

# Application of density functional theory concepts to the study of the chemical reactivity of isomeric thiadiazolines

D. Glossman Mitnik, A. Márquez Lucero

## Abstract

Several useful concepts derived from density functional theory have been applied to the study of the chemical reactivity of the more stable forms of the isomeric thiadiazolines. Dipole moments, total hardness of the molecules in terms of the calculated ionization potentials and electron affinities as a measure of aromaticity and the condensed Fukui functions related to the variation of the net charges of the atoms resulting from a Mulliken population analysis were calculated in order to determine the reactivity of different sites within the molecules studied. The net charges have been obtained from calculations made in the context of the Hartree-Fock and of local (SVWN) and nonlocal (BLYP, B3LYP) density functional approximations. The results were compared with the existing experimental evidence on thiadiazolines and related compounds. Electronic properties calculated using the hybrid B3LYP proved to be the most accurate. It is concluded that the 1, 2, 3-thiadiazoline molecule would be the best starting monomer of the four isomers to be considered for a polymerization reaction.

## Introduction

Organic heterocycles are systems of growing interest in materials science in view of the potential technological applications in fields such as electronics, photonics, sensors, or corrosion protection. Several potentially conducting polymers, optically



nonlinear polymers and biomaterials contain heterocyclic structures [1]. Thiadiazoles, the nitrogen-containing analogs of thiophene, and their derivatives are the structural basis of some of these polymeric materials [2, 3].

Computational chemistry is the quantitative modeling of chemical phenomena by computer implemented techniques [4]. Chemical calculations that can predict the outcome of molecular interactions and allow us to understand chemical reactivity are important tools in chemical research. Electron population analysis [5], the electronegativity as a measure of the tendency of a species to attract electrons [6], global and local hardness and softness [7-9] and Fukui functions [9] are examples of the parameters that characterize the behavior of atoms and molecules, which chemists have extracted from their experience and used for prediction of chemical reactivity.

As a further step in the study of the chemical reactivity of the thiadiazoles and related compounds, some results are presented in this paper on the calculation of such indices for the four unsubstituted isomeric thiadiazoline molecules, following previous work along the same lines [10-13] using Hartree-Fock (HF) and local and nonlocal density functional theory (DFT) calculations [9, 14]. The atomic net charges from a Mulliken population analysis [5], the HOMO-LUMO gap as a measure of aromaticity [15, 16] and related to the energy gap between valence and conduction band of the corresponding polymer [17] and the condensed Fukui functions and condensed local softness indices [18] have been determined in order to find the preferred reactive sites for nucleophilic, electrophilic and radical attacks.

### **Theory and computational details**



The DFT [9] provides a convenient theoretical framework for calculating global and local indices that quantitatively describe the inherent reactivity of chemical species.

The electronegativity  $\chi$  has been identified as the negative of the chemical potential  $\mu$ , which is the Lagrange multiplier in the differential equation in DFT [19]

$\mu = -\chi = (\partial E / \partial N)_{v(\vec{r})}$ , where  $E$  is the total electronic energy,  $N$ , the number of electrons and  $v(\vec{r})$ , the external electrostatic potential that the electrons feel due to the nuclei.

The global hardness is defined as [20]  $\eta = (\partial \mu / \partial N)_{v(\vec{r})}$  (the factor of 1/2 in the original definition [21] has been omitted for convenience) while the global softness  $S$  is the inverse of the global hardness [18]. Both  $\chi$  and  $\eta$  are global properties characterizing the molecules as a whole.

The Fukui function is a local property given by [22]  $f(\vec{r}) = (\partial \rho(\vec{r}) / \partial N)_{v(\vec{r})}$  where  $\rho$  is the electronic density of the system under consideration. The condensed Fukui functions [23] are found by taking the finite difference approximations from Mulliken population analysis of atoms in molecules, depending on the direction of the electron transfer:  $f_k^+ = q_k(N+1) - q_k(N)$  (for nucleophilic attack),  $f_k^- = q_k(N) - q_k(N-1)$  (for electrophilic attack), and  $f_k^0 = [q_k(N+1) - q_k(N-1)]/2$  (for radical attack), where  $q_k$  is the gross charge of atom  $k$  in the molecule. Condensed softness indices allowing the comparison of reactivity between similar atoms of different molecules can be easily calculated starting from the relation between the Fukui function  $f(\vec{r})$ , and the local softness  $s(\vec{r})$ , i.e.  $s(\vec{r}) = f(\vec{r})S$ .

As a high accuracy is needed for a good description of properties that depend on the electronic structure, the condensed Fukui functions and condensed local softness

indices, the electronic density maps, the molecular electrostatic potentials and the gross orbital charges were obtained from HF and local and nonlocal DFT using the 6-31G\*\* basis set through single point calculations on the fully optimized at the same level neutral molecule and the singly ionized positive and negative molecules with the same geometric structure of the neutral molecule.

The local density functional calculations have been performed by resorting to the SVWN functional, which is formed by the exchange part of Slater (S), corresponding to the free-electron gas [24] and the Vosko, Wilk and Nusair (VWN) parametrization of exact uniform gas results [25] for the correlation part. The nonlocal density functional used different combinations of exchange correlation functionals. The functionals used are Becke 88 (B) [26] and the Becke three-parameter hybrid functional (B3) [27] for the exchange part and the Lee, Yang and Parr (LYP) [28] for the correlation part. All the calculations were performed with the GAUSSIAN94W series of programs [29].

## Results and discussion

Thiadiazolines can exist in different tautomeric forms, depending on the position of the double bond. For the purpose of this work, we have considered only the most stable tautomeric forms, characterized for a lower value of total energy.

1, 2, 5-thiadiazoline (I) and 1, 3, 4-thiadiazoline (II) have two tautomeric forms: symmetric, with the double bond between the nitrogen atoms or the carbon atoms in either case, and asymmetric, with the double bond between the nitrogen and the carbon atoms. We have found that the most stable tautomers are the asymmetric forms, lying about 38 kcal/mol off the symmetric form for compound I, and about 2 kcal/ mol for

compound II. Thus, we have chosen the asymmetric forms as the object of our study. 1, 2, 3-thiadiazoline (III) and 1, 2, 4-thiadiazoline (IV) can exist in three tautomeric forms, depending on the position of the double bond. For (III), we have found that the most stable tautomer is that with the double bond between the nitrogen atoms, lying 8.5 and 23 kcal/mol off the other forms. A similar situation is found for 1, 2, 4-thiadiazolidine (IV), where the tautomer with the double bond between the  $\alpha$ -nitrogen and the  $\beta$ -carbon is the one with the lower energy, lying 3.3 and 4.6 kcal/mol off the other forms, and thus, is the more stable geometric structure.

Table 1  
Equilibrium geometry parameters of the 1,2,5-thiadiazoline molecule (system I)

Bond length (Å)					Bond angle (°)						
	HF	SVWN	BLYP	B3LYP	SA <sup>a</sup>		HF	SVWN	BLYP	B3LYP	SA <sup>a</sup>
S–N(1)	1.716	1.709	1.769	1.743	1.734	N(1)–S–N(2)	94.6	95.7	95.6	95.3	95.5
S–N(2)	1.717	1.734	1.792	1.757	1.751	S–N(1)–C(1)	109.7	108.6	108.2	108.7	109.1
N(1)=C(1)	1.252	1.281	1.292	1.278	1.282	S–N(2)–C(2)	105.7	103.6	103.6	104.3	104.5
N(2)–C(2)	1.456	1.450	1.487	1.471	1.476	N(1)–C(1)–C(2)	116.9	116.1	117.8	117.4	116.5
C(1)–C(2)	1.521	1.511	1.539	1.528	1.528	N(2)–C(2)–C(1)	105.3	106.5	107.0	106.4	104.8
N(2)–H(1)	1.002	1.031	1.032	1.021	1.019	N(1)–C(1)–H(2)	120.3	119.7	119.3	119.7	120.1
C(1)–H(2)	1.083	1.102	1.101	1.094	1.088	N(2)–C(2)–H(3)	110.7	110.7	110.1	110.4	110.6

<sup>a</sup> SA = statistical average [30].

Table 2  
Equilibrium geometry parameters of the 1,3,4-thiadiazoline molecule (system II)

Bond length (Å)				Bond angle (°)					
	HF	SVWN	BLYP	B3LYP		HF	SVWN	BLYP	B3LYP
S–C(1)	1.772	1.771	1.808	1.789	C(1)–S–C(2)	87.0	86.8	87.0	87.0
S–C(2)	1.819	1.819	1.865	1.843	S–C(1)–N(1)	116.4	115.8	117.0	116.7
C(1)=N(1)	1.249	1.279	1.289	1.275	S–C(2)–N(2)	103.2	102.7	108.3	103.2
C(2)–N(2)	1.457	1.452	1.493	1.474	C(1)–N(1)–N(2)	112.1	111.3	111.4	111.6
N(1)–N(2)	1.385	1.364	1.412	1.394	C(2)–N(2)–N(1)	112.3	113.4	113.1	113.0
N(2)–H(1)	0.998	1.022	1.024	1.015	N(1)–C(1)–H(1)	122.2	122.8	122.5	122.5
C(1)–H(1)	1.087	1.113	1.099	1.101	N(2)–C(2)–H(3)	110.5	113.6	110.4	110.6

Table 3  
Equilibrium geometry parameters of the 1,2,3-thiadiazoline molecule (system III)

Bond length (Å)				Bond angle (°)					
	HF	SVWN	BLYP	B3LYP		HF	SVWN	BLYP	B3LYP
S–N(1)	1.752	1.802	1.916	1.836	N(1)–S–C(1)	92.3	90.9	89.7	91.1
S–C(1)	1.809	1.804	1.844	1.826	S–N(1)–N(2)	115.3	113.4	112.5	113.7
N(1)=N(2)	1.203	1.229	1.230	1.224	S–C(1)–C(2)	103.2	103.6	105.3	104.3
C(1)–C(2)	1.534	1.522	1.555	1.543	N(1)–N(2)–C(2)	116.7	116.5	118.1	117.3
N(2)–C(2)	1.468	1.456	1.497	1.482	C(1)–C(2)–N(2)	109.7	109.3	109.5	109.7
C(1)–H(1)	1.081	1.103	1.100	1.093	S–C(1)–H(1)	110.1	109.9	109.8	109.9
C(2)–H(3)	1.082	1.102	1.100	1.093	C(1)–C(2)–H(3)	112.8	113.2	113.0	112.9

Table 4  
Equilibrium geometry parameters of the 1,2,4-thiadiazoline molecule (system IV)

Bond length (Å)				Bond angle (°)					
	HF	SVWN	BLYP	B3LYP		HF	SVWN	BLYP	B3LYP
S–N(1)	1.719	1.712	1.772	1.746	N(1)–S–C(1)	93.4	94.4	94.0	93.9
S–C(1)	1.829	1.844	1.887	1.862	S–N(1)–C(2)	109.3	108.3	107.9	108.3
N(1)=C(2)	1.255	1.283	1.295	1.280	S–C(1)–N(2)	101.9	101.0	101.5	101.6
C(1)–N(2)	1.453	1.444	1.477	1.463	N(1)–C(2)–N(2)	120.5	120.2	121.6	121.1
C(2)–N(2)	1.375	1.371	1.398	1.386	C(1)–N(2)–C(2)	111.9	113.3	112.8	112.7
C(1)–H(3)	1.081	1.104	1.101	1.093	S–C(1)–H(3)	110.5	110.1	110.0	110.1
N(2)–H(2)	0.995	1.019	1.021	1.011	C(1)–N(2)–H(2)	117.9	118.8	117.0	117.6

The optimized geometrical bond lengths and bond angles for the 1, 2, 5-(I), 1, 3, 4-(II), 1, 2, 3-(III) and 1, 2, 4-(IV) thiadiazoline molecules are summarized in Tables 1-4, related to the structures shown in Figs. 1-4, respectively. The force constants and vibrational frequencies were determined by the FREQ calculation as implemented in the GAUSSIAN94 series of programs on the stationary point obtained after the optimization in order to check if there was a true minimum.

Although experimental gas-phase data for the compounds studied is not available, a comparison with the theoretical results can be done by resorting to the structures of compounds with related moieties that have been characterized by X-ray diffraction studies. For the moiety that is related to the 1, 2, 5-thiadiazoline molecule,

some statistical analysis has been presented and used to confirm geometrical results provided by the theoretical calculations [30]. The results are shown as statistical average (SA) in Table 1. The agreement of bond lengths and bond angles is in general good, the major discrepancy given for the BLYP functional. Although there are not enough DFT calculations in the literature for sulfur-containing compounds to draw a conclusion, the source of the discrepancy can be attributed to the functional itself, because it has been found that the BLYP functional tends to give bond lengths too long and bond angles too short.

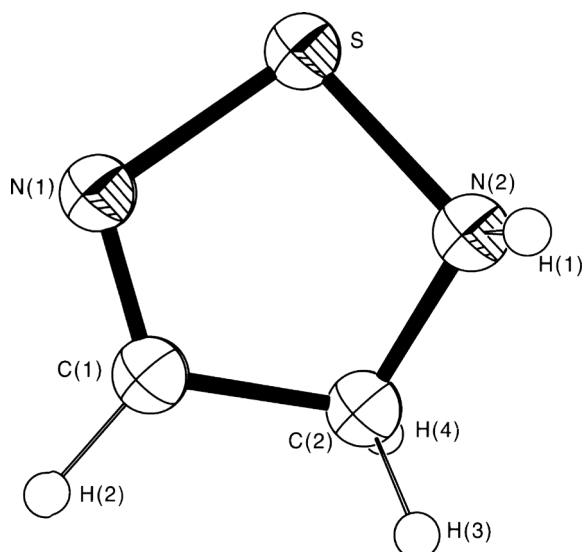


Fig. 1. Molecular structure of 1,2,5-thiadiazoline.

HF and DFT methods predict, in general, N-S-N angles that are in agreement with the statistical averages. The S-N bond lengths (mean 1.734 and 1.751 Å) are well predicted by the B3LYP functional, overestimated by the BLYP model and underestimated by the HF and SVWN models. Meanwhile, the N=C double bond length (mean=1.282 Å) and

the N-C single bond length (1.476 Å) are in perfect agreement with B3LYP predictions. Finally, the C-C bond length is underestimated by BLYP and underestimated by the local SVWN and in perfect agreement for HF and the hybrid B3LYP density functional. The bond angles are predicted to be within 2° of their statistical averages.

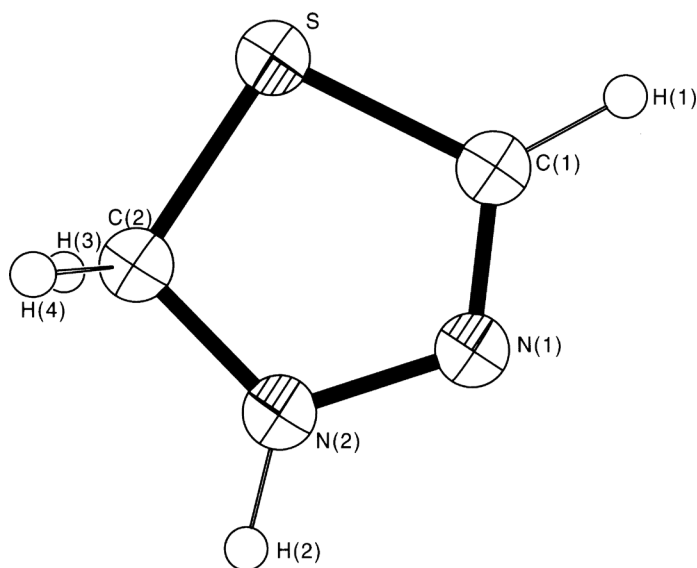


Fig. 2. Molecular structure of 1,3,4-thiadiazoline.

The best match both for bond lengths and bond angles is found for the B3LYP functional. This result is the same that has been arrived at in a previous study and the conclusion is that structural studies of these compounds should be done at the B3LYP level of theory with a 6-31G\*\* basis set. DFT model predictions are in general good, with some particular flaws especially for the local SVWN and the gradient-corrected BLYP functional. The hybrid B3LYP is the DFT model that gives the best agreement with the experimental statistical averages. It is worth noticing that in the case of (I), the B3LYP hybrid functional geometrical parameter prediction is in perfect agreement with the results of more computationally involved correlated MP2 calculations at the same



basis set level [31], which is the usual way to incorporate the electronic correlation effect.

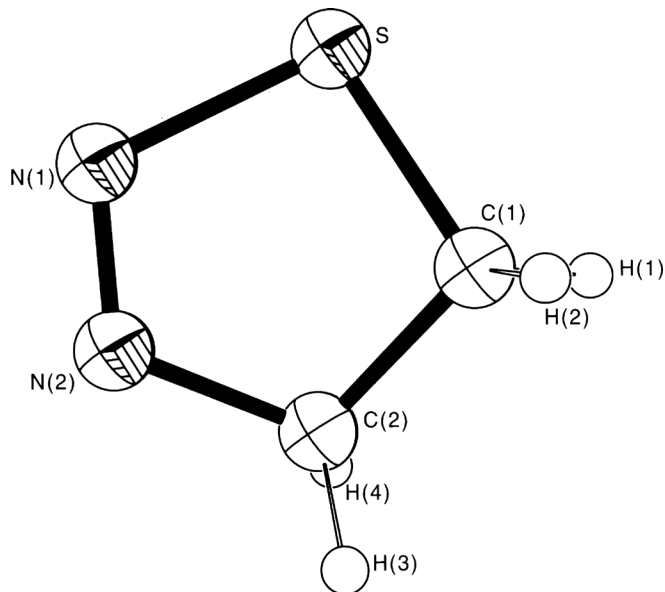


Fig. 3. Molecular structure of 1,2,3-thiadiazoline.

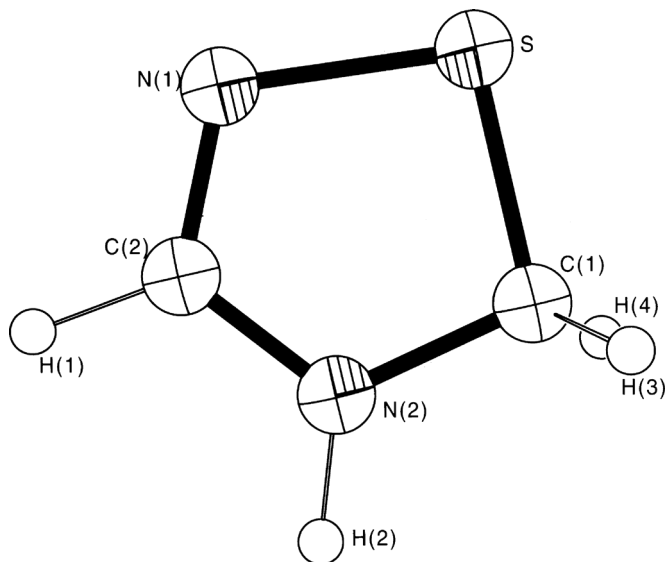


Fig. 4. Molecular structure of 1,2,4-thiadiazoline.

The HOMO-LUMO gap has been considered a measure of aromaticity [15]. The HOMO-LUMO gap is, in turn, related to chemical hardness [16]. The energy gap between valence and conduction bands of a polymer is related to the lowest excitation energy of its monomer units [17]. To design low band gap polymers it is convenient to start with monomer units with small HOMO-LUMO gaps [17], that is, with low hardness  $\eta$  (or great softness  $S$ ). Electronegativities and hardnesses have been calculated using a finite difference approximation, that is,  $\chi=1/2(I+A)$  and  $\eta=(I-A)$  where  $I=E(N+1)-E(N)$  is the ionization potential and  $A=E(N)-E(N-1)$  is the electron affinity of the system,  $E(N)$ ,  $E(N+1)$  and  $E(N-1)$  being the energies of the neutral, anionic and cationic systems, respectively. Total molecular energies, total electronegativities and chemical hardnesses for the molecules under study are presented in Table 5 for the HF and the local and nonlocal density functionals. Inspection of Table 5 reveals that all methods show the same behavior regarding the properties here considered. Thus, only an analysis of the B3LYP results will be done. Total energies indicate that (IV) is the most stable thiadiazoline, with (II) and (III) staying 10 kcal/mol above it (1 hartree 627.5095 kcal/mol). (I) is the less stable isomer, being 12 kcal/mol above (IV). Thus (I) would be more prone to participate in a polymerization reaction providing the attacking molecule is the same in all cases. However, the values of  $\eta$  show the relation (I) > (IV) > (III) > (II) for this property. Moreover,  $\eta(I)=10.44$  eV while  $\eta(IV)=10.40$  eV. All these considerations allow us to conclude that (I) would be the best starting monomer of the four isomers to be considered for a polymerization reaction.

The molecular dipole moment is perhaps the simplest experimental measure of charge density in a molecule. The accuracy of the overall distribution of electrons in a molecule is hard to quantify, since it involves all of the multipole moments. The results of this calculation for the thiadiazoline molecules are shown in Table 5. The different distribution of the nitrogens is revealed in the values of the total dipole moments. However, the small difference in the total values is an indication that the position of the nitrogens in the ring has little effect on the overall dipole moment. As for the case of the geometrical structure, the B3LYP dipole moment prediction for (I) perfectly matches the result from MP2 correlated calculations at the same basis set level [31].

The experimental evidence indicates that the thiadiazolines react with electrophiles at the ring nitrogen atoms or even at the carbon atoms. At the same time, these compounds exhibit greatly enhanced reactivity toward nucleophilic attack at sulfur or even the hydrogen atoms, the site depending on the structure of the substrate and the nature of the nucleophile. The nitrogen atoms of the unsubstituted thiadiazolines are not reactive sites for a nucleophilic attack.

Table 5  
Total energies(in Hartree), electronegativies and hardnesses (in eV), and dipole moments (in Debye) for the isomeric thiadiazolines

	$E$	$\chi$	$\eta$	$\mu$	$E$	$\chi$	$\eta$	$\mu$
	1,2,5-thiadiazoline (I)				1,3,4-thiadiazoline (II)			
HF	-584.4220	2.22	11.11	3.2669	-584.4217	2.15	11.22	1.8722
SVWN	-584.2020	3.86	10.29	2.8729	-584.2076	3.38	10.09	1.9447
BLYP	-586.1822	3.19	10.13	2.8115	-586.1842	2.71	10.09	1.8102
B3LYP	-586.2644	3.33	10.44	2.9168	-586.2667	2.90	10.37	1.8307
	1,2,3-thiadiazoline (III)				1,2,4-thiadiazoline (IV)			
HF	-584.4145	2.65	11.16	3.8426	-584.4422	1.86	10.98	4.3900
SVWN	-584.2036	4.42	10.43	3.6538	-584.2218	3.08	10.21	4.2624
BLYP	-586.1897	3.67	10.21	3.4915	-586.1999	2.51	10.07	4.0649
B3LYP	-586.2667	3.93	10.39	3.5782	-586.2834	2.65	10.40	4.1673

The net charges and condensed Fukui functions determined through Mulliken population analysis as the difference between the gross charges of the atoms in the neutral molecules and ionized species have been used as additional indices to determine the relative softness of each atom in the molecule. The values of the net charges and of the condensed Fukui functions, for the isomeric nine-membered molecules are listed in Tables 6-9. As the results from HF and DFT methods are similar, only the B3LYP values are presented in the tables.

Table 6  
Net charges and condensed Fukui functions for the 1,2,5-thiadiazoline (I) molecule obtained through a B3LYP-DFT calculation

Atom	Net charges	$f^+$	$f^-$	$f^0$
S	0.3653	0.337	0.464	0.401
N(1)	-0.4323	0.131	0.054	0.093
N(2)	-0.5778	0.021	0.065	0.043
C(1)	0.0840	0.142	0.082	0.112
C(2)	-0.1090	-0.060	-0.057	-0.059
H(1)	0.2713	0.071	0.082	0.077
H(2)	0.1231	0.153	0.113	0.133
H(3,4)	0.1277	0.103	0.098	0.101

Table 7  
Net charges and condensed Fukui functions for the 1,3,4-thiadiazoline (II) molecule obtained through a B3LYP-DFT calculation

Atom	Net charges	$f^+$	$f^-$	$f^0$
S	0.1292	0.415	0.381	0.398
C(1)	-0.0718	0.056	0.034	0.045
C(2)	-0.2067	-0.047	-0.076	-0.062
N(1)	-0.2086	0.142	0.111	0.127
N(2)	-0.3506	0.020	0.125	0.073
H(2)	0.2730	0.078	0.089	0.084
H(1)	0.1457	0.126	0.108	0.117
H(3,4)	0.1563	0.126	0.105	0.116

The condensed Fukui functions and condensed local softness indices allow us to distinguish each part of the molecule on the basis of its distinct chemical behavior due to the different substituent functional groups. The site for the electrophilic attack will be the place where the value of  $f^-$  is a maximum. Inspection of the net charges in Tables 6-9 reveals that for the case of (I), the possible sites for electrophilic attack will be the nitrogen atoms or even the  $sp^3$  carbon atom (C(2)). According to the values of  $f^-$  the most reactive site will be that carbon atom. In the case of (II), both carbons and both nitrogens are possible sites of electrophilic attack. Nevertheless, the value of the Fukui

function is a maximum at the  $sp^3$  nitrogen (N(2)), and this will be the preferred reactive site. Using the same criteria one is able to differentiate the behavior of the other thiadiazolines on electrophilic attack. For (III) the situation is similar to the case of (II), but with  $f^-$  values which are almost identical and maximum at both carbon atoms. In the case of the (IV) derivative, the reactivity pattern is even clearer, with the nitrogen in position (N(1)) being the most favorable site for an electrophilic substitution.

Table 8  
Net charges and condensed Fukui functions for the 1,2,3-thiadiazoline (III) molecule obtained through a B3LYP-DFT calculation

Atom	Net charges	$f^+$	$f^-$	$f^0$
S	0.2066	0.276	0.515	0.396
N(1)	-0.2112	0.223	0.069	0.146
N(2)	-0.1349	0.223	0.140	0.182
C(1)	-0.3883	-0.055	0.440	0.193
C(2)	-0.0827	-0.071	0.447	0.188
H(1,2)	0.1544	0.078	0.110	0.094
H(3,4)	0.1468	0.117	0.095	0.106

In turn, the site for nucleophilic attack is controlled by the value of  $f^+$ . From Tables 6-9, the net charges for S and H atoms are positive, thus being possible sites for nucleophilic substitution of the thiadiazolines. However, the value of the Fukui function  $f^+$  is greater for the S than for H in all cases. Thus, the sulfur atoms will be the sites for nucleophilic attack in agreement with the experimental evidence for these unsubstituted molecules.

The condensed local softness indices  $s_k^+$  and  $s_k^-$  are related to the condensed Fukui functions through the value of the total softness S. They are easily calculated by means of the values of 0.0958 (I), 0.0964 (II), 0.0962 (III) and 0.0962 eV (IV) for the

global softness  $S$  of the molecules within the B3LYP approximation together with the condensed Fukui function values shown in Tables 6-9. While the condensed Fukui functions allow us to distinguish between possible reactive sites inside a molecule, the condensed local softness indices allow us to do the same comparison between similar sites of different but analog molecules. As was previously shown the hydrogen atoms are active sites for nucleophilic substitutions. For the molecules here considered, the values of the condensed local softness functions  $s^+$  above the reactive sulfur atoms are 0.0350 eV for (I), 0.0125 eV for (II), 0.0199 eV for (III) and 0.0235 eV for (IV). Thus, the sulfur atom of (I) will be more reactive than the sulfur atoms of the other isomers in a nucleophilic substitution reaction.

Table 9  
Net charges and condensed Fukui functions for the 1,2,4-thiadiazoline (IV) molecule obtained through a B3LYP-DFT calculation

Atom	Net charges	$f^+$	$f^-$	$f^0$
S	0.2439	0.586	0.412	0.499
N(1)	-0.4919	-0.011	0.097	0.043
N(2)	-0.4937	0.010	0.082	0.046
C(1)	-0.2095	-0.053	-0.072	-0.063
C(2)	0.2768	0.055	0.061	0.058
H(3,4)	0.1484	0.090	0.107	0.099
H(1)	0.1338	0.142	0.104	0.123
H(2)	0.2650	0.092	0.082	0.087

## Conclusions

In this work, we have shown calculations of thiadiazolines performed using HF and density functional methods at the 6-31G\*\* basis set level. We have considered several kinds of exchange-correlation functionals, i.e. local SVWN, gradient-corrected BLYP

and hybrid B3LYP functionals. Molecular structures are best predicted with DFT functionals, where geometries are well given by the B3LYP model and with some flaws by the SVWN and BLYP methods. Electronic properties calculated using DFT methods proved to be accurate with the hybrid B3LYP giving results in agreement with those of correlated MP2 calculations at the same basis set level. In conclusion, the best way to study these compounds seems to be accomplishing the geometry optimization of the molecular structures with the 6-31G\*\* basis set at the B3LYP level of theory, and performing single point calculations with the B3LYP model to obtain a good description of electronic properties. Thiadiazolines have been studied as model compounds useful as building blocks of polymeric materials. The dipole moment as a measure of the distribution of charge density has been evaluated. These results allowed us to characterize the different reactive sites within the molecules. Total energies as a measure of stability, and an evaluation of electronegativities and chemical hardnesses and as a measure of the HOMO-LUMO gap useful for the design of low band gap polymers was accomplished. Finally, an order of reactivity of these compounds was obtained, showing (III) to be the most reactive isomer. Moreover, the analysis of DFT reactivity indices, like condensed Fukui functions and condensed local softness allowed us to characterize the sulfur atoms as the active sites for nucleophilic substitutions and those of the 1, 2, 5-derivative as the most prone to be involved this class of reactions.

Atomic charge by itself cannot explain adequately the behavior and chemical reactivity of the molecules. The analysis of the electronic densities and the molecular electrostatic potentials sometimes gives contradicting results. On the contrary, the

relative densities of the frontier orbitals and their relationships and the condensed Fukui functions have proved to be valuable tools to rationalize those concepts and to confirm the known experimental results. These last indices have shown to be the most useful and consequently the most laudable criteria for predicting chemical reactivity.

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