

# Crystallographic study and molecular orbital calculations of thiadiazole derivatives. Part 3: 3,4-diphenyl-1,2,5-thiadiazoline 1,1-dioxide, 3,4-diphenyl-1,2,5-thiadiazolidine 1,1-dioxide and 4-ethoxy-5-methyl-3,4-diphenyl-1,2,5-thiadiazoline 1,1-dioxide

E.E. Castellano<sup>a</sup>, O.E. Piro<sup>b</sup>, J.A. Caram<sup>c</sup>, M.V. Mirífico<sup>c</sup>, S.L. Aimone<sup>c</sup>, E.J. Vasini<sup>c</sup>,  
A. Márquez-Lucero<sup>d</sup>, D. Glossman-Mitnik<sup>d,\*</sup>

<sup>a</sup>Departamento de Física, Instituto de Química y Física de São Carlos, Universidad de São Paulo, C.P. 369, 13560 Sao Carlos (SP), Brazil

<sup>b</sup>Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata and PROFIMO (CONICET), C.C. 67,  
1900 La Plata, Argentina

<sup>c</sup>INIFTA (CONICET), Universidad Nacional de La Plata, Casilla de Correo 16, Suc. 4, 1900 La Plata, Argentina

<sup>d</sup>CIMAV, LAQUICOM, Miguel de Cervantes 120, Complejo Industrial Chihuahua, Chihuahua, Chih 31109, Mexico

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## Abstract

Single-crystal X-ray diffraction studies are reported for 3,4-diphenyl-1,2,5-thiadiazoline 1,1-dioxide (I), 3,4-diphenyl-1,2,5-thiadiazolidine 1,1-dioxide(II) and 4-ethoxy-5-methyl-3,4-diphenyl-1,2,5-thiadiazoline 1,1-dioxide (III). Ab initio MO calculations on the electronic structure, conformation and reactivity of these compounds are also reported and compared with the X-ray results. A charge sensitivity analysis is performed on the results applying concepts derived from density functional theory, 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 moment and the total electron density and electrostatic potential maps, several conclusions have been inferred about the preferred sites of chemical reaction of the studied compounds. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** 1,2,5-Thiadiazole 1,1-dioxide derivatives; Ab initio MO calculations; Single-crystal X-ray diffraction; DFT; Sensitivity analysis

## 1. Introduction

Conjugated 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].

One of the goals of computational chemistry is to understand chemical reactivity and to predict the outcome of molecular interactions [4]. The behavior of atoms and molecules is characterized by some parameters that chemists have extracted from their experience and used for prediction of chemical reactivity.

\* Corresponding author.

E-mail address: glossman@mail.cimav.edu.mx (D. Glossman-Mitnik).

Electron population analysis [5–8], electronic density maps [8], molecular electrostatic potentials (MEP) [9], electronegativities as a measure of the tendency of a species to attract electrons [10], global and local hardness and softness [11–13] and Fukui functions [13] are examples of those parameters.

In relation with our previous studies on kinetics [14,15], UV–VIS and IR spectroscopies [16], electrochemistry [17–20] and theoretical calculations [21–30] of several thiadiazole derivatives, we report here single crystal X-ray diffraction studies on the molecular structure of 3,4-diphenyl-1,2,5-thiadiazoline 1,1-dioxide (I), 3,4-diphenyl-1,2,5-thiadiazolidine 1,1-dioxide (II) and 4-ethoxy-5-methyl-3,4-diphenyl-1,2,5-thiadiazoline 1,1-dioxide (III).

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

## 2. MO theoretical calculations and computational methods

The Density Functional Theory (DFT) [13] 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 [11–13] can be employed to determine the nature of the reactive sites in a given molecule and, from this information, we can infer some aspects of the behavior of the molecule when reacting with other species.

It has been shown [13] that the electronegativity  $\chi$ , that is, the power of an atom in a molecule to attract electrons to itself, is related to the molecular energy  $E$  and the number of electrons  $N$  by  $\chi = -(\partial E/\partial N)_v$ .

The chemical hardness  $\eta$  was introduced as [13]  $\eta = (\partial^2 E/\partial N^2)_v$  (the factor of 1/2 in the original definition has been omitted for convenience [31]). 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 [32].

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 [5–8], can also be employed to determine the relative softness of each atom in the molecule. The corresponding condensed functions are given by [33]  $f_k^+ = q_k(N + 1) - q_k(N)$  (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.  $s(\vec{r}) = (\partial \rho(\vec{r})/\partial N)_{\alpha(\vec{r})}(\partial N/\partial \mu)_{\alpha(\vec{r})} = f(\vec{r})S$ .

To distinguish the behavior of 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. It has been found [27] that the geometries of sulfur compounds with valence other than two are not well described with density functional methods when basis set of 6-31G\*\* quality are used, and that it is necessary to use larger basis sets. This finding precludes the use of density functional theory for calculating the equilibrium geometry of molecules of the size we are considering in this work. In conjunction with the nuclear charges at the equilibrium configuration, the electronic distribution determines the molecular electrostatic potential [9]. 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).

All the MO calculations were performed with

Table 1

Crystal data and structure solution methods and refinement for 3,4-diphenyl 1,2,5-thiadiazoline 1,1-dioxide (I)

Empirical formula	C <sub>14</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> S
Formula weight	272.33
Temperature	295.15 K
Space group	C2/c
Unit cell dimensions <sup>a</sup>	$a = 26.321(2) \text{ \AA}$ , $b = 10.267(1) \text{ \AA}$ , $c = 10.318(7) \text{ \AA}$ , $\beta = 112.558(6)^\circ$
Volume	2574.9(4) $\text{\AA}^3$
Z	8
Density (calculated)	1.405 g/cm <sup>3</sup>
Absorption coefficient	2.383 cm <sup>-1</sup>
Crystal size	0.5 × 0.5 × 0.5 mm
Crystal color/shape	Transparent/spherical fragment
Diffractometer/scan	Enraf-Nonius CAD-4/ $\omega - 2\theta$
Radiation, graphite monochr.	M <sub>o</sub> K $\alpha$ , $\lambda = 0.71069 \text{ \AA}$
Scan width	0.8 + 0.35 tan $\theta$
Standard reflections	(17,7, - 1); (8,2, - 8)
Decay of standards	± 1.0%
$\theta$ range for data collection	2.0 to 58.0°
Index ranges	- 34 ≤ $h$ ≤ 34, 0 ≤ $k$ ≤ 13, 0 ≤ $l$ ≤ 13
Reflections collected	3804
Independent reflections	3098
Observed reflections <sup>b</sup>	2558
Data reduction and correction <sup>c</sup> and	SHELX-76 [38], SHELX-86 [62], and
Structure solution and refinement programs <sup>d</sup>	SDP [40], SHELX-93 [39]
Minimized function	$\sum \omega( F_o  -  F_c )^2$
Weights	$\omega = [\sigma F_o^2 + 0.0001F_o^2]^{-1}$
Number of parameters varied	175
Goodness-of-fit on $F^2$	0.77
$R = \sum  F_o  -  F_c  / \sum  F_o $	0.036
$R_w = \sqrt{w( F_o  -  F_c )^2 / \sum w F_o ^2}$	0.039
Largest feature final difference map	0.27 e. $\text{\AA}^{-3}$

<sup>a</sup> Least-squares refinement of  $((\sin \theta)/\lambda)^2$  values for 25 reflections in the  $16.5 \leq 2\theta \leq 29.1^\circ$  range.<sup>b</sup> Data were corrected for Lorentz, polarization and absorption [63].<sup>c</sup> Neutral scattering factors and anomalous dispersion corrections.<sup>d</sup> Structure solved by Patterson and Fourier methods and the final molecular model obtained by anisotropic full-matrix least-squares refinement of non-hydrogen atoms.

Table 2

Crystal data and structure solution methods and refinement for 3,4-diphenyl 1,2,5-thiadiazolidine 1,1-dioxide (II)

Empirical formula	C <sub>14</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> S
Formula weight	274.34
Temperature	295.15 K
Space group	P2 <sub>1</sub> /c
Unit cell dimensions <sup>a</sup>	$a = 14.760(3) \text{ \AA}$ , $b = 5.526(1) \text{ \AA}$ , $c = 16.580(4) \text{ \AA}$ , $\beta = 109.02(2)^\circ$
Volume	1278.4(6) $\text{\AA}^3$
Z	4
Density (calculated)	1.054 g/cm <sup>3</sup>
Absorption coefficient	1.779 cm <sup>-1</sup>
Crystal size	0.2 × 0.2 × 0.17 mm
Crystal color/shape	Transparent/Parallelepiped
Diffractometer/scan	Enraf-Nonius CAD-4/ $\omega - 2\theta$
Radiation, graphite monochr.	MoK $\alpha$ , $\lambda = 0.71069 \text{ \AA}$
Scan width	0.8 + 0.35 tan $\theta$
Standard reflections	(-5, - 2, 6)
Decay of standards	± 1.7%
$\theta$ range for data collection	2.0 to 58.0°
Index ranges	- 17 ≤ $h$ ≤ 17, 0 ≤ $k$ ≤ 6, 0 ≤ $l$ ≤ 9
Reflections collected	2660
Independent reflections <sup>b</sup>	1893
Observed reflections <sup>c</sup>	1137
Data reduction and correction <sup>d</sup>	SHELX-76 [38], SHELX-86 [62], SDP [40], SHELX-93 [39]
Structure solution and refinement programs <sup>c</sup>	
Minimized function	$\sum \omega( F_o  -  F_c )^2$
Weights	$\omega = [\sigma F_o^2 + 0.0001F_o^2]^{-1}$
Number of parameters varied	173
Goodness-of-fit on $F^2$	1.40
$R = \sum  F_o  -  F_c  / \sum  F_o $	0.0385
$R_w = \sqrt{w( F_o  -  F_c )^2 / \sum \omega F_o ^2}$	0.0408
Largest feature final difference map	0.21 e. $\text{\AA}^{-3}$

<sup>a</sup> Least-squares refinement of  $((\sin \theta)/\lambda)^2$  values for 25 reflections in the  $20.8 \leq 2\theta \leq 30.1^\circ$  range.<sup>b</sup>  $R_{\text{sym}} = 0.0214$ .<sup>c</sup> Data were corrected for Lorentz, polarization and absorption [63].<sup>d</sup> Neutral scattering factors and anomalous dispersion corrections.<sup>e</sup> Structure solved by Patterson and Fourier methods and the final molecular model obtained by anisotropic full-matrix least-squares refinement of non-hydrogen atoms.

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 consid-

ered 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.

Table 3

Crystal data and structure solution methods and refinement for 4-ethoxy-5-methyl-3,4-diphenyl 1,2,5-thiadiazoline 1,1-dioxide (III)

Empirical formula	C <sub>17</sub> H <sub>18</sub> N <sub>2</sub> O <sub>3</sub> S
Formula weight	330.41
Temperature	293.15 K
Space group	<i>Pbca</i>
Unit cell dimensions <sup>a</sup>	<i>a</i> = 9.540(2) Å, <i>b</i> = 16.043(1) Å, <i>c</i> = 21.426(4) Å, β = 90.0°
Volume	3279.3(8) Å <sup>3</sup>
Z	8
Density (calculated)	1.338 g/cm <sup>3</sup>
Absorption coefficient	2.030 cm <sup>-1</sup>
Crystal size	0.5 × 0.35 mm
Crystal color/shape	Orthorhombic/transparent/fragment
Diffractometer/scan	Enraf-Nonius CAD-4/ω – 2θ
Radiation, graphite monochr.	MoK <sub>α</sub> , λ = 0.71073 Å
Scan width	0.8 + 0.35 tan θ
Decay of standards	± 1.0%
θ range for data collection	9.9–17.4°
Index ranges	0 ≤ <i>h</i> ≤ 11, 0 ≤ <i>k</i> ≤ 18, 0 ≤ <i>l</i> ≤ 25
Reflections collected	2454
Independent reflections	2454
Observed reflections <sup>b</sup>	1608
Data reduction and correction <sup>c</sup>	SHELX-76 [38], SHELX-86 [62],
Structure solution and refinement programs <sup>d</sup>	SDP [40], SHELX-93 [39]
Minimized function	$\sum \omega( F_o  -  F_c )^2$
Weights	$\omega = [\sigma F_o^2 + 0.00015 F_o^4]^{-1}$
Number of parameters varied	209
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.62
$R = \sum   F_o  -  F_c   / \sum  F_o $	0.063
$R_w = \sqrt{\sum w( F_o  -  F_c )^2 / \sum \omega  F_c ^2}$	0.064
Largest feature final difference map	0.30 e. Å <sup>-3</sup>

<sup>a</sup> Least-squares refinement of  $(\sin \theta)/\lambda$  values for 25 reflections in the 9.9 ≤ 2θ ≤ 17.4° range.

<sup>b</sup> Data were corrected for Lorentz, polarization and absorption [63].

<sup>c</sup> Neutral scattering factors and anomalous dispersion corrections.

<sup>d</sup> Structure solved by Patterson and Fourier methods and the final molecular model obtained by anisotropic full-matrix least-squares refinement of non-hydrogen atoms.

### 3. Experimental

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

orientation matrix for data collection. Intensities were measured by the ω–2θ scan technique at a rate 2.85–20.0 deg min<sup>-1</sup> determined by a fast prescan of 20.0 deg min<sup>-1</sup>. Reflections were collected in the range 0 < θ < 58 using graphite monochromated MoK<sub>α</sub> radiation. Crystal data, data collection details and structure refinement results for (I), (II) and (III) are shown in Tables 1–3, respectively.

The intensity of one standard reflection selected of each compound was essentially constant over the duration of the experiments. Data were corrected by Lorentz, polarization and absorption effects. Scattering factors taken from Cromer and Waber [36] and the corresponding anomalous dispersion coefficients from Cromer and Ibers [37] were used in the calculations. These were performed with the SHELX [38], SHELXL93 [39] and SDP [40] systems of programs. The stereoscopic projections shown were drawn with the program ORTEP [41,42].

The structures were solved by standard centrosymmetric Direct Methods and Fourier techniques and refined by full-matrix least-squares methods with an isotropic 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 were refined with a common isotropic temperature parameter. Moreover, hydrogen positions were refined by fixing bond distances to the corresponding atoms at their accepted values.

## 4. Results and discussion

### 4.1. Crystallography

Relevant bond distances and angles for compounds (I), (II) and (III) are shown in Tables 4–6 and ORTEP drawings of the molecules showing the labeling of the atoms and their vibrational ellipsoids are shown in Figs. 1–3.

The structural details in Tables 4–6 allow comparisons among these compounds and with reported studies of related compounds, such as thiadiazines [43–47], a 1,1-dioxide thiadiazoline [48], a 1-monoxide thiadiazole [49] and 1,1-dioxide thiadiazole derivatives

Table 4

Relevant bond distances (Å) and angles (°) for 3,4-diphenyl-1,2,5-thiadiazoline 1,1-dioxide (I)

	Experimental <sup>a</sup>	HF/6-31G <sup>**b</sup>
<i>Bond distances</i>		
S–O(1)	1.425(2)	1.424
S–O(2)	1.422(2)	1.422
S–N(1)	1.661(1)	1.660
S–N(2)	1.645(1)	1.658
N(1)–C(1)	1.287(2)	1.263
N(2)–C(2)	1.476(4)	1.459
C(1)–C(11)	1.464(2)	1.479
C(1)–C(2)	1.528(2)	1.539
C(2)–C(21)	1.522(3)	1.524
<i>Bond angles</i>		
O(1)–S–O(2)	117.5(9)	119.4
O(1)–S–N(1)	111.2(8)	111.1
O(1)–S–N(2)	110.5(8)	108.3
O(2)–S–N(1)	106.7(8)	108.0
O(2)–S–N(2)	110.8(8)	111.2
N(1)–S–N(2)	98.4 (8)	96.4
S–N(1)–C(1)	110.0(1)	111.7
S–N(2)–C(2)	109.1(1)	110.6
N(1)–C(1)–C(11)	120.8(1)	120.5
N(1)–C(1)–C(2)	116.5(1)	116.4
C(11)–C(1)–C(2)	122.7(1)	123.1
C(1)–C(11)–C(12)	119.0(1)	118.9
C(1)–C(11)–C(16)	122.0(1)	121.8

<sup>a</sup> X-ray crystallographic determination.<sup>b</sup> HF/6-31G<sup>\*\*</sup> molecular orbital calculation.

Table 5

Relevant bond distances (Å) and angles (°) for 3,4-diphenyl-1,2,5-thiadiazolidine 1,1-dioxide (II)

	Experimental <sup>a</sup>	HF/6-31G <sup>**b</sup>
<i>Bond distances</i>		
S–O(1)	1.434(3)	1.427
S–O(2)	1.418(3)	1.426
S–N(1)	1.649(3)	1.655
S–N(2)	1.640(4)	1.644
N(1)–C(1)	1.482(5)	1.468
N(2)–C(2)	1.475(5)	1.465
C(1)–C(2)	1.561(2)	1.569
C(1)–C(3)	1.500(5)	1.519
C(2)–C(9)	1.517(5)	1.513
<i>Bond angles</i>		
O(1)–S–O(2)	115.6(2)	118.9
O(1)–S–N(1)	113.2(2)	112.6
O(1)–S–N(2)	108.7(2)	107.4
O(2)–S–N(1)	110.1(2)	107.2
O(2)–S–N(2)	112.5(2)	112.6
N(1)–S–N(2)	95.0(2)	95.8
S–N(1)–C(1)	107.5(2)	109.6
S–N(2)–C(2)	112.7(2)	113.2
N(1)–C(1)–C(2)	102.3(3)	103.2
N(1)–C(1)–C(3)	113.5(3)	112.3
C(2)–C(1)–C(3)	114.9(3)	117.0
N(2)–C(2)–C(1)	102.5(3)	105.6
N(2)–C(2)–C(9)	112.7(3)	112.6
C(1)–C(2)–C(9)	115.1(3)	118.7

<sup>a</sup> X-ray crystallographic determination.<sup>b</sup> HF/6-31G<sup>\*\*</sup> molecular orbital calculation.

[24,30] and suggest relations with their experimental chemical behavior.

From Tables 4–6, we can conclude for these compounds:

- S=O double bond length values vary from 1.417(4) to 1.438(4) Å, i.e. in about  $2\sigma$  (where  $\sigma = 0.005$  Å is the standard error) around the mean value (= 1.428(3) Å).
- S–N single bond lengths vary from 1.606(4) to 1.661(1) Å, i.e. in about  $4\sigma$  ( $\sigma = 0.007$  Å) around the mean value (= 1.634(3) Å).
- C=N double bond lengths in compounds (I) and (III) are practically equal within experimental error (average = 1.287(2) Å).
- C–N single bond lengths vary from 1.463(5) to 1.482(5) Å, i.e. in about  $2\sigma$  ( $\sigma = 0.005$  Å) around the mean value (= 1.473(5) Å).
- C(1)–C(2) single bond lengths of compounds (I)

and (III) are practically equal within experimental error (average = 1.528(5) Å), while in compound (II) it is slightly longer.

- C(1)–C(11) single bond lengths of compounds (I) and (III) are almost equal (= 1.4642 Å), while C(2)–C(21) are 1.522(3) and 1.530(6) Å for I and III respectively. These results are an indication of the different hybridization of C(1) ( $sp^2$ ) and C(2) ( $sp^3$ ) and constitute an evidence of some double-bond character for the C(1)–C(11) bonds in I and III. Together with the coplanarity of the phenyl ring, this accounts full delocalization interaction of its  $\pi$  system with the corresponding C=N double bond. Meanwhile, C(1)–C(3) and C(2)–C(9) in compound (II) vary from 1.500(5) to 1.517(5) Å, i.e. in about  $2\sigma$  ( $\sigma = 0.004$  Å) around the mean value (= 1.508(5) Å).
- C–C resonant bond lengths in the six-membered

Table 6  
Relevant bond distances (Å) and angles (°) for 4-ethoxy-5-methyl-3,4-diphenyl-1,2,5-thiadiazoline 1,1-dioxide (III)

	Experimental <sup>a</sup>	HF/3-21G <sup>**b</sup>
<i>Bond distances</i>		
S–O(1)	1.438(4)	1.427
S–O(2)	1.417(4)	1.430
S–N(1)	1.648(4)	1.643
S–N(2)	1.606(4)	1.626
O(3)–C(2)	1.405(5)	1.411
O(3)–C(4)	1.458(6)	1.462
N(1)–C(1)	1.286(6)	1.270
N(2)–C(2)	1.463(5)	1.476
N(2)–C(3)	1.423(6)	1.454
C(1)–C(2)	1.529(5)	1.553
C(1)–C(11)	1.464(6)	1.464
C(2)–C(21)	1.530(6)	1.521
C(4)–C(5)	1.477(8)	1.528
<i>Bond angles</i>		
O(1)–S–O(2)	117.1(2)	118.6
O(1)–S–N(1)	110.2(2)	110.2
O(1)–S–N(2)	110.8(2)	111.3
O(2)–S–N(1)	108.5(2)	109.8
O(2)–S–N(2)	112.0(2)	110.0
N(1)–S–N(2)	96.2(2)	94.3
C(2)–O(3)–C(4)	114.9(3)	117.4
S–N(1)–C(1)	113.3(3)	113.9
S–N(2)–C(2)	113.8(3)	115.1
S–N(2)–C(3)	122.2(3)	121.9
C(2)–N(2)–C(3)	122.5(3)	122.5
N(1)–C(1)–C(2)	116.4(4)	115.2
N(1)–C(1)–C(11)	120.1(4)	121.6
C(2)–C(1)–C(11)	123.4(3)	123.2
O(3)–C(2)–N(2)	111.2(3)	113.1
O(3)–C(2)–C(1)	113.5(3)	112.3
O(3)–C(2)–C(21)	107.6(3)	108.8
N(2)–C(2)–C(1)	102.0(3)	101.3
N(2)–C(2)–C(21)	109.9(3)	110.5
C(1)–C(2)–C(21)	112.6(3)	110.6
O(3)–C(4)–C(5)	108.7(4)	106.2

<sup>a</sup> X-ray crystallographic determination.

<sup>b</sup> HF/3-21G<sup>\*\*</sup> molecular orbital calculation.

rings (not shown) vary from 1.360(5) to 1.421(4) Å, i.e. within  $6\sigma$  ( $\sigma = 0.009$  Å) around the mean value ( $= 1.39(2)$  Å).

Although not shown in the tables, an analysis of the torsional angles reveals that the heterocycle rings of compound (I), (II) and (III) are not planar. As already found in the related six-membered heterocyclic compounds 1,2,6-thiadiazine 1,1-dioxides [43–47]

and 1,2,5-thiadiazole 1,1-dioxides [24,25,30], 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.

#### 4.1.1. Compound I

The heterocyclic ring deviates slightly from planarity (maximum and minimum departures from the least-squares plane of 0.068(2) and 0.016(2) Å. As expected, both phenyl rings are planar to within experimental accuracy. The phenyl group attached to the heterocyclic sp<sup>2</sup> carbon C(1) deviates from coplanarity with the heterocycle least-squares plane in 7.6(2)° while the other phenyl ring is nearly perpendicular to either of the latter planes (subtending dihedral angles with the heterocycle and the other phenyl ring of 89.23(9) and 96.58(8)° respectively).

#### 4.1.2. Compound II

Both phenyl rings are practically planar with maximum deviation from the corresponding mean planes of about three times the standard error. The heterocyclic ring is not planar.

#### 4.1.3. Compound III

The heterocyclic ring departs slightly from planarity (maximum and minimum deviations from the mean plane of 0.033(3) and 0.017(4) Å). Again, the phenyl rings are planar to within experimental accuracy. The ethoxy backbone atoms are approximately on a plane with the heterocyclic carbon atom (maximum and minimum deviations of 0.076(3) and 0.054(5) Å). The phenyl group attached to the heterocyclic sp<sup>2</sup> carbon C(1) departs from coplanarity with the heterocyclic plane in 10.7(6)°. The other phenyl ring and the ethoxy group, which are coplanar, are perpendicular to the heterocyclic least-squares plane to within experimental errors.

#### 5.2. Theoretical calculations

The results for the equilibrium conformation of the neutral molecule (I) and (II) (HF-LCAO with 6-31G<sup>\*\*</sup> basis set) are included in Tables 4 and 5 along with the experimental X-ray results. Due to the larger size of (III), the geometry optimization has been done by resorting to a smaller basis set, i.e. 3-21G<sup>\*\*</sup> and the results are included in Table 6. The agreement is

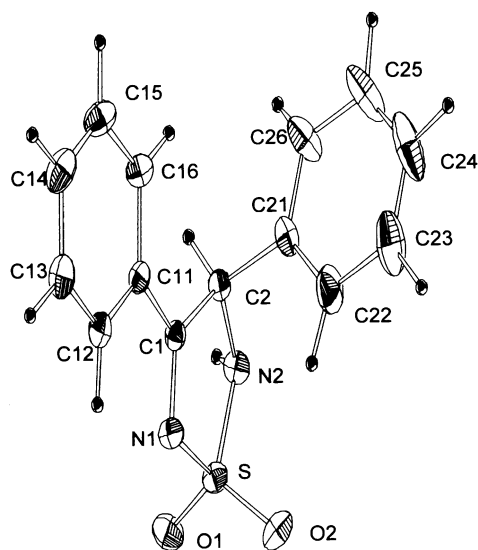


Fig. 1. ORTEP representation of the molecular structure of 3,4-diphenyl-1,2,5-thiadiazoline 1,1-dioxide (I).

in general good for these ab initio calculations; the standard error of the differences between the experimental and the calculated bond lengths is ca  $8 \times 10^{-3}$  for all methods. The corresponding value for the bond angles is  $0.73^\circ$ .

The molecular dipole moment is perhaps the

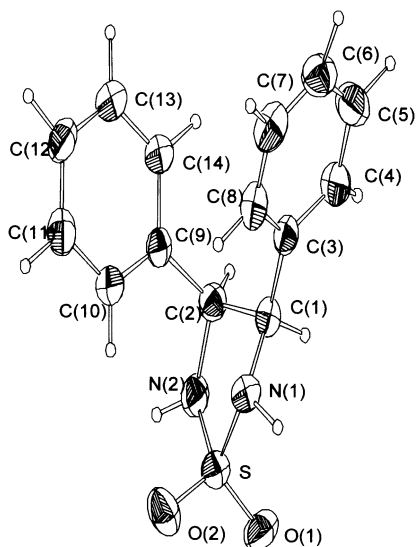


Fig. 2. ORTEP representation of the molecular structure of 3,4-diphenyl-1,2,5-thiadiazolidine 1,1-dioxide (II).

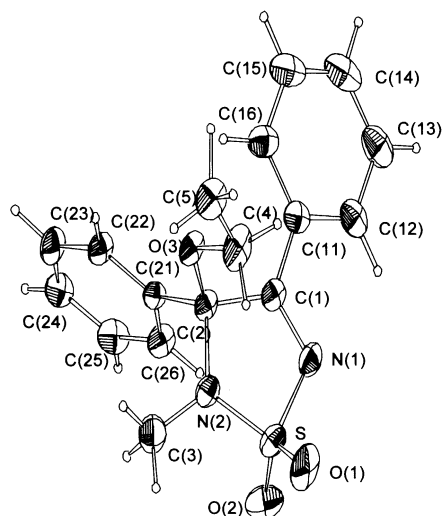


Fig. 3. ORTEP representation of the molecular structure of 4-ethoxy-5-methyl-3,4-diphenyl-1,2,5-thiadiazoline 1,1-dioxide (III).

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 compounds (I), (II) and (III) are shown in Table 7. The small difference in the total values is an indication that the atomic distribution in the substituent moieties has little effect on the overall dipole moment.

The HOMO–LUMO gap has been considered a measure of aromaticity [50]. The HOMO–LUMO gap is, in turn, related to chemical hardness [51]. The energy gap between valence and conduction band of a polymer is related to the lowest excitation energy of its monomer units [52]. To design low band gap polymers it is convenient to start with monomer

Table 7

Total energies  $E$  (a.u.), dipole moments  $\mu$  (debye), electronegativities  $\chi$  (eV) and hardnesses  $\eta$  (eV) for 3,4-diphenyl-1,2,5-thiadiazoline 1,1-dioxide (I), 3,4-diphenyl-1,2,5-thiadiazolidine 1,1-dioxide (II) and 4-ethoxy-5-methyl-3,4-diphenyl-1,2,5-thiadiazoline 1,1-dioxide (III)

Compound	$E$	$\mu$	$\chi$	$\eta$
I	– 1193.2198	8.4467	4.454	9.343
II	– 1194.3854	7.0333	2.698	10.156
III	– 1385.1737	7.2889	2.970	9.916

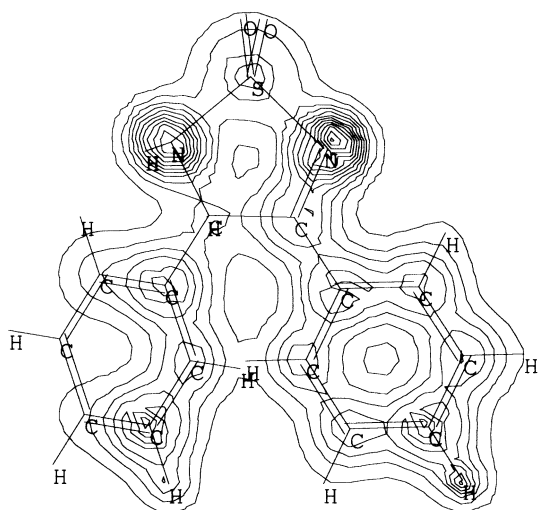


Fig. 4. HF/6-31G\*\* electron density of 3,4-diphenyl-1,2,5-thiadiazoline 1,1-dioxide (I) on the molecular plane.

units with small HOMO–LUMO gaps [52], 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

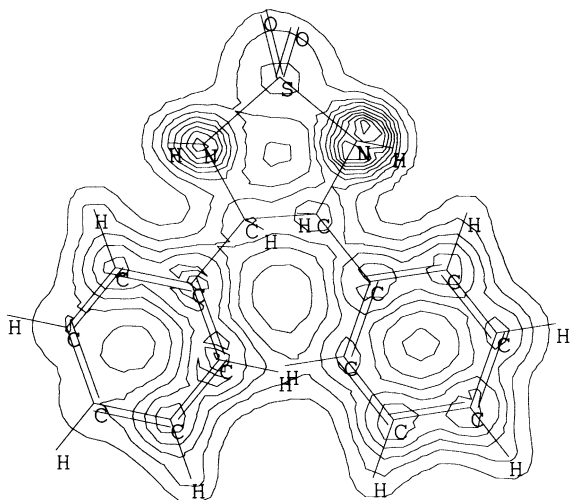


Fig. 5. HF/6-31G\*\* electron density of 3,4-diphenyl-1,2,5-thiadiazolidine 1,1-dioxide (II) on the molecular plane.

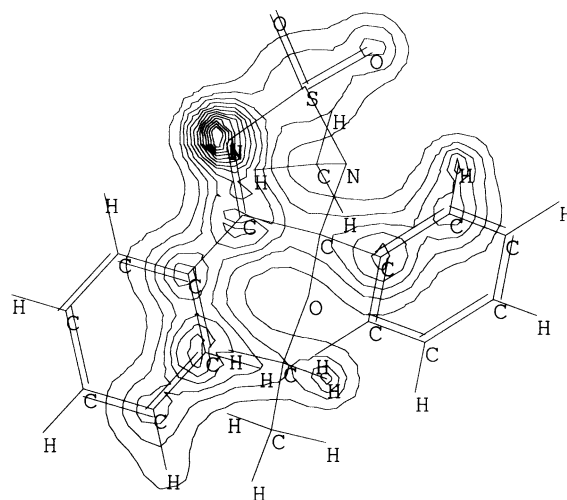


Fig. 6. HF/6-31G\*\* electron density of 4-ethoxy-5-methyl-3,4-diphenyl-1,2,5-thiadiazoline 1,1-dioxide (III) on the molecular plane.

neutral, anionic and cationic systems, respectively. Total molecular energies, total electronegativities and chemical hardnesses for the molecules under study are presented in Table 7.

The condensed Fukui functions can be applied, as shown in previous work [21–30], to the study of the behavior of substances under nucleophilic or electrophilic attack. Figs. 4–6 display a planar representation of the calculated electron density of (I), (II) and (III) and Figs. 7–9 shows two-dimensional isosurfaces renderings of the electrostatic potential of (I), (II) and (III), respectively. All these figures show that the electrophilic attack would occur preferentially in the oxygen or nitrogen atoms and nucleophilic attack will take place at the heterocyclic ring in the sulfur or carbon atoms.

These reactive sites can also be identified by an analysis based on frontier orbitals [13,53]. Tables 8–10 show the net atomic charges for the ring atoms of the neutral molecules (I), (II) and (III), obtained by a Mulliken population analysis, together with the  $f^+$ ,  $f^-$  and  $f^0$  Fukui functions. A small or negative value of the Fukui function over an atom is an indication that the site is unlikely reactive and this is an overall conclusion for molecules (II) and (III) from Tables 9 and 10. The sites for electrophilic attack will be those atoms bearing a negative charge and where the Fukui function  $f^-$  is a maximum. From



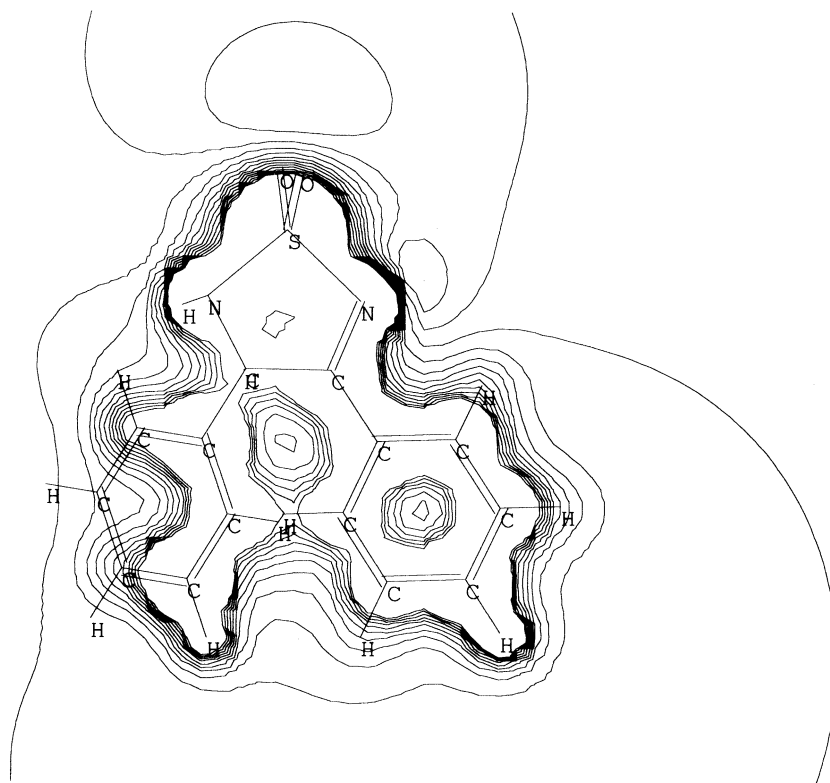


Fig. 7. Two-dimensional isosurface rendering of the electrostatic potential of the 3,4-diphenyl-1,2,5-thiadiazoline 1,1-dioxide molecule (I).

Table 8, these values confirm that the site for the electrophilic attack in molecule (I) will be the nitrogen atom N(1). 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 value of  $f^+$  on C(1) is larger than the corresponding value on the sulfur atom. Therefore, in this molecule, the heterocycle carbon C(1) would be more susceptible than the sulfur to nucleophilic interactions. Finally, from Table 8, the nitrogen atom N(1) will be the place for radical attack.

The condensed local softness indices  $s_k^+$  and  $s_k^-$  are related to the condensed Fukui functions through the global softness  $S$ . They are easily calculated by mean of the values of 0.10703 eV (I), 0.09846 eV (II) and 0.10084 eV (III) for the global softnesses  $S$  of the molecules. As it has been remarked [54–56], 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 [13] and analytically proved by Gázquez and Méndez [57]. This idea has been extensively exploited in the past for the study of the nucleophilic addition to  $\alpha,\beta$ -unsaturated compounds [58], in the interpretation of the effect of alkyl substitution on the basicity of amines [59,60], as a measure of the acidity of substituted acetic acids [61], as reactivity indices for predicting reactivity sequences of carbonyl compounds toward nucleophilic attack [55] and for studying the site of protonation of substituted anilines [56]. As shown, the carbon atom C(1) of molecule (I) will be the active site for nucleophilic interactions. The values of the condensed softness function  $s_k^-$

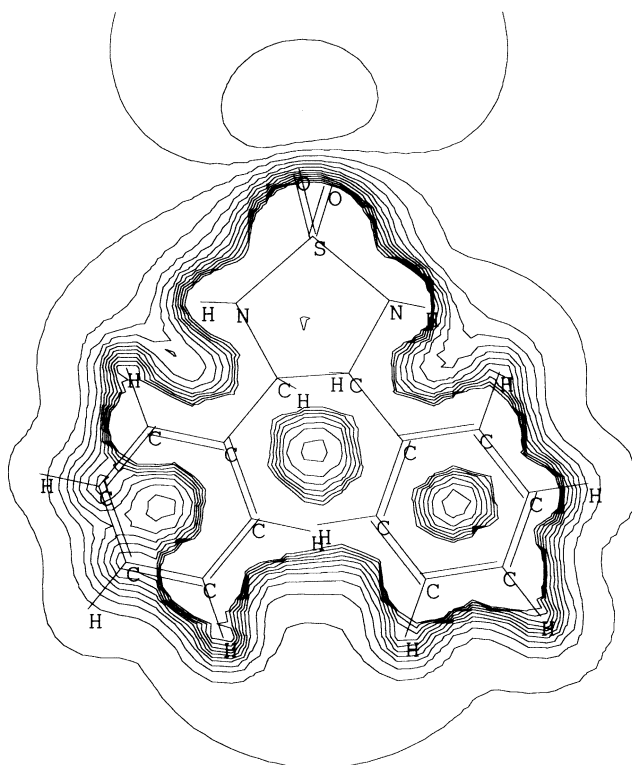


Fig. 8. Two-dimensional isosurface rendering of the electrostatic potential of the 3,4-diphenyl-1,2,5-thiadiazolidine 1,1-dioxide molecule (II).

above the reactive nitrogen N(1) atoms are 0.03928 eV for (I) and 0.00403 eV for (III). Thus, the nitrogen atom N(1) of (I) will be more reactive than the nitrogen atom N(1) of (III) in a electrophilic attack.

## 5. Conclusions

In this work, single-crystal X-ray diffraction studies have been reported for 3,4-diphenyl-1,2,5-thiadiazoline 1,1-dioxide (I), 3,4-diphenyl-1,2,5-thiadiazolidine (II) and 4-ethoxy-5-methyl-3,4-diphenyl-1,2,5-thiadiazoline (III). We have also shown calculations on this molecule performed using Hartree-Fock method at the 6-31G\*\* basis set level (some at the 3-21G\*\* basis set level). The molecular structure is well predicted in good agreement with crystallographic results, specially when it is considered that the ab initio results correspond to gas phase calculations.

(I), (II) and (III) 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, and electrostatic potential plots allowed to characterize the different reactive sites of the molecules. Total energy as a measure of stability, and an evaluation of electronegativity and chemical hardness 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 heterocyclic ring sp<sup>2</sup> carbon atom as the active site for nucleophilic interactions and the heterocyclic ring sp<sup>2</sup> nitrogen atoms as the active sites for electrophilic attacks in perfect agreement with the experimental evidence. These same nitrogen atoms will also be the place for radical interactions.

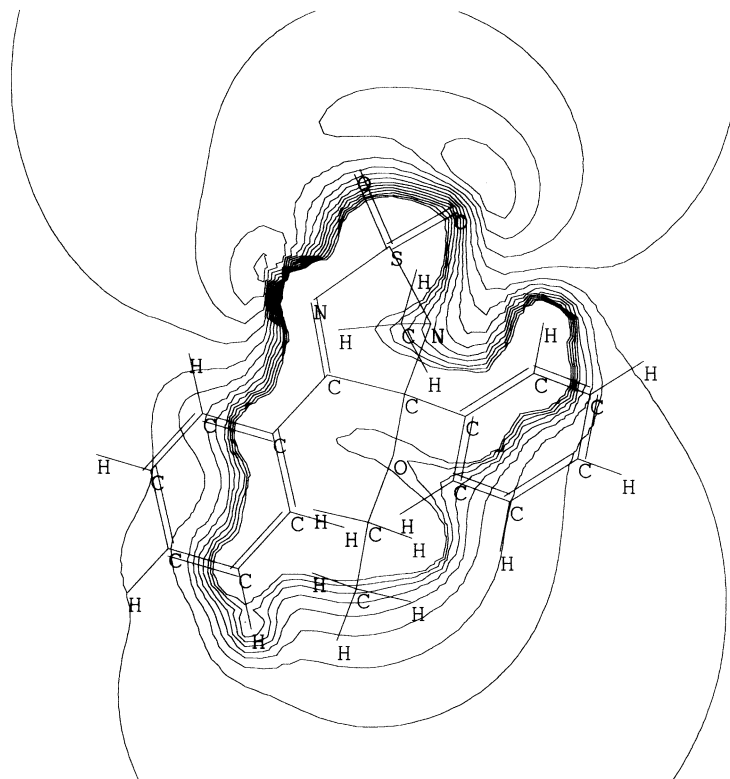


Fig. 9. Two-dimensional isosurface rendering of the electrostatic potential of the 4-ethoxy-5-methyl-3,4-diphenyl-1,2,5-thiadiazoline 1,1-dioxide molecule (III).

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 show sometimes contradictory results. On the contrary, the relative densities of the frontier orbitals and their mutual relations, 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.

Table 8

Net atomic charges and Fukui functions for the ring atoms of the 3,4-diphenyl-1,2,5-thiadiazoline 1,1-dioxide (I)

Atom	$q$	$f^+$	$f^-$	$f^0$
O(2)	-0.641	0.050	0.074	0.062
S	1.676	0.045	-0.006	0.020
O(1)	-0.640	0.052	0.092	0.072
N(1)	-0.772	0.026	0.367	0.196
N(2)	-0.642	0.137	0.048	0.092
C(2)	-0.044	-0.029	-0.099	-0.064
C(1)	0.299	0.151	0.027	0.089

Table 9

Net atomic charges and Fukui functions for the ring atoms of the 3,4-diphenyl 1,2,5-thiadiazolidine 1,1-dioxide (III)

Atom	$q$	$f^+$	$f^-$	$f^0$
O(1)	-0.6640.0140.0150.015			
S	1.723	0.013	0.007	0.010
O(2)	-0.652	0.030	0.031	0.030
N(1)	-0.804	-0.010	-0.002	-0.006
N(2)	-0.765	0.020	0.023	0.022
C(1)	0.040	-0.019	-0.033	-0.026
C(2)	0.008	-0.013	-0.008	-0.011

Table 10

Net atomic charges and Fukui functions for the ring atoms of the 4-ethoxy-5-methyl-3,4-diphenyl-1,2,5-thiadiazoline 1,1-dioxide (III)

Atom	$q$	$f^+$	$f^-$	$f^0$
O(1)	-0.645	0.033	0.032	0.033
S	1.742	0.010	0.006	0.008
O(2)	-0.672	0.014	0.014	0.014
N(1)	-0.671	0.038	0.040	0.039
N(2)	-0.857	-0.007	0.003	-0.002
C(1)	0.297	0.008	-0.027	-0.009
C(2)	0.575	0.018	-0.008	0.005
C(3)	-0.119	-0.015	-0.011	-0.013
O(3)	-0.713	-0.000	0.003	0.001
C(4)	0.084	-0.023	-0.021	-0.022
C(5)	-0.347	-0.006	-0.006	-0.006

## 6. Supplementary material

Fractional coordinates and equivalent isotropic temperature parameters for the non-H atoms in compounds (I), (II) and (III) can be obtained from the authors on request. A list of atomic anisotropic thermal parameters, of hydrogen atoms positions, and listing of observed and calculated structure factor amplitudes can also be obtained from the authors on request.

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