2,4-oxadiazole.

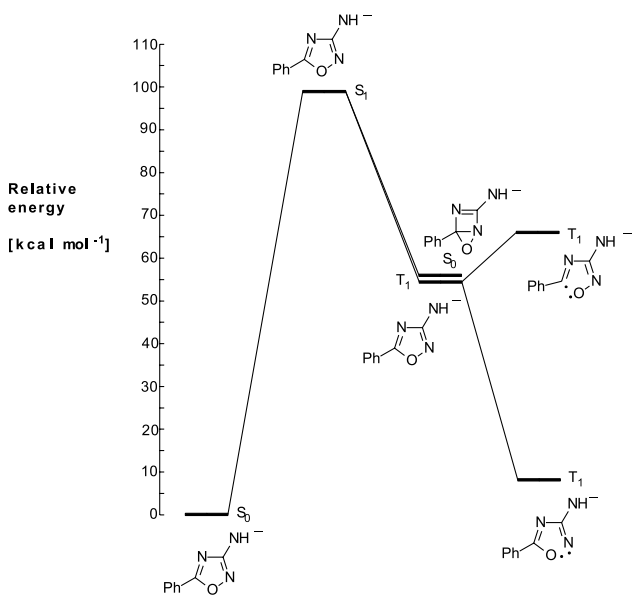


Figure 8. Relative energies of the species involved in the photoisomerization of the conjugated base of 3-amino-5-phenyl-1,2,4-oxadiazole.

computational study clearly explained the absence of the internal cyclization–isomerization route due to a more favored route through the formation of the 1,2-biradical leading to the diazirine intermediate and therefore to the 1,3,4-oxadiazole as the only product. This appears valid both for neutral and anionic forms. For the 5-methyl series, the computational model on the neutral form still showed that the ring contraction-ring expansion route is the favoured one. In the presence of a base, instead, we witness an inversion in the relative stability of the Dewar isomer and the first triplet state intermediate; the formation of the more stable 1,2-biradical still drives the reaction mainly towards the formation of the 1,3,4-oxadiazole ring, but the formation of the 1,2,4-oxadiazole regioisomer is now present as the result of a more competitive process.

As a comment on the role of the base, the authors believe that the involvement of the base in the deprotonation of the excited state cannot be excluded: besides the process described, a deprotonation of the oxadiazole excited state can lead to the formation of the deprotonated anion that can evolve into the final products.

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