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Some Tautomers of 5-Nitriminotetrazole - A DFT Study

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Abstract

Tetrazole compounds having high-nitrogen content, thermal and kinetic stability are usually desired energetic materials. In the present study, various proton tautomers of 5-nitriminotetrazole, including 1,3-types and others, have been investigated within the constraints of density functional theory at the level of B3LYP/6-31++G(d,p). Some structural, spectral, physico chemical and quantum chemical data have been collected and discussed.

1. Introduction

It is known that triazole compounds are often not energetic enough and pentazoles are kinetically too labile, whereas terazole derivatives usually possess both the desired endothermicity and kinetic stability [1]. Also, tetrazole compounds seem to be a good choice for having high-nitrogen content with rational stability in accord. Moreover, tetrazole derivatives possess the remarkable property that they often combine having high nitrogen contents and high heats of formation with acceptable thermal stability and sensitivities [2]. The thermal stability of tetrazole compounds usually can be increased by deprotonation and salt formation [1,2]. Despite the fact that, deprotonation also improves sensitivity. Introduction of functional side chains at the carbon and/or nitrogen atoms of the tetrazole compounds is another way of controlling the performance and sensitivity. Usually, pronounced performances have been accomplished with tetrazoles consisting of nitrogen and oxygen-containing functional groups, for instance nitro groups, [3] and nitramine functionalities. Besides, the formation of tetrazolium salts with oxygen-rich counter anions are in the focus of research because of their characteristic of having

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balanced oxygen contents [2]. Recent years have evidenced some intense research on nitriminotetrazoles [4-11]. The physical and explosive properties of tetrazole derivatives can be improved by the replacement of substituents with various functional groups. Usually the thermal stability of tetrazole compounds can be increased by deprotonation and salt formation. Despite that, deprotonation also improves sensitivity [2]. Energetic materials based on salts often have advantages over non-ionic molecules since these salts tend to exhibit lower vapor pressure and higher densities than neutral derivatives [11].

Since, tautomers having different structures possess dual reactivity, it is anticipated that 5-nitriminotetrazole which exhibits 1,3- and 1,5-proton tautomerisms should display variable properties depending on its tautomer content (allelotropic mixture [12,13]). Note that substances which are isomeric under certain conditions are tautomeric under more drastic conditions [12,13].

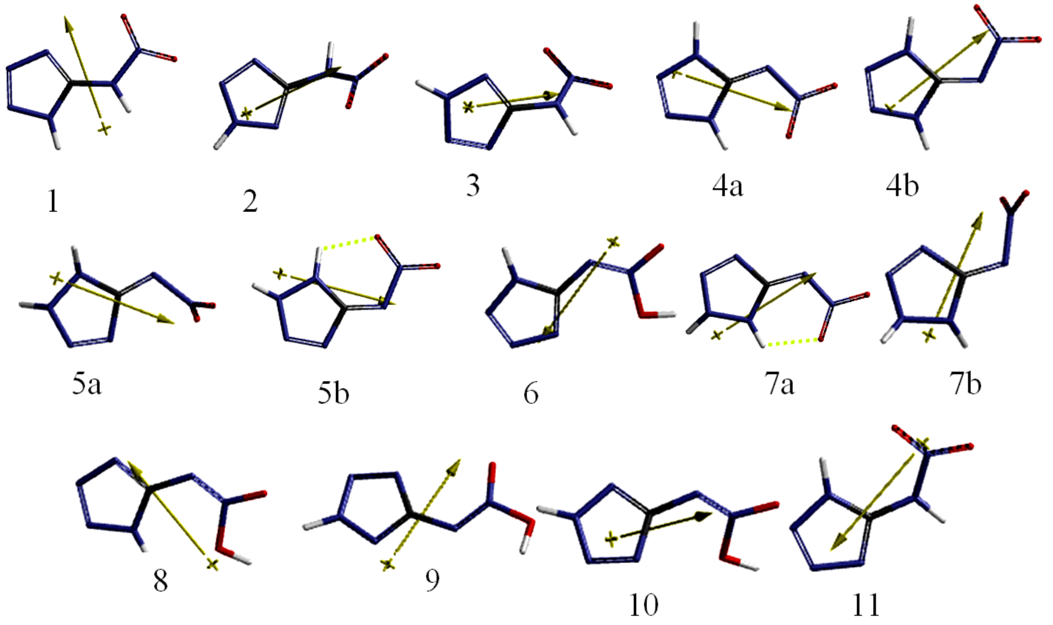
In the present study, various tautomers of 5-nitriminotetrazole have been studied within the constraints of density functional theory and the basis set employed.

2. Method of Calculations

All the structures of present interest were subjected to the geometry optimizations leading to energy minima. The optimizations have been achieved first by using MM2 method which has been followed by semi-empirical PM3 self consistent fields molecular orbital (SCF MO) method [14,15] at the restricted level [16,17]. Subsequent optimizations were performed at Hartree-Fock level employing various basis sets. Afterwards, geometry optimizations were managed within the framework of density functional theory [18,19] at the level of B3LYP/6-311++G(d,p) [16,20]. It is worth mentioning that the exchange term of B3LYP consists of hybrid Hartree-Fock and local spin density (LSD) exchange functions with Becke's gradient correlation to LSD exchange [19,21]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [22] and Lee, Yang, Parr (LYP) correlation correction functional [23]. Also, vibrational analyses have been done on the optimized structures. The total electronic energies were corrected for the zero point vibrational energy (ZPE). The normal mode analysis for each structure yielded no imaginary frequencies for the $3N-6$ vibrational degrees of freedom, where N stands for the number of atoms in the system. This has indicated that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. All these calculations have been done by using the Spartan 06 package program [24].

3. Results and Discussion

Figure 1 shows the optimized structures of the tautomers of 5-nitriminotetrazole, as well as the direction of the dipole moment vectors. If it exists hydrogen bonding is also shown in the figure (5b and 7a) by a dashed line. Structures 4a- and 4b- stand for the 5-nitriminotetrazole in two different geometrical isomers. Although, the starting Lewis structures of some of the tautomers are convertible to each other via some symmetry operations, the optimized structures shown in the figure and indicated such as a- or b-types exhibit some differences and consequently some properties of them differ. The direction of the dipole moment vectors are highly sensitive to the optimized structure, position of the hydrogens and the geometrical isomerism present. In most of the cases the tail of the vector originates from somewhere in or nearby the tetrazole moiety. In the cases of tautomers 6 and 8 (which show tautomerism like nitro-*aci* pair) but not in 9 and 10 the tail of the dipole moment vector originates from nearby the *aci* moiety.



1 2 3 4a 4b

5a 5b 6 7a 7b

8 9 10 11

Figure 1. Optimized structures of the tautomers of present interest.

Figure 2 shows the side views of the optimized structures of the tautomers having side group or hydrogen(s) not coplanar with the ring. Also note that tautomers 7a and 7b have slightly puckered ring systems to minimize the lone pair-lone pair repulsive interaction between the adjacent ring nitrogens. A similar situation also happens in 5a but less pronounced.

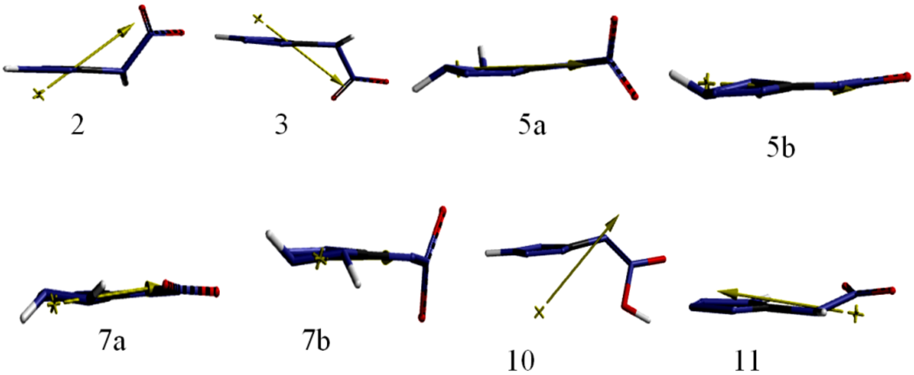


Figure 2. Side views of the optimized structures of the tautomers not coplanar.

Table 1 lists some properties of the tautomers considered. Again it is observed that geometrical isomers possess rather different properties as expected. Tautomers 5a and 7b have the greatest dipole moment values whereas tautomer-11 has the smallest one.

Table 1. Some properties of the tautomers considered.

Tautomer	Eaq (kJ/mol)	Dipole (debye)	Polarizability	Log P
1	-1360655.85	6.34	47.52	1.31
2	-1360688.14	3.69	47.37	1.31
3	-1360688.22	3.72	47.36	1.31
4a	-1360678.62	4.11	47.44	1.01
4b	-1360678.66	4.12	47.44	1.01
5a	-1360602.22	7.89	47.82	1.31
5b	-1360642.04	7.48	47.64	1.31
6	-1360637.79	3.12	47.66	2.87
7a	-1360642.06	7.48	47.64	1.31
7b	-1360602.32	7.89	47.82	1.31
8	-1360660.54	6.37	47.65	2.87
9	-1360666.86	4.10	47.59	2.87
10	-1360660.39	2.80	47.51	2.87
11	-1360669.52	2.24	47.54	1.31

Polarizabilities in 10^{-30} m^3 units.

The polarizabilities differ in small range after the digit only. On the other hand, the polarizability is defined according to the formula [24].

$$\text{Polarizability} = 0.08*V - 13.0353*h + 0.979920*h2 + 41.3791$$

where V and h are the Van der Waals volume and hardness, respectively. Hardness is defined as,

$$\text{Hardness} = -(\varepsilon_{HOMO} - \varepsilon_{LUMO})/2$$

where ε_{HOMO} and ε_{LUMO} are the molecular orbital energies of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbital energies.

As for the log P values, the partition coefficients (P) are important property and useful, especially in estimating the distribution of drugs within the body. Hydrophobic drugs with high octanol-water partition coefficients are mainly distributed to hydrophobic areas such as lipid bilayers of cells. Conversely, hydrophilic drugs (low octanol/water partition coefficients) are found primarily in aqueous regions such as blood serum. The present log P values vary in the range of 1.0-2.9.

It should be noted that the “energy aqueous (Eaq)” is the sum of the base energy and the energy of solvation. The program calculates the solvation energy using SM54A method (Ghose-Crippen method) [24,25].

Table 2 lists some energies of the isomers considered where E, ZPE and E_C stand for the total electronic energy, zero point vibrational energy and the corrected total electronic energy, respectively. E_C values follow the algebraic order of 4b< 4a< 11< 2< 3< 9< 1< 10< 8< 6< 7a< 7b< 5b< 5a. Thus, tautomers 4b and 5a are the most and the least stable ones, respectively. Note that although tautomers 4 and 7 (a and b forms) differ only in terms of the positions of hydrogens however they have highly different stability orders. This fact should arise from the difference in 7a and 7b forms where adjacent nitrogens possibly exert an α-effect [26] affecting the conjugation somewhat. Also note that tautomers 6, 8, 9 and 10 are in the *aci* form.

The two nitrimino pairs, structures 4 and 5, appear at the extreme ends of the order sequence. Most probably due to lone pair-lone pair repulsive interaction occurs in tautomers 5a and 5b (also in 7a and 7b). Also not that in 5b and 7a hydrogen bonding occurs between the ring hydrogen and the nitro group. Those hydrogen bonded structures (see Figure 1) are more stable (characterized with more negative E_C values) than their geometrical isomers (namely, 5b< 5a and 7a< 7b).

Table 2. Some energies of the tautomers considered.

Tautomer	E	ZPE	E_c
1	-1360594.94	169.48	-1360425.46
2	-1360637.74	175.26	-1360462.48
3	-1360637.67	175.22	-1360462.45
4a	-1360641.15	173.79	-1360467.36
4b	-1360641.12	173.69	-1360467.43
5a	-1360521.21	171.27	-1360349.94
5b	-1360550.04	170.69	-1360379.35
6	-1360583.50	170.62	-1360412.88
7a	-1360550.01	170.76	-1360379.25
7b	-1360521.22	171.24	-1360349.98
8	-1360582.81	169.43	-1360413.38
9	-1360598.66	172.97	-1360425.69
10	-1360590.00	172.59	-1360417.41
11	-1360637.09	173.43	-1360463.66

Energies in kJ/mol.

Note that in the table all the structures, except 4, 5 and 7 (their a and b types) possess a ring containing 6π-electrons in cyclic conjugation, thus they are expected to be aromatic.

Figure 3 shows the electrostatic potential (ESP) charges on atoms of the tautomers considered. It is worth noting that the ESP charges are obtained by the program based on a numerical method that generates charges that reproduce the electrostatic potential field from the entire wavefunction [24].

Figure 4 displays the electrostatic potential maps of the tautomers considered. As seen in the figure, negative (red/ reddish regions) and positive potential (blue/bluish regions) parts vary depending on the position of the hydrogens and the structural form of the ring and the substituent in each tautomer.

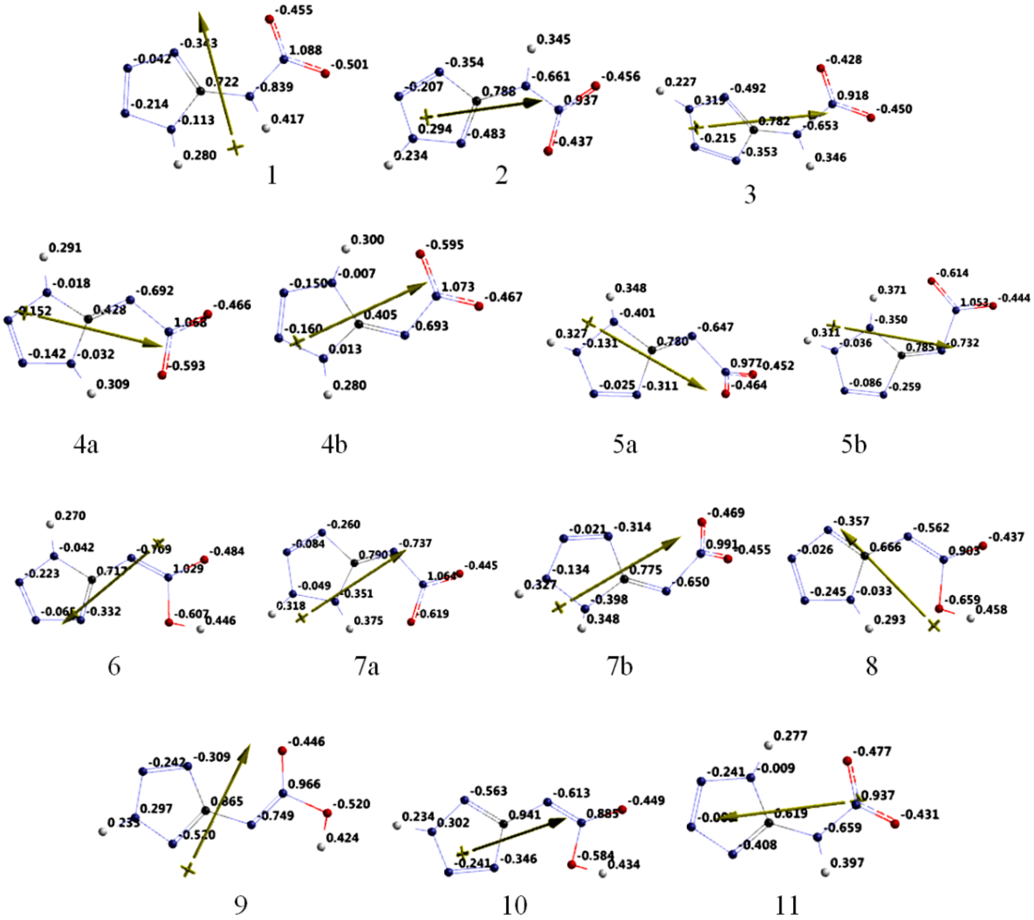


Figure 3. The ESP charges on atoms of the tautomers considered.

Table 3 shows the N-H and O-H stretching frequencies of the tautomers considered. In the tautomers considered there are two hydrogen atoms which one or two of them have bound to the ring nitrogens (tautomers 4,5 and 7) and in some cases one of them linked to the ring and the other to the nitramine nitrogen atom (tautomers 1,2,3 and 11). Whereas in tautomers 6,8,9 and 10 one of the hydrogens binds the nitro oxygen atom forming the *aci* form (nitro-aci tautomers). Note that nitramine N-H stretchings occur at lower frequencies as compared to the ring N-H stretchings because of the prevailing conjugative effects. On the other hand, the O-H stretchings occur at higher frequencies than the N-H stretchings, simply because of the values of reduced masses of O-H and N-H bonds [27].

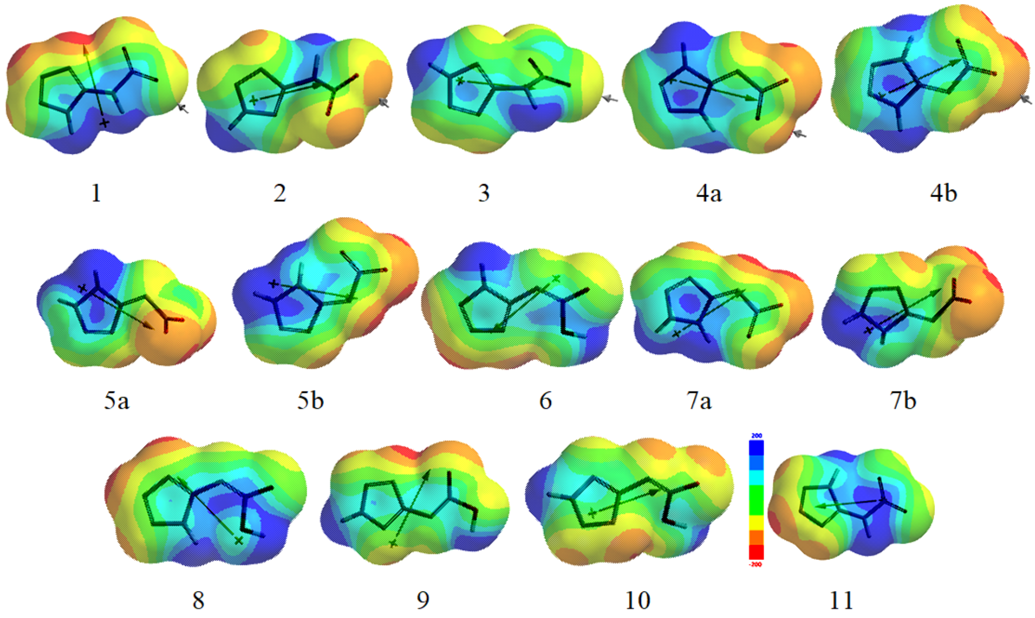


Figure 4. The electrostatic potential maps of the tautomers considered.

Table 3. The N-H and O-H stretching frequencies of the tautomers considered.

Tautomer	N-H (Ring)	N-H (Nitramine)	O-H (*aci*)
1	3635	3621	
2	3620	3571	
3	3621	3572	
4a	3651, 3618		
4b	3649, 3619		
5a	3573, 3529		
5b	3567, 3530		
6	3633		3706
7a	3565, 3530		
7b	3573, 3527		
8	3647		3727
9	3625		3716
10	3624		3729
11	3626	3582	

Frequencies in cm^{-1} units.

Table 4 tabulates the HOMO, LUMO energies (ε_{HOMO} and ε_{LUMO}) and the interfrontier molecular orbital energy gap values ($\Delta\varepsilon = \varepsilon_{LUMO} - \varepsilon_{HOMO}$) of the tautomers considered. The tautomers possessing cyclic conjugation of 6π-electrons in the ring, such as 1,2,3 have lower HOMO energies than that of 4a, 4b and 5a, 5b (nitriminotetrazoles). Tautomers 7a and 7b have slightly puckered ring systems. However, in the present case of tautomeric systems, the HOMO and LUMO energies are dictated by not only the electron donors or attracters attached to the conjugated system(s) in the structures but also degree of aromatic character of the ring in each aromatic case. In the side chain, the nitrogen linked to the ring is acting as an amino group (actually a nitramine, in 1,2,3 and 11) or nitrimino group (4,5 and 7) or N=NO(OH) group (in tautomers 8,9 and 10). So, an overall effect dictates the raising or lowering of the frontier molecular orbitals with respect to a reference structure. In general, electron donating groups raise both the HOMO and LUMO energies at unequal extents and the electron attractors have the opposite effect. Whereas an increased conjugation raises the HOMO but lowers the LUMO energy [26]. In general, the present tautomers having an aromatic ring (they have nitramine substituent) possess, lower HOMO energies as compared to the nitrimino

Table 4. The HOMO, LUMO energies and **Δε** values of the tautomers considered.

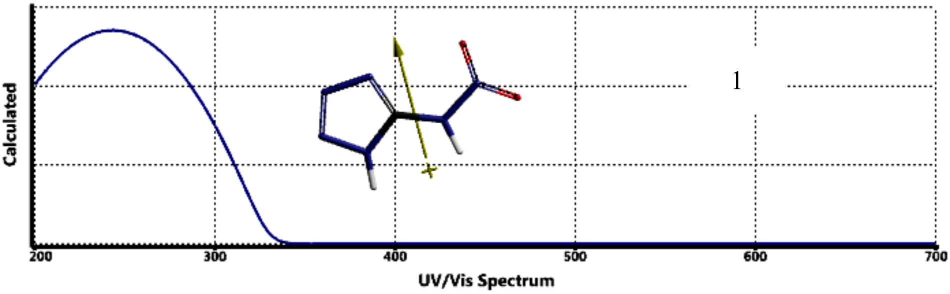
Tautomer	ε_{HOMO}	ε_{LUMO}	**Δε**
1	-806.32	-272.08	534.24
2	-822.28	-237.15	585.13
3	-823.94	-237.04	586.90
4a	-773.39	-237.89	535.50
4b	-773.34	-237.86	535.48
5a	-724.23	-300.12	424.11
5b	-762.39	-311.65	450.74
6	-775.92	-306.52	469.40
7a	-762.30	-311.57	450.73
7b	-723.95	-299.98	423.97
8	-792.22	-325.89	466.33
9	-754.87	-254.59	500.28
10	-773.35	-248.19	525.16
11	-819.69	-311.40	508.29

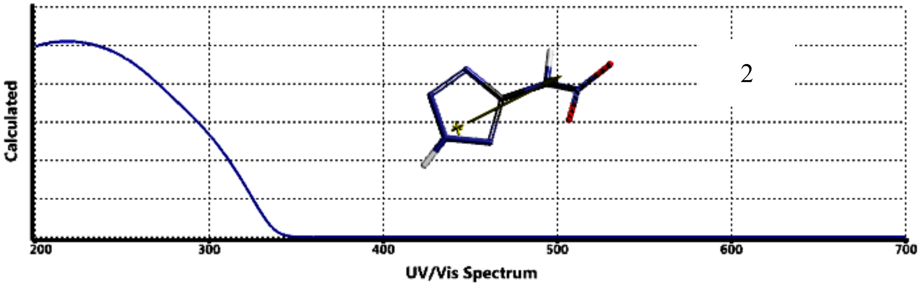
Energies in kJ/mol.

types. It is also valid for the LUMO energies with the exception of 11. The *aci* type tautomers are characterized with higher HOMO but lower LUMO energies as compared to the nitramine types. It is worth mentioning that hydrogen bonded tautomers (5b and 7a) have lower HOMO and LUMO energies than their geometrical isomers 5a and 7b, respectively.

Many properties of the molecules including explosives are dictated by molecular orbital energies up to a certain extent, for example the impact sensivities [28-30] or electric discharge sensivities [31] of explosives.

Figure 5 displays some typical UV-VIS spectra (time-dependent density functional) exhibited by the tautomers considered. Tautomers 1 and 2 are aromatic nitramine-type structures. Tautomers 4a and 4b have quite similar spectra and they are nitriminotetrazoles. Tautomers 5a and 5b are also nitriminotetrazoles, however their spectra are somewhat different from each other. It reflects how apparently small perturbations in the σ-skeleton (like proton tautomerism) or geometrical isomerism of these systems affect the spectral behavior. Spectrum of tautomer-8 is an example for an *aci*-form in the set considered. The common feature of all these tautomers is that they all absorb in the ultraviolet region. Tautomers 5a and 5b, in contrast to 4a and 4b, somewhat exhibit bathochromic effect implying a better conjugation occurs in them to narrow the interfrontier molecular orbital energy gap, thus shifting the absorption relatively to longer wavelengths.





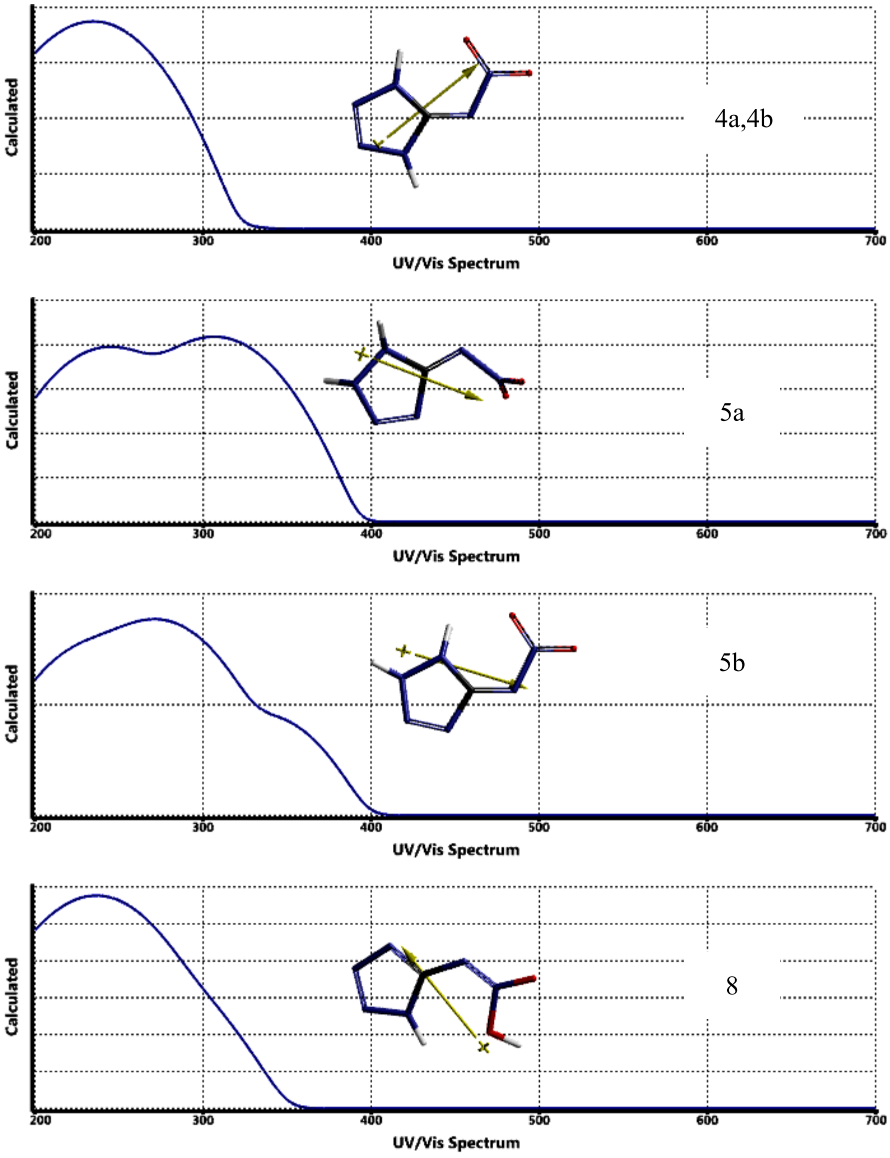
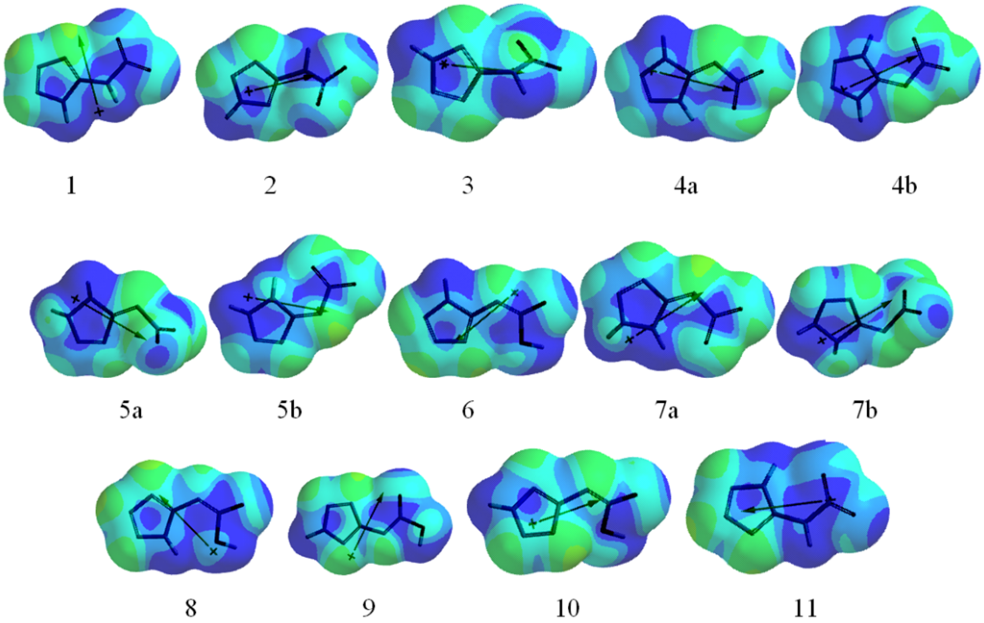


Figure 5. Some typical UV-VIS spectra exhibited by the tautomers considered.

Figure 6 shows the local ionization potential maps of the tautomers considered. In the local ionization potential map, conventionally red/reddish regions (if any exists) on the density surface indicate areas from which electron removal is relatively easy, meaning that they are subject to electrophilic attack.

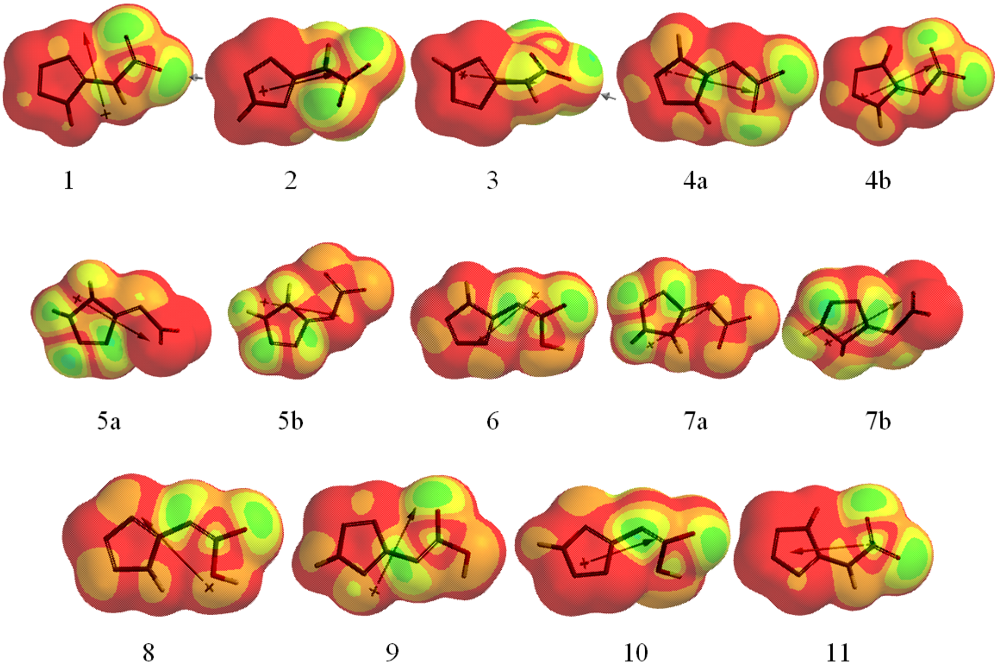

1 2 3 4a 4b

5a 5b 6 7a 7b

8 9 10 11

Figure 6. The local ionization potential maps of the tautomers considered.

Figure 7 shows the LUMO maps of the tautomers considered. A LUMO map displays


1 2 3 4a 4b

5a 5b 6 7a 7b

8 9 10 11

Figure 7. The LUMO maps of the tautomers considered.

the absolute value of the LUMO on the electron density surface. The blue color stands for the maximum value of the LUMO and the color red, the minimum value. Thus, by inspecting the figure, it is possible to follow the variation of the locations of the nucleophilic sites as the tautomerism happens.

4. Conclusion

The present DFT study within the constraints of the theory and the level of application indicate that in vacuum conditions, 5-nitriminotetrazole tautomers are structurally and electronically stable. Most of them have coplanar geometry exhibiting diversity of quite high dipole moments. Whereas the polarizability and log P values vary in rather narrow range. The HOMO and LUMO energies as well as the interfrontier molecular orbital energy gap values are highly sensitive to structural variations in these tautomers. In general, the tautomers having an aromatic ring possess lower HOMO energies as compared to the nitrimino types. It is also generally valid for their LUMO energies. On the other hand, the *aci* type tautomers are characterized with higher HOMO but lower LUMO energies as compared to the nitramine types.

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