AN EXPERIMENTAL AND THEORETICAL STUDY ON 4-AMINO-1,2,3-TRIAZOLO-1,2,6-THIADIAZINE 2,2-DIOXIDE TAUTOMERS AND THEIR *N*-AMINO AND *N*-METHYL DERIVATIVES

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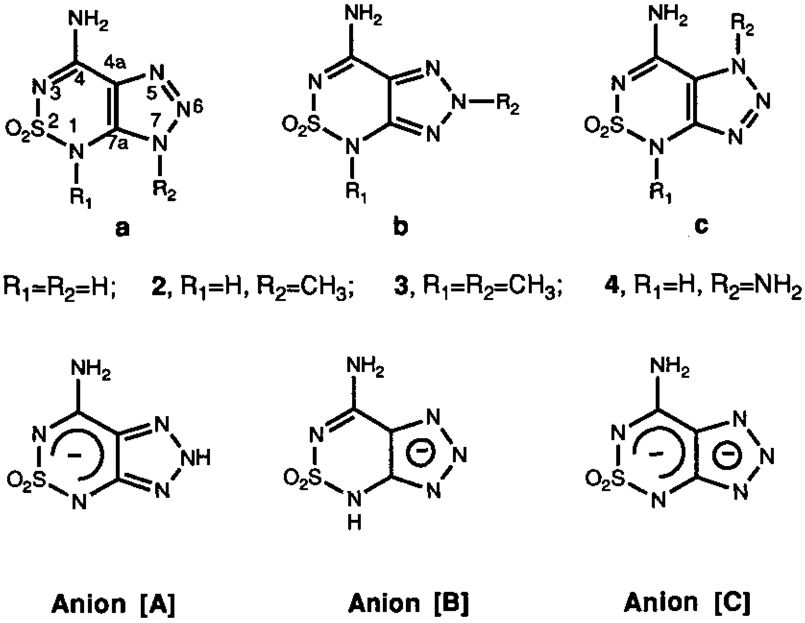
Abstract - The synthesis of 4,5-diaminotriazolothiadiazine dioxide (**4c**) is described. The carbon-13 and nitrogen-15 chemical shifts of 4-amino-1,2,3-triazolo-1,2,6-thiadiazine 2,2-dioxide (**1**), its 1,6-dimethyl derivative(**3b**) and **4c** are reported. Compound (**4c**) has been studied by X-ray crystallography. The experimental preference for the 1*H*, 6*H*-tautomer, 1,6-dimethyl and 5-amino isomers is discussed.

Continuing with our studies on 1,2,6-thiadiazine 1,1-dioxides and fused derivatives,[1] our interest was focused on physicochemical properties and reactivity of *vic*-triazolo-1,2,6-thiadiazine 2,2-dioxide system. Thus, geometry, tautomerism and reactivity of 4-amino-1,2,3-triazolo[4,5-*c*][1,2,6]thiadiazine 2,2-dioxides (**1**) towards electrophiles have been studied by experimental methods complemented by *ab initio* calculations.

The title compound (**1**) had been previously synthesized[2] and the preference for the 1*H*,6*H* tautomer (**1b**) in solid state and water solution confirmed by X-ray[3] and uv spectroscopic studies.[4] Methylation and glycosylation of **1** yielded only the 1,6-disubstituted derivatives (**b**)[4] in spite of several nitrogens in the molecule.

Amination had not been previously achieved in 1,2,6-thiadiazine 1,1-dioxides, and also, it had not been attempted before in fused derivatives. In this work, *N*- amination of **1** has been carried out and surprisingly, only the 5-amino derivative (**4c**) has been found.

In order to find some reasons for the preference of tautomer (**1b**) and for the different regiochemistry of alkylation and amination in triazolothiadiazine dioxides, a theoretical study using *ab initio* calculations of triazolothiadiazine dioxide tautomers (**1a**, **1b**, and **1c**) and the corresponding *N*-methyl (**2a**, **2b**, **2c**, **3a**, **3b**, and **3c**) and *N*-amino (**4a**, **4b**, and **4c**) isomers together with different anionic forms has been performed.



1, $R_1=R_2=H$; **2**, $R_1=H, R_2=CH_3$; **3**, $R_1=R_2=CH_3$; **4**, $R_1=H, R_2=NH_2$

Scheme

Synthesis and spectroscopic study - For the first time, synthesis of *N*-amino derivatives of fused 1,2,6-thiadiazine 1,1-dioxides was achieved by amination of **1** with *o*-mesitylensulfonylhydroxylamine (MSH) in aqueous sodium hydroxide, while the use of hydroxylamine *O*-sulfonic acid (HOSA) was unsuccessful. In the reaction mixture only one monosubstituted derivative was detected. Assignment of the site of amination was made on the basis of uv, ^{13}C- and ^{15}N-nmr spectroscopies and the structure of **4c** was confirmed by X-ray analysis.

Previous attempts to synthesize *N*-amino derivatives of 1,2,6-thiadiazine 1,1-dioxides had been unsuccessful and thus the nitrogens at the thiadiazine ring seem to be less probable sites of amination. So, the three *N*-amino isomers at the triazole ring (**4a**, **4b**, and **4c**) are possible for the reaction product. The structure of the 6-amino isomer (**4b**) was excluded by comparison of uv data (Table l) with those reported[4] for **lb** and its 1,6-dimethyl derivative (**3b**).

Table 1. Uv Spectroscopic Data[a]

Compd	λmax (nm) ($\varepsilon 10^{-3}$)			
1b	225(10.0)	242(7.5)	292(6.9)	-
3b	225(10.3)	250(7.7)	293(7.2)	-
4c	210(6.1) 222(sh)	245(5.0)	-	322(4.7)

a) In H_2O.

Table 2. Nmr Data[a] of **1**, **3b** and **4c**

	^{13}C Chemical Shifts (ppm)				
Compd	C-4	C-4a	C-7a	$CH_3(1)$	$CH_3(6)$
1	155.1	120.8	148.4	-	-
3b	154.3	121.1	151.8	38.7	40.3
4c	151.8	108.8	150.0	-	-

	^{15}N Chemical Shifts[b] (ppm)						
Compd	N-1	N-3	N-5	N-6	N-7	$NH_2(8)$	$NH_2(9)$
1	269.2	-	53.4	-	-	281.9	-
3b	279.0	158.0	51.7	136.5	84.0	278.4	-
4c	268.5	184.6	78.6	15.8	69.2	283.4	298.7

a) DMSO. b) Chemical shifts are referred to neat nitromethane, an increase in shielding being a positive increment. $Cr(acac)_3$ was added as relaxation reagent.

The ^{13}C- and ^{15}N-nmr data of **1b**, **3b** and **4c** are gathered in Table 2. Chemical shifts were assigned on the basis of reported data of oxadiazolo- and thiadiazolothiadiazine dioxides[5] and ^{13}C and ^{15}N-nmr data of benzotriazole[6] and its methyl and amino derivatives.[7] The ^{13}C-nmr chemical shift values of **1** and **3b** are very similar and it is in agreement with the fact that 1*H*,6*H* tautomer (**1b**) predominates in DMSO solution.

Due to the problem of prototropy that exists in compound (**1**), in its ^{15}N-nmr spectrum only the signals corresponding to N-1 and NH_2 and a broad signal at 53.4 ppm, which was assigned to N-5 by comparison to the spectrum of **3b**, could clearly be seen. In the ^{15}N-nmr spectrum of the amination compound (**4c**), the chemical shift of the sp^3 nitrogen at triazole ring has a lower value than that corresponding to the N-7 and higher than the corresponding to the N-5 sp^2 nitrogens in **3b** and so, it must correspond to the N-5 atom in agreement to the structure of 5-amino isomer (**4c**).

X-Ray Crystallography of 4C - Final atomic fractional coordinates are given in Table 3, (see Experimental part). The least squares estimated standard deviations for bond lengths and angles were less than 0.003 Å and 0.2° respectively. The geometry describing the molecular constitution (see Table 4) agrees with that in the literature (see, for example, ref. 8) of thiadiazine derivatives, with N-8 planar and N-9 pyramidal, the angles around adding up to 358(4) and 324(5) respectively (see Figure 1). The thiadiazine ring adopts the usual envelope E^s conformation.

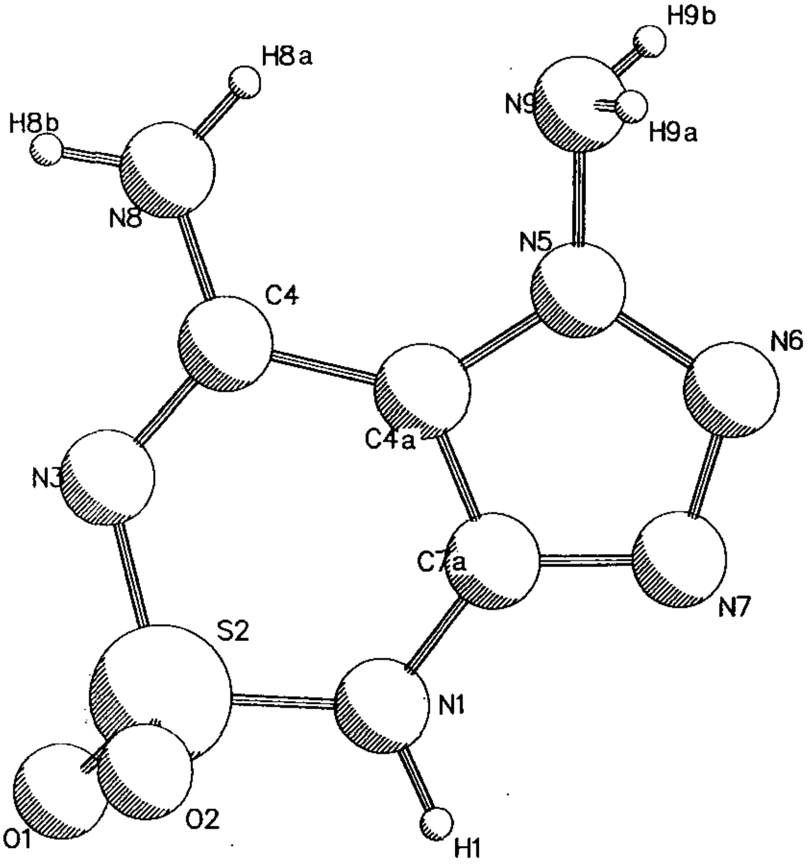


Figure 1- The molecular structure of **4c** showing the atomic numbering

Table 4. Selected Experimental and Calculated Bond Distances (Å) and Angles (deg)

	1b	**1b**^{a}	**3a**	**3b**	**3b**^{b}	**3c**	**4a**	**4b**	**4c**	**4c**^{c}
N1-S2	1.734	1.666	1.749	1.733	1.671	1.717	1.764	1.735	1.733	1.652 (2)
S2-N3	1.699	1.583	1.675	1.699	1.599	1.705	1.670	1.698	1.703	1.598 (2)
N3-C4	1.301	1.329	1.314	1.301	1.329	1.298	1.316	1.302	1.303	1.327 (2)
C4-C4a	1.485	1.454	1.464	1.482	1.430	1.477	1.469	1.484	1.477	1.444 (3)
C4a-C7a	1.419	1.399	1.376	1.416	1.388	1.361	1.363	1.413	1.355	1.368 (2)
C7a-N1	1.424	1.376	1.405	1.424	1.384	1.421	1.407	1.426	1.426	1.376 (2)
C4a-N5	1.337	1.338	1.398	1.340	1.348	1.391	1.406	1.344	1.387	1.356 (2)
N5-N6	1.364	1.322	1.305	1.363	1.312	1.378	1.306	1.363	1.387	1.325 (2)
N6-N7	1.390	1.352	1.417	1.392	1.350	1.324	1.419	1.391	1.322	1.331 (2)
N7-C7a	1.333	1.331	1.374	1.334	1.328	1.396	1.378	1.338	1.402	1.346 (3)
S2-O1	1.444	1.442	1.443	1.444	1.429	1.443	1.443	1.444	1.443	1.433 (2)
S2-O2	1.438	1.431	1.439	1.438	1.428	1.438	1.438	1.437	1.437	1.426 (2)
C4-N8	1.409	1.321	1.401	1.412	1.323	1.430	1.390	1.409	1.408	1.318 (2)
N1-R1^d	1.032	-	1.480	1.468	1.323	1.485	1.032	1.033	1.032	0.93
N5-R5^d	-	-	-	-	-	1.477	-	-	1.436	1.396 (2)
N6-R6^d	1.028	-	-	1.479	1.459	-	-	1.454	-	-
N7-R7^d.	-	-	1.479	-	-	-	1.432	-	-	-
C1-H1a	1.025	-	1.023	1.025	0.856	1.027	1.021	1.024	1.025	0.88
C1-H1b	-	-	1.092	1.092	0.944	1.092	-	-	-	-
C1-H1c	-	-	1.089	1.089	0.966	1.089	-	-	-	-
N9-H9a	-	-	-	-	-	-	1.039	1.043	1.040	0.89
N9-H9b	-	-	-	-	-	-	1.039	1.041	1.040	0.90
C6-H6a	-	-	1.085	1.089	0.889	1.089	-	-	-	-
C6-H6b	-	-	1.091	1.090	0.947	1.092	-	-	-	-
C6-H6c	-	-	1.090	1.091	0.946	1.091	-	-	-	-

Bond and Torsion Angles

N1-S2-N3	101.7	108.2	103.0	102.3	106.4	101.3	102.9	101.4	101.5	105.7 (1)
S2-N3-C4	119.4	124.8	117.8	119.1	123.7	119.9	119.9	118.8	118.9	122.3 (2)
N3-C4-C4a	123.4	119.6	124.0	123.4	119.3	122.6	123.7	123.4	122.3	118.2 (2)
C4-C4a-C7a	120.8	121.8	121.9	120.9	122.3	121.2	120.8	120.7	122.6	123.1 (2)
C4a-C7a-N1	120.1	124.5	121.8	120.8	124.4	122.5	124.6	120.3	121.3	123.4 (2)
C7a-N1-S2	112.8	117.1	113.5	112.2	114.7	113.1	113.2	112.1	112.0	115.1 (2)
C7a-C4a-N5	109.7	108.8	109.8	109.6	108.4	104.3	109.6	109.7	104.4	103.3 (2)

Table 4 (Cont.)

	1b	**1b**[a]	**3a**	**3b**	**3b**[b]	**3c**	**4a**	**4b**	**4c**	**4c**[c]
C-4a-N5-N6	102.1	103.0	108.5	102.6	102.9	109.5	108.8	102.0	109.9	111.7 (2)
N5-N6-N7	116.4	116.6	107.7	115.7	116.9	108.6	107.0	116.5	107.8	107.3 (2)
N6-N7-C7a	101.1	102.0	109.4	101.6	101.8	107.1	109.6	100.9	107.4	107.8 (2)
N7-C7a-C4a	110.6	109.6	104.7	110.5	110.1	110.5	105.0	110.8	110.4	109.9 (1)
C4-C4a-N5	129.4	129.4	128.1	129.5	129.2	134.4	129.5	129.6	132.9	133.2 (2)
N1-C7a-N7	129.1	125.8	133.4	128.5	125.4	126.8	130.0	128.8	128.3	126.5 (2)
O1-S2-O2	122.4	116.5	121.9	122.2	115.3	122.2	122.1	122.4	122.4	116.6 (1)
N1-S2-O1	105.5	106.9	104.5	105.4	106.5	106.1	104.9	105.8	105.9	104.9 (1)
N3-S2-O2	107.6	109.5	108.9	108.3	110.9	110.1	109.7	107.8	107.4	110.3 (1)
N3-C4-C8	119.3	120.1	118.5	119.1	119.8	117.8	118.7	119.0	120.3	120.1 (2)
N8-C4-C4a	117.0	120.2	117.2	117.2	120.8	119.2	117.6	117.3	117.1	118.2 (2)
N1-S2-N3-C4	-38.8	-21.4	-	-38.8	-30.3	-	-	-	-32.9	-34.5 (2)
S2-N3-C4-C4a	+10.0	+11.3	-	+10.5	+12.9	-	-	-	+11.4	+14.7 (2)
N3-C4-C4a-C7a	+13.2	+0.9	-	+12.7	+5.1-	-	-	-	+12.4	+6.9 (3)
C4-C4a-C7a-N1	-3.0	-1.2	-	-2.8	-0.7	-	-	-	-2.5	-1.6 (3)
C4a-C7a-N1-S2	-37.3	-13.7	-	-36.2	-21.5	-	-	-	-36.2	-22.5 (2)
C7a-N1-S2-N3	+51.2	+21.5	-	+50.2	+32.7	-	-	-	50.0	36.7 (2)

[a] Experimental from ref. 3. [b] experimental from ref. 8. [c]This work. Least squares e.s.d. in parenthesis. [d] Representing H, C or N depending on the compound.

The large value of the density, 1.92 gr cm^{-3}, describes the tight crystal packing produced by the H-bonds (see Table 5). The strongest interaction gives rise to dimers through a symmetry center, N-l being the donor and N-7 the acceptor.

Optimized Geometries - The optimized bond lengths and bond angles for **1b**, **3b** and **4c**, of which experimental data are available, are given in Table 4. We have found that, as in the reported study[9] on imidazothiadiazine dioxides, calculated bond lengths are in agreement with experimental data (error < 0.05Å) excepting S2-Nl, S2-N3 and C4-N8. In general, the theoretical values are slightly longer than experimental ones. However, the N3-C4 bond is shorter in the three cases. This fact may be due to that the minimal basis overstimates the double bond of N3-C4 and the single bond character of C4-N8, whereas the experimental value correspond to a more delocalizated double bond among N3, C4 and N8. The shorter theoretical value of the N6-N7 bond indicates that minimal basis is not able to delocalize the double bond in the triazole ring for **4c**. For the hydrogen atoms, the calculated X-H bond lengths are longer (between 0.2 and 0.1 Å) than experimental, showing that the STO-3G* calculations underestimate X-H distances.

Most significant bond angle distorsions are in the O1-S2-O2, N1-S2-N3, S2-N3-C4 and N3-C4-C4a angles while in torsion angles the major differences between theoretical and experimental values are found in the angles bearing the N1-S2 moiety such as N1-S2-N3-C4, S2-N1-C7a-C4a and N3-S2-N1-C7a. This significant discordance could be explained by the crystal structure distorsions which are not present in the gas phase, and by the lack of flexibility of minimal basis set.

As in imidazothiadiazine dioxides STO-3G* geometries[9] the sulfur atom is out of the molecular plane in all triazolothiadiazines studied which is in good agreement with experimental findings. Finally, the conformation adopted by 4-amino and 5-amino groups of **4c** is the same in the experimental as in the calculated structures.

Energies and Dipole Moments - Total SCF energy, and dipole moments of triazolothiadiazine dioxides are gathered in Table 6.

Table 6. STO-3G* Calculated Dipole Moments, Total Energy and Relative Stability of Triazolothiadiazine Dioxides

Compd.	μ(D)	E_T(au)	Relative Stability (kcal/mol)
1a	2.97	-977.902756	0.00
1b	5.08	-977.902253	0.31 (**1a** over **1b**)
1c	5.12	-977.892182	6.63 (**1a** over **1c**)
2a	3.59	-1016.487013	1.42 (**2b** over **2a**)
2b	5.79	-1016.489248	0.00
2c	5.72	-1016.477407	7.45 (**2b** over **2c**)
3a	3.82	-1055.064825	3.60 (**3b** over **3a**)
3b	5.61	-1055.070594	0.00
3c	5.26	-1055.058766	7.42 (**3b** over **3c**)
4a	2.46	-1032.194335	2.08 (**4b** over **4a**)
4b	5.72	-1032.197652	0.00
4c	6.19	-1032.196497	0.72 (**4b** over **4c**)
Anion [A]	-	-977.237886	22.89 (**B** over **A**)
Anion [B]	-	-977.274387	0.00
Anion [C]	-	-976.435732	

The stability order changes upon substitution. Methyl substitution increases stability of isomer (**b**). In *NH*, *N*-methyl and *N,N'*-dimethyl compounds (**1**, **2**, and **3**) 5-substituted derivatives (**c**) are the least stable, about 7 kcal/mol. This relative stability drastically changes in the case of the *N*-amino compounds (**4**), in which **4c** is only 0.7 kcal/mol less stable than the most stable **4b**. The greater stability of 6-substituted derivatives (**2b**, **3b**, **4b**) must be due, in part, to the non existence of lone pair/lone pair repulsions of adjacent sp^2 nitrogens as in the case of 2*H*-1,2,3-triazole itself.[10]

Concerning the 5-substituted derivatives (**c**) their highest energy in the case of **1**, **2**, and **3** must be due to steric effects between the 4-amino and 5-substituted groups; likewise in benzotriazoles a highest energy for 1-substituted derivatives in the case of 4- and 7-substitution has been described.[11] However, when the substituent at 5 position is an amino group, the conformation adopted by this group (see Figure 1) favors a interaction between a hydrogen atom of 4-amino and the lone pair of 5-amino groups increasing the stability of the compound. The greater stability of **3a** in comparison to **3c** can be explained by the fact that 1- and 7-methyl groups of **3a** are in different planes with lower steric hindrance than that 4-amino and 5-methyl groups show in **3c**.

Concerning dipole moments, **a** derivatives have the lowest values, while **b** and **c** exhibit similar dipole moments.

Tautomerism - The preference for the 1*H* tautomer of the thiadiazine ring has previously been shown[5,6] and it is in agreement with experimental uv and nmr data of **1**. Prototropy at the triazole ring will now be discussed.

It is known that in polar solvents the tautomeric equilibrium can be shifted towards the higher dipole moment tautomer if the difference in energy allows it. Although we have no experimental data about triazolothiadiazine dioxides in the gas phase, the preference of **1b** over **1a** in water solution and solid state[3] (crystallized from water) is explained by the higher value of its dipole moment ($\Delta\mu$=2.11, ΔE=0.31 kcal/mol).

Reactivity: Acidity and Basicity - In triazolothiadiazine dioxides the relative stability of anion [**B**] over [**A**] (see Table 6) indicates that the proton at the triazole ring is more acid than the proton at the thiadiazine ring. The higher acidity of the triazole proton in comparison to that of the thiadiazine one is in agreement with the values of net charges calculated[12] for these protons in the three tautomers (Table 7).

In a previous paper,[2] the two pKa values of **1** (2.26 and 8.70) were reported together with that of its 6-phenyl derivative (3.21). From these pKa values, the greater acidity of the thiadiazine proton was admitted. Now, in the light of our theoretical calculations, the 2.26 value must be regarded as belonging to the loss of the triazole proton from the neutral form and 8.70 to the loss of the thiadiazine proton from monoanion [**B**], to give [**C**] whereas the 3.21 value is due to the loss of the thiadiazine proton in derivatives substituted at the triazole ring.

Table 7. Nitrogen and Hydrogen Net Charges (q) Obtained from Mulliken Population Analysis of Triazolothiadiazine Dioxide Tautomers and Their Anions.

Compd	q H-N1	q H-Nx	q N1	q N3	q N5	q N6	q N7
1a	+0.209	+0.254	-0.339	-0.317	-0.134	-0.027	-0.247
1b	+0.214	+0.264	-0.336	-0.297	-0.105	-0.145	-0.145
1c	+0.221	+0.256	-0.336	-0.286	-0.226	-0.007	-0.159
Anion [A]	-	+0.188	-0.401	-0.303	-0.170	-0.188	-0.220
Anion [B]	+0.176	-	-0.344	-0.356	-0.233	-0.153	-0.279
Anion [C]	-	-	-0.444	-0.378	-0.300	-0.217	-0.336

By comparison of the positive net charge of the triazole proton in the three tautomers (**1a**, **1b** and **1c**) it is concluded that **1b** is the most acidic tautomer.

To explain the different isomers obtained under methylation and amination reactions in the case of triazolothiadiazines, several factors have been taken into account: (i) net charges (ii) E_{1s} orbital energies (iii) relative stability of isomers obtained and (iv) dipole moment values.

(i) Prediction of the site of either nucleophilic or electrophilic substitution on the basis of relative charge distribution calculated in isolated molecule should be used with care since reactivity depends on the properties of the molecule in the transition state and it must also be kinetically controlled.

The order of nitrogen basicity of triazolothiadiazine dioxides can be predicted from the value of their negative net charges in dianion [**C**]. This order is as follows N1 > N3 > N7 > N5 > N6 and so, thiadiazine ring nitrogens are more basic than triazole ring ones. The value of the nitrogen net charges explains only the attack of CH_3^+ to N-1 to give the 1,6-dimethyl derivative (**3b**).

(ii) In azoles there is a good correlation between proton affinities (intrinsic basicity) and 1s orbital energy (E_{1s}) of the basic centers.[13,14] This correlation is completely valid if nitrogens with the same hybridization are compared. In our case by comparison of E_{1s} of non hydrogenated nitrogens of neutral forms **1a**, **1b**, **1c** and anion [**A**] in each system, yield the same nitrogen basicity order than in (i). However, the formation of the anion at the triazole ring (anions [**B**] and [**C**]) decreases the relative intrinsic basicity of N3 (see Table 8).

On the other hand, the 1s orbital energy of a center gives some relative information on its hardness.[15] Thus from the E_{1s} values of nitrogens the increasing order of their hardness is the same as the above mentioned basicity for **1a**, **1b**, **1c** and anion [**A**] and N1 > N7 > N5 > N3 > N6 for anions [**B**] and [**C**].

Table 8. N_{1s} Orbital Energies of Basic Centers (au) of Triazolothiadiazine Dioxide Tautomers and Their Anions

Compd	E_{1s} N1	E_{1s} N3	E_{1s} N5	E_{1s} N6	E_{1s} N7
1a	-	-15.33299	-15.41980	-15.45065	-
1b	-	-15.34522	-15.45603	-	-15.41903
1c	-	-15.36073	-	-15.47014	-15.40469
Anion [A]	-15.05164	-15.15522	-15.24928	-	-15.17802
Anion [B]	-	-15.15101	-15.14860	-15.15552	-15.11784
Anion [C]	-14.84600	-14.93829	-14.93657	-14.95011	-14.89411

It is known that hard and soft acids (cations) attack hard and soft bases respectively.[16] Since methylation and amination reactions were carried out in alkaline medium, anions [**B**] or [**C**] must be considered the species under reaction. Again, the formation of the 1,6-dimethyl derivative (**3b**) is in agreement with the electrophilic attack of the hard acid CH_3^+ to the hardest center N1 but it is not with the attack to the least hard center N-6. However, the relative lower hardness of NH_2^+ could account for the attack to the moderate hard center N5.

(iii) The 1,6-dimethyl isomer (**3b**) is 7.4 kcal/mol more stable than 1,5-dimethyl (**3c**) and 3.6 kcal/mol than **3a** and only compound (**3b**) is obtained.

Concerning the case of amino derivatives, **4c** increases its relative stability about 7 kcal/mol in comparison to *NH* and *N*-methyl derivatives (**1**, **2** and **3**). STO-3G* calculations indicate that the **4c** isomer is only 0.7 kcal/mol less stable than **4b**. Due to the well known fact that minimal basis understimate hydrogen bond interactions, it is presumable that a more precise basis set will stabilize **4c** over **4b** due to its better description of the hydrogen bond between both amino groups in **4c**.

(iv) In polar solvents compounds with higher dipole moments are more stables. The calculated values of dipole moments are in agreement with the preference for compounds with higher dipole moments, when the difference in energy is not too large, such as the case of **4c** over **4b** and **1b** over **1a.**

In conclusion the experimental preference for 1*H*,6*H*-tautomer (**1b**) and 1,6-dimethyl isomer (**3b**) can be explained by the value of dipole moments and SCF energy while net charges and E_{1s} orbital energies of nitrogens do not quite agree. The small energy difference between **4b** and **4c** and the slightly higher dipole moment of **4c** can be taken into account to explain the predominancy of **4c**. The conformation adopted by the 5-amino group would explain why **4b** and **4c** are of similar energy.

The differences in energy and dipole moment values between **4b** and **4c** are exclusively thermodynamic criteria about the relative stability of both isomers. Although, these criteria agree with the formation of **3b** in methylation and **4c** in amination reactions, these kind of reactions are evidently controlled by kinetic factors, and in our case they must induce the formation of **4c**, since it is obtained. Unfortunately, the size of the system under study and our computational capability prevent a kinetic study using reaction surfaces.

EXPERIMENTAL

Chemistry - The melting point is uncorrected. DC-Aulofolien silica gel 60 F254 (Merck, layer thickness 0.2 mm) was used for analytical tlc in the reaction mixture, in order to check all reaction products. ^{1}H- and ^{13}C-nmr spectra were recorded at 200 and 50 MHz respectively on a Bruker AM-200 spectrometer. Chemical shifts are reported as δ values (ppm) relative to Me_4Si as internal standard. The natural abundance ^{15}N-nmr spectra were obtained at 30.41 MHz on a Varian XL 300 spectrometer using 1.0 M solutions in a mixture of DMSO and DMSO-d_6 (10%) to provide the locking signal. Chemical shifts were determined with respect to external neat nitromethane in the σ scale (shielding being a positive increment). The ir and uv spectra were registered on a Perkin Elmer 257 and a Perkin Elmer 550 SE spectrophotometers respectively.

4,5-Diamino-1H-1,2,3-triazolo[4,5-c][1,2,6]thiadiazine 2,2-Dioxide **(4c)** - To a solution of **1** (0.5 g, 2.6 mmol) in 5 ml of 1.5 N sodium hydroxide, MSH (0.6 g, 2.7 mmol) in 10 ml of ethanol was added. The solution was stirred at room temperature for 2 h. The precipitate which appeared was filtered and washed with ethanol. The solid was dissolved in water and acidified with concentrated hydrochloric acid to pH 1. Compound **(4c)** (0.15 g, 30%) crystallized from the acid solution as white plates, mp > 265°C (decomp.) (from water); ^{1}H nmr (DMSO-d_6) δ: 11.57 (s, 1H, NH), 8.77, 7.70 (br s, 2H, NH_2), 7.51 (s, 2H, NH_2); ir (nujol) ν: 3400, 3300 (NH_2), 3200 (NH), 1300, 1180-1120 cm^{-1} (SO_2). Anal. Calcd for $C_3H_5N_7O_2S$: C, 17.73; H, 2.48; N, 48.26; S, 15.78. Found: C, 17.71; H, 2.56; N, 48.68; S, 16.03.

Crystal Structure Determination - Crystals were prepared from water. They present good stability at room temperature. Crystal data are: $C_3H_5N_7O_2S$, M=203.2, monoclinic, $P2_1/c$, Z=4, Dc=1.92 g cm^{-3}, a=6.6884(3), b=8.9503(4), c=12.1971(6) Å, β =105.469(4)°, V=703.71 Å^3 (by least squares fit of the diffractometer settings of 53 reflections, λ=1.5418 Å), transparent colourless prism of dimensions 0.2 x 0.3 x 0.4 mm. Data were collected on a PW1100 diffractometer: ω /2θ scans, with ω =1.5° and ω speed of 3°/min, graphite monochromated CuKα radiation, 1193 measured reflections

($2<\theta<65°$, +h,k,l), 1126 observed ones at 3σ (I) level. No absorption correction was applied. The structure was solved by direct methods and refined by full-matrix least-squares with anisotropic non-H atoms and isotropic H atoms (from difference synthesis). Empirical weights give no trends in $<w\,^{2}F>$ when analyzed vs. either <Fo> or <sinθ/λ>. Final R and Rw values, for the observed data, were 0.029 and 0.032. Programs used, on a Vax 6410, are given in references 17 to 20. Atomic scattering factors were taken from reference 21.

Table 3 Final Atomic Parameters
Thermal Parameters as:
$U_{eq}=(1/3).\Sigma[U_{ij}.a_i.a_j.\cos(a_i,a_j)].10^4$
and as:
$\exp[-8.\pi^2.U.(\sin\theta/\lambda)^2.10^3]$ *for H Atoms*

Atom	x	y	z	Ueq/U
N1	0.6800 (3)	0.1266 (2)	0.4529 (1)	292 (5)
S2	0.74984 (6)	0.29094 (5)	0.41374 (4)	225 (5)
O1	0.6958 (2)	0.2858 (2)	0.2925 (1)	344 (5)
O2	0.6542 (2)	0.4061 (2)	0.4639 (1)	385 (5)
N3	0.9964 (2)	0.2979 (2)	0.4625 (1)	282 (5)
C4	1.0965 (3)	0.2358 (2)	0.5605 (1)	229 (5)
C4a	0.9862 (3)	0.1295 (2)	0.6118 (1)	237 (5)
N5	1.0416 (2)	0.0454 (2)	0.7076 (1)	259 (5)
N6	0.8927 (3)	0.0490 (2)	0.7142 (1)	295 (5)
N7	0.7362 (2)	0.0292 92)	0.6216 (1)	279 (5)
C7a	0.7915 (3)	0.0789 (2)	0.5588 (2)	240 (5)
N8	1.2958 (3)	0.2625 (2)	0.6042 (2)	307 (5)
N9	1.2302 (3)	0.0561 (3)	0.7908 (2)	365 (6)
H1	0.541 (5)	0.099 (3)	0.426 (2)	22 (7)
H8a	1.360 (4)	0.225 (3)	0.671 (3)	16 (6)
H8b	1.350 (5)	0.337 (4)	0.577 (3)	32 (8)
H9a	1.200 (5)	0.085 (40)	0.854 (3)	38 (9)
H9b	1.284 (5)	0.037 (4)	0.797 (3)	36 (9)

Table 5. Experimental Hydrogen Interactions Å and º of **4c**

X-H...Y	X-H	X..Y	X-H...Y	H...
N8-H8a...O1 (i)	0.88 (3)	3.056 (2)	139 (3)	2.34 (3)
N8-H8b...O2 (ii)	0.89 (4)	3.123 (2)	146 (3)	2.35 (4)
N9-H9a...N3 (iii)	0.89 (4)	3.207 (3)	155 (3)	2.37 (4)
N9-H9b...O1 (iv)	0.90 (4)	3.303 (3)	148 (3)	2.50 (4)
N1-H1...N7 (v)	0.93 (3)	2.826 (2)	176 (3)	1.89 (3)

Other non-hydrogen interactions

N6...O1 (vi)	2.978 (2)	O2...O1 (vii)	2.971 (2)

Symmetry operations

(i)	1+x, 0.5-y, 0.5+z	(v)	1-x, -y, 1-z
(ii)	2-x, 1-y, 1-z	(vi)	x, 0.5-y, 0.5+z
(iii)	2-x,0.5-y,0.5-z	(vii)	1-x, 1-y, 1-z
(iv)	2-x, -y, 1-z		

Computational Aspects - HONDO 7 program[22] was used on a IBM 4381 system to perform the present calculations. Due to the size of the systems under study and our lack of supercomputer power, fully geometry optimizations by using a suitable gradient method[23] were performed at STO-3G*.[24] This basis set has proved its suitable accuracy for imidazothiadizine dioxides[9] and other heterocycles with the SO_2 moiety.[25] Other basis sets such as 6-31G* or even 3-21G(*) are beyond our computational capabilities. Anions **[A]**, **[B]** and **[C]** were fully optimized at STO-3G* level. Although split valence plus polarization are necessary for anions, minimal basis set can be used for relative energies[26].

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