

Crystallographic study and molecular orbital calculations of thiadiazole derivatives. 1. Phenanthro[9,10-c]-1,2,5-thiadiazole 1, 1-dioxide and acenaphtho[1,2-c]-1,2,5-thiadiazole 1,1-dioxide

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Abstract

Single-crystal X-ray diffraction studies are reported for phenanthro[9,10-c]-1,2,5-thiadiazole 1,1-dioxide (I) and acenaphtho[1,2-c]-1,2,5-thiadiazole 1,1-dioxide (II). Ab initio molecular orbital (MO) calculations on the electronic structure, conformation and reactivity of I and II are also reported and compared with the X-ray results. A charge sensitivity analysis of the studied molecules has been performed by resorting to density functional theory (DFT), obtaining several sensitivity coefficients such as the molecular energy, net atomic charges, global and local hardness, global and local softness and Fukui functions. With these results and the analysis of the dipole moments and the total electron density maps, several conclusions have been inferred about the preferred sites of chemical reaction of the studied compounds.

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 [5-7], the electronegativity as a measure of the tendency of a species to attract electrons [8], global and local hardness and softness [9-11] and Fukui functions [11] 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.

In relation with our previous studies on kinetics [12,13], UV-VIS and IR spectroscopies [14], electrochemistry [15-18] and theoretical calculations [19-22] of several 3,4 substituted 1,1-dioxide derivatives of 1,2,5-thiadiazole, we report here a single crystal X-ray diffraction study on the molecular structure of the following derivatives: phenanthro[9,10-c]-1,2,5-thiadiazole 1,1-dioxide (I) and acenaphtho[1,2-c]-1,2,5-thiadiazole 1,1-dioxide (II).

2. We also report ab initio HF/6-31G** Hartree-Fock-LCAO molecular orbital (MO) calculations on the electronic structure, conformation and reactivity of compounds (I) and (II), as well as results of a charge sensitivity analysis performed by resorting to several concepts derived from density functional theory (DFT). MO theoretical calculations and computational methods

The DFT [11] provides a convenient theoretical framework to calculate global and local indexes that quantitatively describe the inherent reactivity of chemical species. In particular, the Fukui and local softness functions [9,10,23] can be employed to determine the nature of the reactive sites in a given molecule and, from this information, to infer about some aspects of the behavior of the molecule when reacting with other species.

It has been shown [11] that the electronegativity χ , i.e. the power of an atom in a molecule to attract electrons, is related to the molecular energy E and the number of electrons N by $\chi = -(\partial E/\partial N)_v$.

The chemical hardness η was introduced as [11] $\eta = (\partial^2 E/\partial N^2)_v$ (the factor of 1/2 in the original definition has been omitted for convenience [24]). The hardness measures a chemical species's resistance to charge transfer, whereas the electronegativity expresses its initial attraction towards electronic charge. Both quantities have been shown to be very important in the elucidation and interpretation of chemical reactivity [25].

Using a finite difference approximation and a quadratic relationship between the energy E and the number of electrons N , both definitions are transformed into the working equations $\chi = (I + A)/2$ and $\eta = (I - A)$, with I and A the ionization energy and electron affinity, respectively.

The condensed Fukui functions, which are determined by a Mulliken population analysis [5-7,26], can also be employed to determine the relative softness of each atom in the molecule. The corresponding condensed

functions are given by [27] $f^+ = q(N+1) - q_k(N)$ (for nucleophilic attack),

$f_k^- = q_k(N) - q_k(N-1)$ (for electrophilic attack), and $f_k = [q_k(N+1) - q_k(N-1)]/2$

(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 $f(r)$, and the local

$$\text{softness } s(r), \text{ i.e. } s(r) = \frac{\partial p(r)/\partial N}{f(r)} = \frac{\partial N/\partial \mu}{f(r)}$$

To distinguish the behavior of the different atoms in a molecule by employing the condensed Fukui functions, it is necessary to obtain the electronic densities of the molecule as a neutral entity as well as the corresponding anionic and cationic moieties. These densities may be calculated within the ab initio Hartree-Fock-LCAO approximation employing the 6-31G** basis set, while the net atomic charges of the anion, cation and neutral molecule are obtained through a Mulliken population analysis. In conjunction with the nuclear charges at the equilibrium configuration, the electronic distribution determines the molecular electrostatic potential [28]. This potential, in turn, provides a guide to find the reaction sites on the molecule: positively (negatively) charged reagents, i.e. electrophiles (nucleophiles), tend to attack at places where the electrostatic potential is strongly negative (positive).

Experimental

Single crystals of compounds (I) and (II) were grown from ethanolic solutions and mounted on glass fibers on an Enraf-Nonius CAD-4 X-ray diffractometer. In both cases, 25 centered reflections using least squares refinement gave the unit cell dimensions

Table 1
Crystal data, data collection details and structure refinement results for the phenanthro[9,10-*c*] (I) and acenaphtho[1,2-*c*] (II) derivatives of 1,2,5-thiadiazole 1,1-dioxide

Parameter	C ₁₄ H ₈ N ₂ O ₂ S (I)	C ₁₂ H ₆ N ₂ O ₂ S (II)
Molecular weight	268.3	242.3
Space group	<i>P2₁/n</i>	<i>P2₁/a</i>
Temperature (°C)	22	22
<i>a</i> (Å)	7.043(1)	8.384(2)
<i>b</i> (Å)	17.209(3)	14.825(4)
<i>c</i> (Å)	9.914(2)	8.433(2)
β (°)	108.86(2)	103.88(1)
Cell volume (Å ³)	1137.1(7)	1017.6(8)
Formula units/units cell	4	4
D_{calc} (g cm ⁻³)	1.567	1.862
μ_{calc} (cm ⁻¹)	2.69	3.44
2θ range (°)	$2 \leq 2\theta \leq 30$	$2 \leq 2\theta \leq 60$
Reflections observed	2358	1404
$[F_0 \geq 6\sigma(F_0)]$		
Minimized function	$\sum w(F_0 - F_c)^2$	$\sum w(F_0 - F_c)^2$
$R = \sum[F_0 - F_c] / \sum F_0 $	0.0454	0.0445

and the orientation matrix for data collection. Intensities were measured by the $\omega - 2\theta$ scan technique at a rate between 2.85–20.0° min⁻¹

determined by a fast prescan of $20.0^\circ \text{ min}^{-1}$. Reflections were collected in the range $0 < \theta < 30$ using graphite monochromated MoK α radiation. Crystal data, data collection details and structure refinement results for compounds (I) and (II) are summarized in Table 1.

The intensity of one standard reflection selected for each compound was essentially constant over the duration of the experiments. Data were corrected by Lorentz and polarization effects but not for absorption or extinction. Scattering factors taken from Cromer and Waber [29] and the corresponding anomalous dispersion coefficients from Cromer and Ibers [30] were used in the calculations. These were performed with the SHELX [31] and SDP [32] systems of programs. The stereoscopic projections shown were drawn with the program ÜRTEP [33,55].

The structures were solved by standard centrosymmetric Direct Methods and Fourier techniques and refined by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms. Most hydrogen atoms were located from difference Fourier maps. However, they were positioned on stereochemical grounds and incorporated to the final molecular model. The positions of the hydrogen atoms in each of the two compounds were refined with a common isotropic temperature parameter. In both cases, hydrogen positions were refined by fixing bond distances to the corresponding atoms at their accepted values.

All the MO calculations were performed with the GAUSSIAN 98 series of programs [34]. Single determinantal wavefunctions of the restricted Hartree-Fock type were used for the closed-shell system, and those of the unrestricted

Hartree-Fock (UHF) type were considered for the open-shell systems, with orbitals being the solutions of the Roothaan equations [35]. The equilibrium conformations of the neutral molecules were calculated by the gradient method.

Relevant bond distances and angles for compounds (I) and (II) are in Tables 2 and 3 and ÜRTEP drawings of these molecules showing the labeling of the atoms and their vibrational ellipsoids are in Figs. 1 and 2.

The structural details in Tables 2 and 3 allow comparisons among these compounds and with reported studies of related compounds, such as thiadiazines [36-40], thiadiazole 1,1-dioxides [22], a thiadiazoline 1,1 dioxide [41] and a thiadiazole 1- monoxide [42] and suggest relations with their experimental chemical behavior.

From Tables 2 and 3 we can conclude for both compounds:

- S=O double bond length values vary from 1.413(3) to 1.426(2) Å, i.e. in about 2σ (where $\sigma = 0.003$ Å is the standard error) around their mean value [=1.419(5) Å].
- S–N single bond lengths vary from 1.681(2) to 1.704(3) Å, i.e. in about 4σ ($\sigma = 0.003$ Å) around the mean value [=1.691(1) Å].
- C=N double bond lengths vary from 1.270(4) to 1.287(3) Å, i.e. in about 2σ ($\sigma = 0.004$ Å) around the mean value [=1.279(7) Å].
- C(1)–C(2) single bond lengths of compounds I and II are practically equal to within experimental error [average = 1.511(5) Å].
- C(1)–C(3) and C(2)–C(9) single bond lengths vary from 1.437(3) to

1.464(4) Å, i.e. within 3.5σ ($\sigma = 0.004$ Å) around the mean value [=1.45(1) Å].

- C–C resonant bond lengths in the 6-membered rings vary from 1.360(5) to 1.421(4) Å, i.e. within 6σ ($\sigma = 0.009$ Å) around the mean value [=1.39(2) Å].

Table 2.

Interatomic bond distances (Å) and bond angles (°) for phenanthro[9<comma>1(

	Bond distance		Bond angle		
	Exp.a	HFb	Exp.a	HFb	
S–O(1)	1.426(2)		1.418 O(1)–S–O(2)	119.1(1)	120.8
S–O(2)	1.419(2)		1.418 O(1)–S–N(1)	109.7(1)	109.1
S–N(1)	1.681(2)		1.684 O(1)–S–N(2)	108.6(1)	109.1
S–N(2)	1.686(2)		1.684 O(2)–S–N(1)	109.3(1)	109.1
N(1)–C(1)	1.283(3)		1.259 O(2)–S–N(2)	109.0(1)	109.1
N(2)–C(2)	1.287(3)		1.259 N(1)–S–N(2)	99.3(1)	97
C(1)–C(2)	1.508(3)		1.51 S–N(1)–C(1)	106.0(1)	107.8
C(1)–C(3)	1.451(3)		1.459 S–N(2)–C(2)	106.1(2)	107.8
C(2)–C(9)	1.437(3)		1.459 N(1)–C(1)–C(2)	114.6(2)	113.7
C(3)–C(4)	1.394(3)		1.391 N(1)–C(1)–C(3)	125.3(2)	126.6
C(3)–C(8)	1.407(3)		1.402 C(2)–C(1)–C(3)	120.0(2)	119.7
C(4)–C(5)	1.377(3)		1.374 N(2)–C(2)–C(3)	114.0(2)	113.7
C(5)–C(6)	1.382(4)		1.387 N(2)–C(2)–C(4)	126.0(2)	126.6
C(6)–C(7)	1.378(3)		1.382 C(1)–C(2)–C(4)	120.0(2)	119.7
C(7)–C(8)	1.398(3)		1.394 C(1)–C(3)–C(4)	120.0(2)	119.5
C(8)–C(10)	1.485(3)		1.499 C(1)–C(3)–C(8)	118.6(2)	119
C(9)–C(10)	1.418(3)		1.421 C(4)–C(3)–C(8)	121.3(2)	121.5
C(9)–C(14)	1.397(3)		1.391 C(3)–C(4)–C(5)	120.0(2)	120.2
C(10)–C(11)	1.393(3)		1.394 C(8)–C(10)–C(9)	121.2(2)	121.3
C(11)–C(12)	1.387(4)		1.382 C(9)–C(10)–C(11)	117.0(2)	117.1
C(12)–C(13)	1.381(4)		1.387 C(8)–C(10)–C(12)	121.8(2)	121.6
C(13)–C(14)	1.380(3)		1.377 C(3)–C(8)–C(7)	117.1(2)	117.1
C–H	–		1.074 C(7)–C(8)–C(11)	121.5(2)	121.6
			C(2)–C(9)–C(11)	118.8(2)	119
			C(2)–C(9)–C(12)	120.3(2)	119.5
			C(10)–C(9)–C(12)	120.8(2)	121.5

Although not shown in the tables, an analysis of the torsional angles reveals that

the heterocycle rings of compounds (I) and (II) are planar to within experimental accuracy. As already found in the related six-membered heterocyclic compounds 1,2,6-thiadiazine 1,1-dioxides [36-40] and 1,2,5-thiadiazole 1,1-dioxides [22], the geometry around the S atom corresponds to a distorted tetrahedron, with the O-S-O angle larger than the other bond angles around S. Compound I. Both phenyl rings of the Phenanthromoiety are practically planar with maximum deviation from the corresponding mean planes of about three times the standard error. These planes are coplanar with each other and with the heterocycle ring within a few standard deviations of dihedral angles.

Compound II. The complete molecular skeleton is practically planar with deviations from mean plane of less than seven standard errors.

Table 3.

Interatomic bond distances (Å) and bond angles (°) for acenaphtho[1,2-*b*]quinoline

	Bond distance		Bond angle		HFb
	Exp.a	HFb	Exp.a	HFb	
S–O(1)	1.413(3)		1.417 O(1)–S–O(2)	118.9(1)	120.9
S–O(2)	1.420(2)		1.417 O(1)–S–N(1)	108.7(1)	108.9
S–N(1)	1.697(2)		1.705 O(1)–S–N(2)	109.8(1)	108.9
S–N(2)	1.704(3)		1.705 O(2)–S–N(1)	108.8(1)	108.9
N(1)–C(1)	1.270(4)		1.252 O(2)–S–N(2)	109.0(1)	108.9
N(2)–C(2)	1.278(3)		1.252 N(1)–S–N(2)	100.0(1)	97.9
C(1)–C(2)	1.515(4)		1.519 S–N(1)–C(1)	104.6(2)	106.2
C(1)–C(3)	1.464(4)		1.465 S–N(2)–C(2)	104.7(2)	106.2
C(2)–C(9)	1.455(4)		1.465 N(1)–C(1)–C(2)	115.9(2)	114.9
C(3)–C(4)	1.362(4)		1.36 N(1)–C(1)–C(3)	136.9(2)	137.8
C(3)–C(8)	1.413(4)		1.419 C(2)–C(1)–C(3)	107.2(2)	107.4
C(4)–C(5)	1.406(4)		1.419 N(2)–C(2)–C(1)	114.8(2)	114.9
C(5)–C(6)	1.360(5)		1.367 N(2)–C(2)–C(3)	137.4(3)	137.8
C(6)–C(7)	1.421(4)		1.421 C(1)–C(2)–C(3)	107.8(2)	107.3
C(7)–C(8)	1.397(4)		1.389 C(1)–C(3)–C(4)	134.9(2)	134.7
C(7)–C(12)	1.412(4)		1.421 C(1)–C(3)–C(8)	104.9(2)	105.3
C(8)–C(9)	1.417(4)		1.419 C(4)–C(3)–C(8)	120.2(2)	120
C(9)–C(10)	1.374(4)		1.36 C(3)–C(4)–C(5)	118.2(3)	118.2
C(10)–C(11)	1.399(4)		1.419 C(8)–C(9)–C(10)	119.4(2)	120
C(11)–C(12)	1.368(5)		1.367 C(2)–C(9)–C(10)	135.8(2)	134.7
C–H	–	1.075	C(6)–C(7)–C(8)	115.8(3)	116.4
			C(2)–C(9)–C(8)	104.8(2)	105.3
			C(8)–C(7)–C(11)	116.7(3)	116.4
			C(3)–C(8)–C(7)	122.4(2)	122.6
			C(3)–C(8)–C(9)	115.4(2)	114.7
			C(7)–C(8)–C(9)	122.2(3)	122.6

Theoretical calculations

The results for the equilibrium conformation of the neutral molecules (I) and (II) (HF/LCAO with 6-31G** basis set) are included in Tables 2 and 3 along with the experimental X-ray results. The agreement is in general good for these ab initio calculations (the standard error of the differences between the experimental and the calculated bond lengths is ca. 4×10^{-3} for all methods. The

corresponding value for the bond angles is 0.3° .

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 result of this calculation for compounds (I) and (II) are shown in Table 4. The small difference in the total values is an indication that the atomic distribution in the phenanthro and acenaphtho moieties has little effect on the overall dipole moment. The HOMO–LUMO gap has been considered a measure of aromaticity [43]. The HOMO–LUMO gap is, in turn, related to chemical hardness [44]. The energy gap between valence and conduction band of a polymer is related to the lowest excitation energy of its monomer units [45]. To design low band gap polymers it is convenient to start with monomer units with small HOMO–LUMO gaps [45], that is, with low hardness η (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 4.

The condensed Fukui functions can be applied, as it has been shown in previous work, [19]; [20]; [21] ; [22] to the study of the behavior of substances under nucleophilic or electrophilic attack. Fig. 3 ; Fig. 4 display a planar

representation of the calculated electron densities of (I) and (II). These figures show that the electrophilic attack would occur preferentially at the nitrogens and nucleophilic attack at the heterocyclic ring carbons.

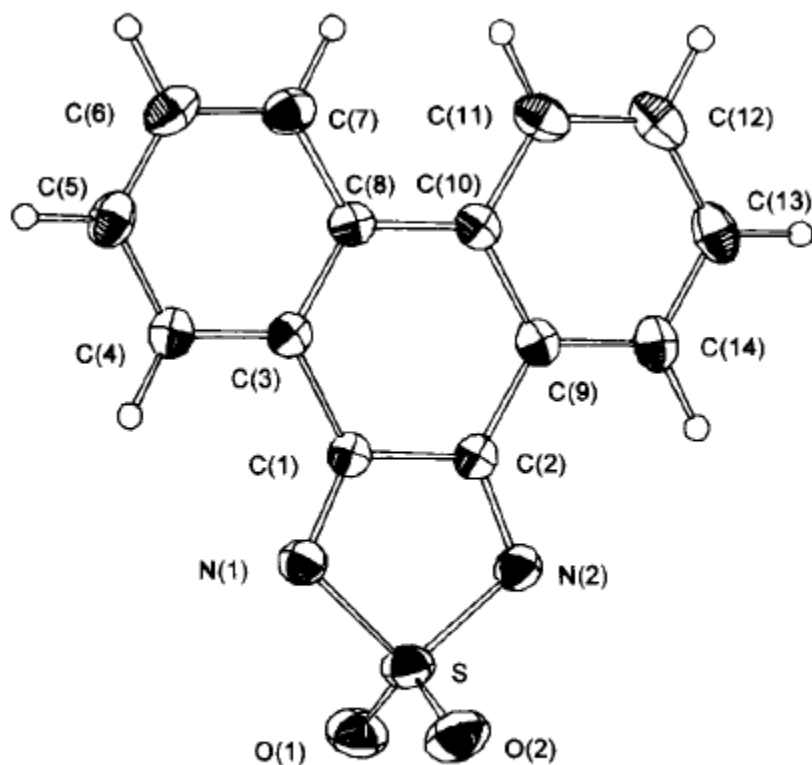


Fig. 1. Molecular structure of phenanthro[9,10-c]-1,2,5-thiadiazole 1,1-dioxide (I).

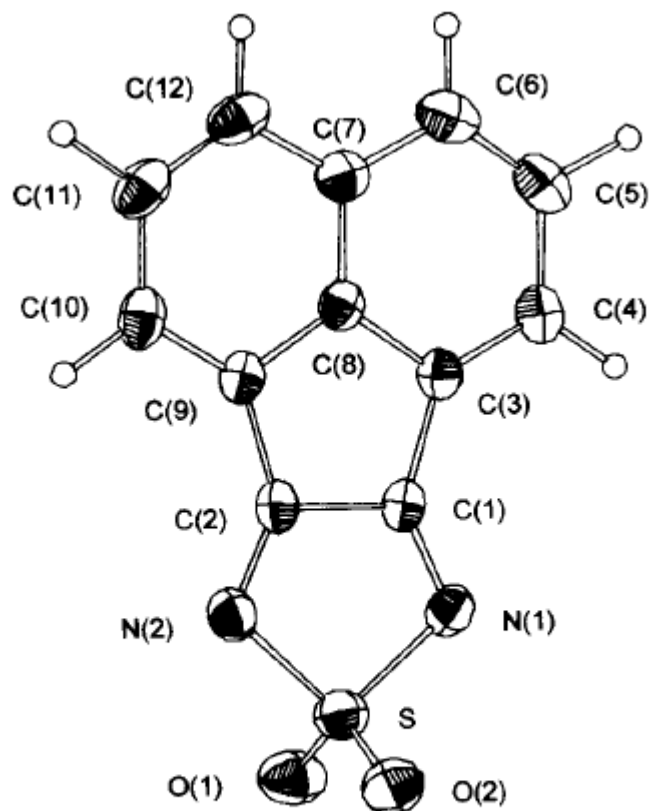


Fig. 2. Molecular structure of acenaphtho[1,2-c]-1,2,5-thiadiazole 1,1-dioxide (II).

Table 4.

Compound	Total energies E (a.u.)	dipole moments μ (debye)	χ	η
I	-1190.892777	10.5507	4.26	6.7
II	-1113.966887	11.0207	4.002	7.802

These reactive sites can also be identified by an analysis based on frontier orbitals [11,46]. Tables 5 and 6 show the net atomic charges of the neutral molecules for (I) and (II), respectively, by a Mulliken population analysis, together with the $f+$, $f-$ and $f0$ Fukui functions. The site for electrophilic attack will be those atoms bearing a negative charge and where

Table 5.

Net atomic charges and Fukui functions of phenanthro[9<comma>

Atom	q	f+	f-	f0	
O(1)	-0.610		0.056	0.039	0.048
O(2)	-0.610		0.056	0.039	0.048
S		1.619	0.037	0.015	0.026
N(1)	-0.646		0.102	0.064	0.083
N(2)	-0.646		0.102	0.064	0.083
C(1)		0.294	0.078	-0.017	0.031
C(2)		0.294	0.078	-0.017	0.031
C(3)	-0.057	-0.026		0.052	0.013
C(4)	-0.083		0.035	0.005	0.02
C(5)	-0.163	-0.003		0.053	0.025
C(6)	-0.131		0.04	-0.003	0.019
C(7)	-0.155	-0.008		0.041	0.017
C(8)		0.01	0.029	0.04	0.034
C(9)	-0.057	-0.026		0.051	0.013
C(10)		0.01	0.029	0.04	0.034
C(11)	-0.155	-0.008		0.041	0.017
C(12)	-0.131		0.04	-0.003	0.019
C(13)	-0.163	-0.003		0.055	0.025
C(14)	-0.083		0.035	0.04	0.02
H(4)		0.216	0.032	0.045	0.038
H(5)		0.175	0.05	0.064	0.057
H(6)		0.173	0.057	0.057	0.057
H(7)		0.168	0.038	0.052	0.045
H(11)		0.168	0.038	0.052	0.045
H(12)		0.173	0.057	0.057	0.057
H(13)		0.175	0.051	0.064	0.057
H(14)		0.216	0.032	0.045	0.038

Table 5

Net atomic charges and Fukui functions of phenanthro[9,10-c] 1,2,5-thiadiazole 1,1-dioxide (I)

Table 6.

Net atomic charges and Fukui functions of acetonafto[1,2-c]

Atom	q	f+	f-	f0	
O(1)	-0.609		0.043	0.041	0.042
O(2)	-0.609		0.043	0.041	0.042
S		1.613	0.024	0.014	0.019
N(1)	-0.639		0.075	0.073	0.074
N(2)	-0.639		0.075	0.073	0.074
C(1)		0.29	-0.003	-0.011	-0.007
C(2)		0.29	-0.003	-0.011	-0.007
C(3)		0.055	0.104	0.068	0.086
C(4)	-0.105		0.046	0.039	0.042
C(5)	-0.168		0.004	0.025	0.014
C(6)	-0.107		0.051	0.09	0.07
C(7)		0.002	-0.023	-0.050	-0.037
C(8)	-0.168		-0.062	-0.022	-0.042
C(9)		0.055	0.104	0.068	0.086
C(10)	-0.105		0.046	0.039	0.042
C(11)	-0.168		0.004	0.025	0.014
C(12)	-0.107		0.051	0.09	0.07
H(4)		0.207	0.071	0.061	0.066
H(5)		0.175	0.072	0.071	0.071
H(6)		0.178	0.068	0.072	0.07
H(10)		0.207	0.071	0.061	0.066
H(11)		0.175	0.072	0.071	0.071
H(12)		0.178	0.068	0.072	0.07

Table 6

Net atomic charges and Fukui functions of acetonafto[1,2-c]- 1,2,5-thiadiazole 1,1-dioxide(II)

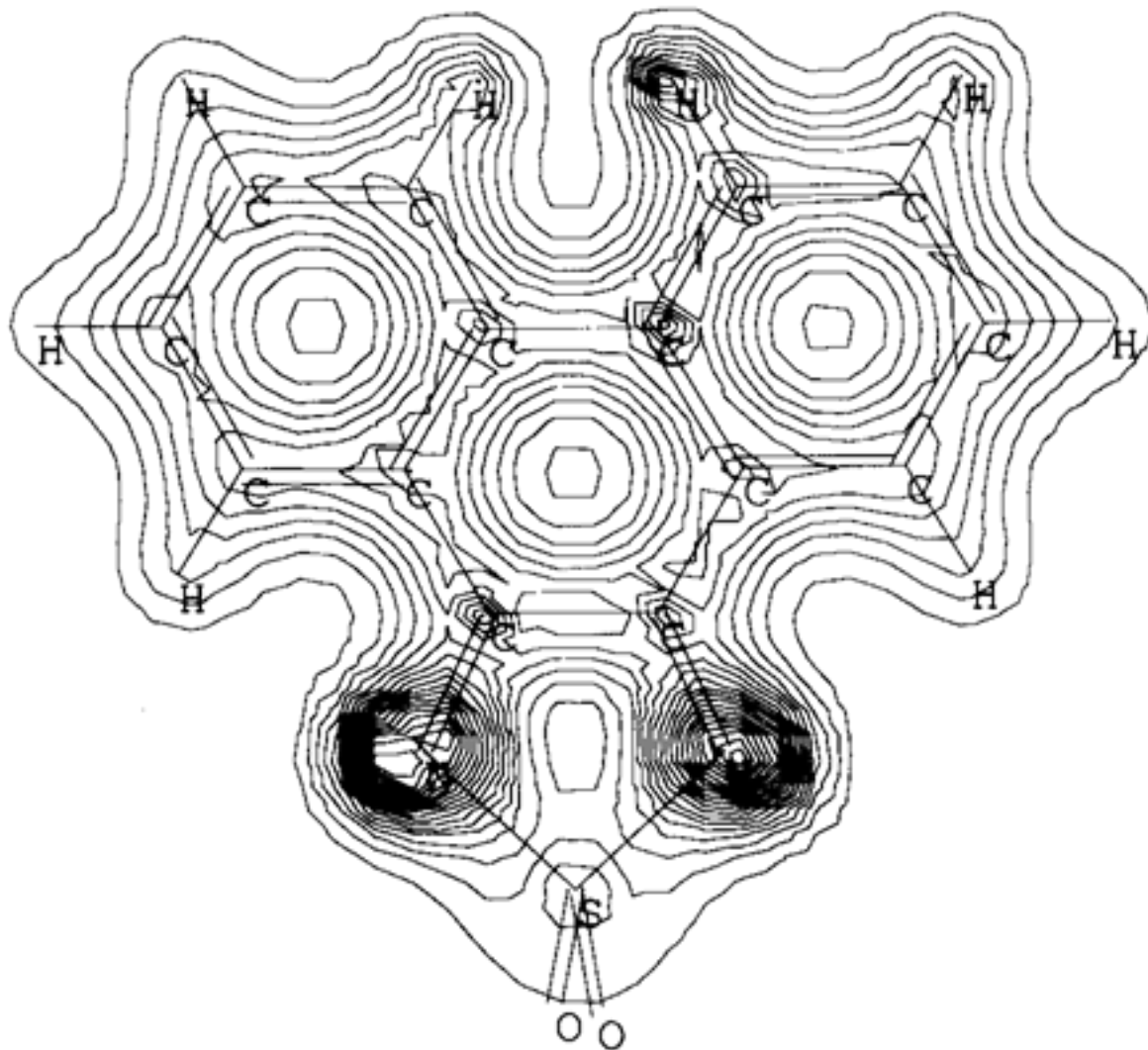


Fig. 3. HF/6-31G** electron density of phenanthro[9,10-c]-1,2,5- thiadiazole 1,1-dioxide (I) on the molecular plane.

the Fukui function f^- is a maximum. These values confirm that for both compounds, the sites for the electrophilic attack are the nitrogen atoms. The site for potential nucleophilic attack would depend on the values of f^+ on the atoms with a positive charge density. Although the net positive charge on the sulfur atom is larger than that on the heterocyclic carbons, the values of f^+ on these atoms are much larger than the corresponding value on the sulfur atom.

However, while in compound (I), carbons C(1) and C(2) will be the site for nucleophilic attack, a different situation will happen in compound (II), where carbons C(1) and C(2) will not be reactive sites, and the nucleophilic attack will take place at carbons C(3) and C(9). As for radical reactions, the nitrogen atoms in compound (I) will be the most prone to be attacked. An inverse situation is found for compound (II) where the carbon atoms C(3) and C(9) are the most reactive sites.

The condensed local softness indices s^+ and s^- are

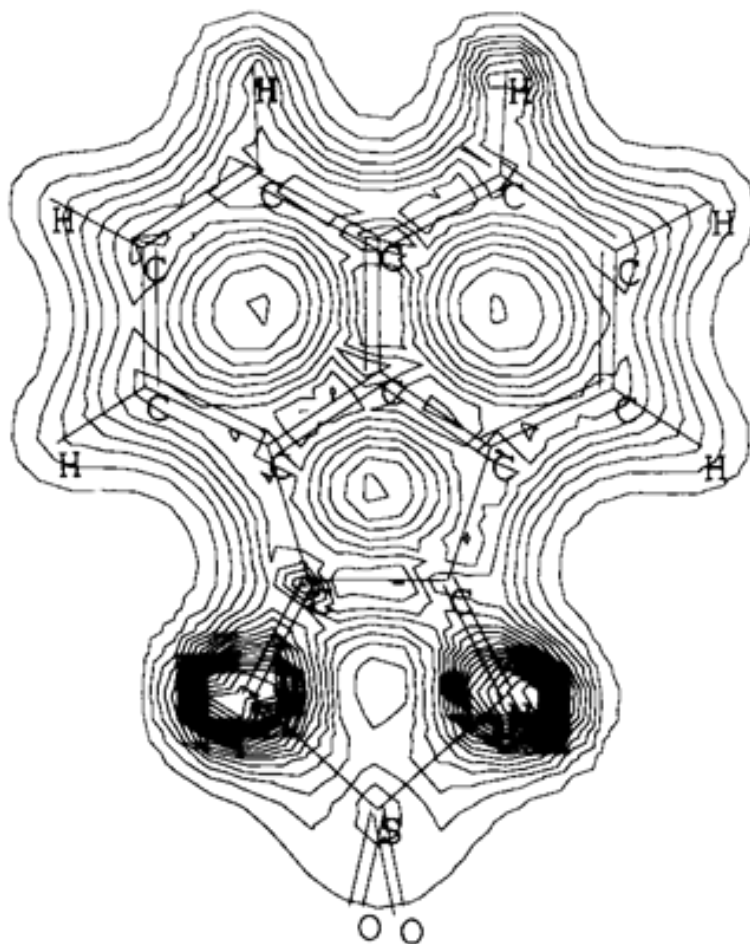


Fig. 4.

HF/6-31G** electron density of acenaphtho[1,2-c]-1,2,5-thiadiazole 1,1-dioxide (II) on the molecular plane related to the condensed Fukui functions through the global softness S . They are easily calculated by mean of the values of 0.1493 eV (phenanthro[9,10-c]-1,2,5-thiadiazole 1,1-dioxide (I)) and 0.1282 eV (acenaphtho[1,2-c]-1,2,5-thiadiazole 1,1-dioxide (II)) for the global softnesses S of the molecules. As it has been remarked, [47-49], it is obvious that both $s(\vec{r})$ and $f(\vec{r})$ may be used in the study of intramolecular reactivity sequences for finding reactive sites in a molecule, but only $s(\vec{r})$, which contains in its definition the information of global softness S , can be used for the comparison of the reactivity of different molecules with respect to a common reaction partner. This is a consequence of the local Hard and Soft Acids and Bases (HSAB) principle, which was originally proposed by Parr and Yang[11] and analytically proved by Gázquez and Méndez [50]. This idea has been extensively exploited in the past for the study of the nucleophilic addition to α,β -unsaturated compounds [51], in the interpretation of the effect of alkyl substitution on the basicity of amines [52] ; [53], as a measure of the acidity of substituted acetic acids [54], as reactivity indices for predicting reactivity sequences of carbonyl compounds toward nucleophilic attack [48] and for studying the site of protonation of substituted anilines [49]. As was previously shown, the carbon atoms of the molecules considered in the present work are the active sites for nucleophilic reactions. The values of the condensed softness function sk above the reactive nitrogen atoms are 0.01522 eV for (I) and 0.00961 eV for (II). Thus, the nitrogen atoms of (I) will be more reactive than the

nitrogen atoms of (II) in a electrophilic reaction.

.Conclusions

In this work, single-crystal X-ray diffraction studies have been reported for phenanthro[9,10-c]-1,2,5-thiadiazole 1,1-dioxide (I) and acenaphtho[1,2-c]-1,2,5-thiadiazole 1,1-dioxide (II) molecules. We have also shown calculations on both molecules performed using Hartree–Fock method at the 6-31G** basis set level. Molecular structures are well predicted in good agreement with crystallographic results, especially when it is considered that the ab initio results correspond to gas phase calculations.

(I) and (II) have been studied as model compounds useful as building blocks of polymeric materials with potentially conducting behavior. The dipole moment as a measure of the distribution of charge density has been evaluated. These results together with the analysis of electron density plots are allowed to characterize the different reactive sites within the molecules. Total energies as a measure of stability, and an evaluation of electronegativities and chemical hardnesses as an indication of aromaticity and as a measure of the HOMO–LUMO gap useful for the design of low band gap polymers had been accomplished. The analysis of DFT reactivity indices, like condensed Fukui functions and condensed local softnesses allowed to characterize the carbon atoms as the active sites for nucleophilic and the nitrogen atoms as the active sites for electrophilic attacks in perfect agreement with the experimental evidence.

Atomic charges alone cannot explain adequately the behavior and

chemical reactivity of these molecules. The analysis of the electronic densities and the molecular electrostatic potentials show contradicting results sometimes. On the contrary, the relative densities of the frontier orbitals and its 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.

Supplementary material

Fractional coordinates and equivalent isotropic temperature parameters [55] for the non-H atoms in compounds (I) and (II) are given in Tables 7 and 8, and can be obtained from the authors on request. A list of atomic anisotropic thermal parameters (Table 9), of hydrogen atoms positions (Table 10), and listings of observed and calculated structure factor amplitudes (Table 11) can also be obtained from the authors on request.

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References

- [1] H.S. Nalwa (Ed.), Handbook of Organic Conductive Molecules and Polymers, Wiley, Chichester, UK, 1997.
- [2] L.M. Weinstock, I. Shinkai, in: K.T. Potts (Ed.), Comprehensive Heterocyclic Chemistry, 6, Pergamon Press, Oxford, UK, 1984.
- [3] K. Müllen, G. Wegner, Electronic Materials: The Oligomer Approach, Wiley, Weinheim, FRG, 1998.
- [4] K.B. Lipkowitz, D.B. Boyd, in: K.B. Lipkowitz, D.B. Boyd (Eds.), Reviews in Computational Chemistry, 1, VCH Publishers, New York, 1990.
- [5] R.S. Mulliken, J. Chem. Phys. 23 (1955) 1833.
- [6] R.S. Mulliken, J. Chem. Phys. 23 (1955) 1841.
- [7] R.S. Mulliken, J. Chem. Phys. 23 (1955) 2338.
- [8] R.S. Mulliken, J. Chem. Phys. 2 (1934) 782.
- [9] R.G. Pearson, J. Am. Chem. Soc. 85 (1963) 3533.
- [10] R.G. Pearson, Science 151 (1966) 172.
- [11] R.G. Parr, W. Yang, Density Functional Theory of Atoms and Molecules, Oxford University Press, New York, 1989.
- [12] M.V. Mir'nfico, E.J. Vasini, J.E. Sicre, Int. J. Chem. Kinet. 23 (1991) 197.

- [13] M.V. Mir'nfico, E.J. Vasini, An. Quim. 91 (1995) 557.
- [14] M.V. Mir'nfico, J.A. Caram, E.J. Vasini, J.E. Sicre, J. Phys. Org. Chem. 6 (1993) 341.
- [15] M.V. Mir'nfico, J.A. Caram, E.J. Vasini, Electrochim. Acta 36 (1991) 167.
- [16] J.A. Caram, M.V. Mir'nfico, E.J. Vasini, Electrochim. Acta 39 (1994) 939.
- [17] S.L. Aimone, M.V. Mir'nfico, J.A. Caram, E.J. Vasini, J. Phys. Org. Chem. 13 (2000) 272.
- [18] S.L. Aimone, M.V. Mir'nfico, J.A. Caram, D. Glossman Mitnik, O.E. Piro, E.E. Castellano, E.J. Vasini, Tetrahedron Lett. 41 (2000) 3531.
- [19] M.D. Glossman, J. Mol. Struct. (Theochem) 330 (1995) 385.
- [20] M.D. Glossman, Atualidades de Fisicoqu'nmica Orga'nica 1995, Universidade Federal de Santa Catarina Press, Santa Catarina, Brazil, 1996.
- [21] M.D. Glossman, J. Mol. Struct. (Theochem) 390 (1997) 67.
- [22] E.E. Castellano, O.E. Piro, J.A. Caram, M.V. Mir'nfico, S.L. Aimone, E.J. Vasini, M.D. Glossman, J. Phys. Org. Chem. 11 (1998) 91.
- [23] R.G. Parr, W. Yang, J. Am. Chem. Soc. 106 (1984) 4049.
- [24] J.L. Ga'zquez, C. Pa'rka'nyi (Eds.), Theoretical Organic Chem- istry - Theoretical and Computational Chemistry, 5, Else- vier, Amsterdam, 1998, p. 135.
- [25] R.G. Parr, W. Yang, Annu. Rev. Phys. Chem. 46 (1995) 701.
- [26] S.M. Bachrach, in: K.B. Lipkowitz, D.B. Boyd (Eds.), Reviews in

Computational Chemistry, 5, VCH Publishers, New York, 1994.

- [27] W. Yang, W.J. Mortier, J. Am. Chem. Soc. 108 (1986) 5708.
- [28] P. Politzer, D.G. Truhlar (Eds.), Chemical Applications of Atomic and Molecular Electrostatic Potentials, Plenum Press, New York, 1981.
- [29] D.T. Cromer, J.T. Waber, International Tables for X-ray Crystallography, IV, Kinoch Press, Birmingham, UK, 1974, p. 71.
- [30] D.T. Cromer, J.T. Ibers, International Tables for X-ray Crystallography, IV, Kinoch Press, Birmingham, UK, 1974, p. 149.
- [31] G.M. Sheldrick, SHELX, A Program for Crystal Structure Determination, University of Cambridge, Cambridge, UK, 1974.
- [32] A.B. Frenz, Enraf-Nonius Structure Determination Package, Enraf-Nonius, Delft, The Netherlands, 1983.
- [33] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.
- [34] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith,

- M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez,
M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L.
Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN
98 Revision A. 7, Gaussian Inc., Pittsburgh PA, 1998.
- [35] C.C.J. Roothaan, Rev. Mod. Phys. 23 (1951) 69.
- [36] C. Foces-Foces, F.H. Cano, S. Garc'na, Blanco, Acta Crystal-
logr. B 31
(1975) 2310.
- [37] C. Foces-Foces, J. Fayos, F.H. Cano, S. Garc'na, Blanco, Acta Crystallogr.
B 33 (1977) 910.
- [38] C.E. Caldero'n, M.M. Ripoll, S.G. Blanco, Acta Crystallogr. B
35 (1979) 2795.
- [39] C.E. Caldero'n, M.M. Ripoll, S.G. Blanco, Acta Crystallogr. B 38 (1982)
2296.
- [40] C.E. Caldero'n, M.M. Ripoll, S.G. Blanco, Acta Crystallogr. B 38 (1982)
1340.
- [41] R.J. Baker, S. Chiu, C. Klein, J.W. Timberlake, L.M.
Trefonas, J. Am. Chem. Soc. 45 (1980) 482.
- [42] J.S. Amato, S. Karady, A.A. Reamer, H.B. Schlegel, J.P. Spriger, L.M.
Weinstock, J. Org. Chem. 104 (1982) 1375.
- [43] Z. Zhou, R.G. Parr, Tetrahedron Lett. 29 (38) (1988) 4843.
- [44] R.G. Pearson, J. Chem. Educ. 64 (1987) 561.
- [45] U. Salzner, J.B. Lagowski, P.G. Pickup, R.A. Poirier, J. Comp. Chem. 18
(15) (1997) 1943.

- [46] K. Fukui, Theory of Orientation and Stereoselection, Springer, Berlin, 1973.
- [47] W. Langenaeker, F. De Proft, P. Geerlings, J. Phys. Chem. 99 (1995) 6424.
- [48] R.K. Roy, S. Krishnamurti, P. Geerlings, S. Pal, J. Phys. Chem. 102 (1998) 3746.
- [49] R.K. Roy, F. De Proft, P. Geerlings, J. Phys. Chem. 102 (1998) 7035.
- [50] J.L. Ga'zquez, F. Me'ndez, J. Phys. Chem. 98 (1994) 4591.
- [51] W. Langenaeker, K. Demel, P. Geerlings, J. Mol. Struct. (Theochem) 259 (1992) 317.
- [52] A. Baeten, F. De Proft, P. Geerlings, Chem. Phys. Lett. 235 (1995) 17.
- [53] Baeten, F. De Proft, W. Langenaeker, P. Geerlings, J. Mol. Struct. (Theochem) 306 (1994) 203.
- [54] F. De Proft, S. Amira, K. Choho, P. Geerlings, J. Phys. Chem. 98 (1994) 5227.
- [55] C.K. Johnson, ÜRTEP Report ORNL-3794, Oak Ridge, TN, USA, 1965.