Journal of Molecular Structure 978 (2010) 67–73

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Synthesis and characterization of the first phosphonic diamide containing thiazolyl groups: Structural properties and tautomeric equilibrium

Khodayar Gholivand [a,*], Sedighe Farshadian [a], Mauricio F. Erben [b], Carlos O. Della Védova [b,c,*]

[a] Department of Chemistry, Tarbiat Modares University, P.O. Box: 14115-175, Tehran, Iran
[b] CEQUINOR (UNLP-CONICET, CCT-La Plata), Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, CC 962, 47 esq. 115, (1900) La Plata, Argentina
[c] Laboratorio de Servicios a la Industria y al Sistema Científico UNLP-CIC-CONICET), Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata, Argentina

ARTICLE INFO

Article history:
Received 30 October 2009
Received in revised form 4 December 2009
Accepted 4 December 2009
Available online 13 January 2010

Specially dedicated to our friend Prof. Dr. Heinz Oberhammer.

Keywords:
2-Aminothiazole
Hydrogen bonds
Tautomerism
Phosphonic diamide

ABSTRACT

A new phosphonic diamide containing thiazolyl rings, *N,N′* bis(2-thiazolyl) phenylphosphonic diamide, with general formula $H_5C_6P(O)[NHCN(CH)_2S]_2$ (**1**), was synthesized and characterized by NMR, IR, UV, EI mass-spectrometry and elemental analysis. The X-ray diffraction structure obtained for **1** shows that the crystalline compound exists in the imine form, forming centro-symmetric dimers which are produced by intermolecular cooperative hydrogen bonds leading to a two-dimensional polymeric chain. The preferred tautomeric and conformational equilibria have also been identified in solution. Thus, a tautomeric equilibrium of 97:3% between the amine:imine form is observed in DMSO-d_6. Structural and conformational properties are analyzed using a combined approach involving crystallographic data, vibrational spectra and theoretical calculations at the B3LYP and MP2 (with 6-311++G** and CBSB7 basis sets) level of approximations.

1. Introduction

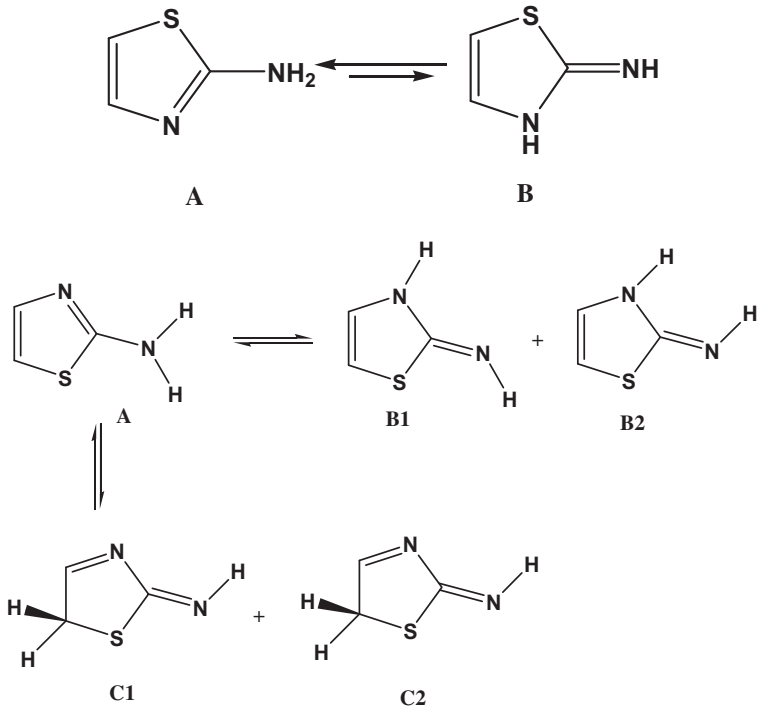
Thiazole and its derivatives show biological significance, e.g., they are found in the penicillin and vitamin B1 molecules and in coenzyme cocarboxylase [1]. The chemistry of 2-thiazolines, including new methodologies for their preparation, and recent applications, such as their growing use in organic synthesis in the biological field and asymmetric catalysis as ligands has been recently reviewed [2]. 2-Aminothiazoles are known mainly as biologically active compounds with a broad range of activity and as intermediates in the synthesis of antibiotics and dyes [3]. Several papers have been published on the use of these compounds as antimicrobial [4–6], antifungal [7], anti-inflammatory activity [8,9], anesthetic [10] and antiviral drugs [11].

Plausible tautomeric equilibria of 2-aminothiazole are illustrated in Scheme 1 [12]. Numerous experimental studies, including infrared (IR) [13,14] ultraviolet (UV) [15,16], and nuclear magnetic resonance (^{1}H NMR) [17] spectra, indicate that 2-aminothiazole derivatives exist in solution preferentially in the amino form, based on the analysis of the reactivity data. Additionally, the pK_{BH+} values of a number of 2-aminothiazoles and their derivatives showed that these generally exist in the amino aromatic form and are protonated at the aza-nitrogen [18]. The amine/imine tautomeric equilibrium (Scheme 1A and B) in the isolated, mono-, di-, and trihydrate forms and dimmer of 2-aminothiazole and the effects of hydration or self assistance on the transition state structures corresponding to proton transfer from the amine to imine form, was calculated in the gas phase as well as in solution [19]. The results showed that the amine form is always the predominant tautomer, whereas the stability of the imine form is enhanced in polar solvents. Moreover, molecular orbital calculations were performed on 2-, 4- and 5-aminothiazoles using different calculation levels in order to study the 1,3-hydrogen transfer between the amino group and the endocyclic nitrogen atom or carbon atom at position five (Scheme 1) [10]. The effect of type and substituent position on the tautomeric equilibrium was also studied at the DFT and MP2 levels in the gas and solution phases [20].

Only few examples of molecules containing the thiazole ring and the phosphoramidate group are known. Although the pesticidal and herbicidal utility of phosphorus containing thiazoles and thiazolines have been reported in a patent [21], chemical structures and spectroscopic studies for these compounds were not investigated so far. Woollins et al. reported the synthesis of three phosphines containing aminothiazole [22]. Very recently, in the frame of our work concerning the synthesis and structural

* Corresponding authors. Tel.: +98 21 82884422 (K. Gholivand), +54 221 4259485; fax: +54 221 4714527 (C.O. Della Védova).
E-mail addresses: gholi_kh@modares.ac.ir (K. Gholivand), carlosdv@quimica.unlp.edu.ar (C.O. Della Védova).

0022-2860/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2009.12.018



Scheme 1. Tautomeric equilibrium of 2-aminothiazole.

study of carbacylamidophosphate compounds, a number of new species has been reported [23–25]. In this work, the synthesis of the first phosphonic diamide containing the 2-aminothiazole moiety is described. The X-ray structural determination, including the study of the conformational and tautomeric equilibria, has been performed by using experimental and quantum chemical methods.

2. Experimental

2.1. Materials and methods

All reagents and solvents were purchased from Merck. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker (Advance DRS) 500 MHz spectrometer. ^{1}H, ^{13}C and ^{31}P chemical shifts were obtained in DMSO-d_6 relative to TMS and 85% H_3PO_4 as external standards, respectively. IR spectrum was obtained using KBr pellets on a Shimadzu IR-60 model spectrometer. Elemental analysis was performed using a Heraeus CHN—O— RAPID and melting point was obtained with an Electrothermal instrument. Electronic spectra were recorded on a Shimadzu UV-2100 spectrometer. Mass spectrum was obtained on a MS Model 5973 Network apparatus at ionization potential of 70 eV.

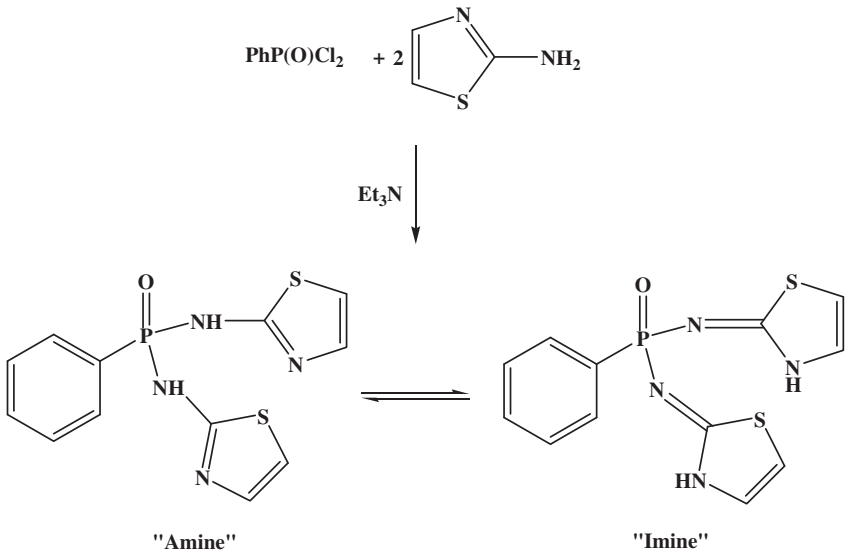
X-ray data of compound **1** were collected on a Bruker SMART 1000 CCD single crystal diffractometer with graphite monochromated MoKα radiation (k = 0.71073 Å). The structure was refined with SHELXL-97 [26] by full matrix least squares on F^2. The positions of hydrogen atoms were obtained from the difference Fourier map.

All quantum chemical calculations were performed with the GAUSSIAN 03 program package [27]. Gradient techniques were used for the geometry optimizations and vibrational calculations. The stationary structures are confirmed by ascertaining that all ground states have only real frequencies. The three-parameter B3LYP hybrid density functional theory method was used in conjunction with standard Gaussian basis sets up to the extended valence triple-ζ basis sets augmented with polarization and diffuse functions for both hydrogen and non-hydrogen atoms [6-311++G (3df,2p)]. This basis set has been shown to be near the basis set saturation limit when used with the B3LYP functional [28]. Additionally, the CBSB7 basis set was used. The CBSB7 has the form 6-311G(2d,d,p) and has been developed by Petersson and coworkers as a part of the complete basis set CBS-QB3 energy compound method [29,30]. The combination of the B3LYP functional in connection with the CBSB7 basis set was recommended for studying spectroscopic properties of related thiadiazole derivatives [31]. Single point energy calculations were performed for the B3LYP fully optimized geometry employing the MP2 treatment of the electronic correlation.

2.2. Chemical synthesis and characterization

The thiazolyl phosphonic diamide have been synthesized essentially by following the reaction procedure shown in Scheme 2. A mixture of 2-aminothiazole (0.817 g, 8 mmol) and triethylamine (0.801 g, 8 mmol) in 30 cm^3 of chloroform was added dropwise to a chloroform solution of phenylphosphonic dichloride (0.78 g, 4 mmol) at 0 °C. The mixture was subsequently allowed to warm to room temperature. After stirring for 2 days, the product was filtered off and then washed with $CHCl_3$, CH_3CN and H_2O. The compound was recrystallized from methanol. Yield: 80%, m.p. 220–222 °C. Compound **1** is soluble in DMSO and DMF, and less soluble in methanol and insoluble in $CHCl_3$, CH_2Cl_2, acetone and hydrocarbons. The product was characterized by ^{13}C, ^{31}P, ^{1}H NMR, IR, UV–vis absorption spectrum, mass-spectrometry, elemental analyses and X-ray diffraction.

Physical and spectroscopic data of the title compound are as below: Anal. Calc. for $C_{12}H_{11}N_4OPS_2$ (322.34): C, 44.71; H, 3.44; N, 17.38; found: C, 44.69; H, 3.43; N, 17.39%. ^{1}H NMR (500.14 MHz, DMSO-d_6, 25 °C): δ = 6.7 (d, $^{3}J_{H,H}$ = 3.9 Hz, 2H, thiazolyl), 7.1 (d, $^{3}J_{H,H}$ = 4.1 Hz, 2H, thiazolyl), 7.4 (m, $J_{P,H}$ = 3.6 Hz, $^{3}J_{H,H}$ = 7.5 Hz, 3Ar-H), 7.8 (dd, $^{3}J_{H,H}$ = 6.9 Hz, $^{3}J_{P,H}$ = 13.0 Hz, 2Ar-H), 10.7 (br, 2NH). $^{1}H\{^{31}P\}$ NMR, (500.13 MHz, DMSO-d_6, 25 °C): δ = 6.7 (d, $^{3}J_{H,H}$ = 4.1 Hz), 7.1 (d, $^{3}J_{H,H}$ = 4.1 Hz), 7.4 (m, $^{3}J_{H,H}$ = 7.5 Hz), 7.47



Scheme 2. Preparation of compound **1**.

(m, $^3J_{H,H}$ = 7.2 Hz), 7.8 (d, $^3J_{H,H}$ = 6.9 Hz), 10.7 (br). ^{13}C NMR (125.8 MHz, DMSO-d_6, 25 °C): 106.5, 109.0, 127.9 (d, $^3J_{P,C}$ = 13.6 Hz), 131.0 (d, $^2J_{P,C}$ = 9.7 Hz), 131.1 (d, $^4J_{P,C}$ = 2.1 Hz), 131.7, 133.4 ($^1J_{P,C}$ = 162.3 Hz), 138.0, 165.3. ^{31}P NMR (202.5 MHz, DMSO-d_6, 25 °C): 12.1 (m, J = 12.3 Hz). IR (KBr, cm^{-1}): 3407 cm^{-1} (w), 3020 (m), 2750 (s), 1565 (vs), 1528 (vs), 1471 (s), 1426 (s), 1312 (m), 1247 (w), 1179 (s), 1146 (s), 1111 (s), 1062 (w), 962 (s), 932 (m), 882 (w), 840 (s), 723 (m), 686 (s), 634 (s), 601 (m), 521 (m).

The electronic spectra of **1** were studied in the UV and visible regions in methanol and DMSO solutions. A very strong band at λ_{max} 302 and 305 nm was observed in the spectra of the compound, respectively, which is attributed to the π–π^* transition in the thiazole rings.

In the mass spectrum of **1** the molecular ion is present at m/z = 322 and the base peak is the aminothiazole fragment with m/z = 100. Relevant fragments originated from logical ruptures are (%): 322(8) M$^+$, 223(33), 183(21), 100(100), 73(24), 58(82), 45(20).

3. Results and discussion

3.1. Multinuclear NMR spectroscopy

By using experimental UV–vis and NMR techniques, Forlani et al. discussed the amide/imide tautomeric equilibrium of 2-aminoazoles derivatives (acetamidothiazole) in terms of external (hydrogen bond interactions, polarity of the medium, acidity) and internal (energy of isolated molecule, molecular geometry and intramolecular hydrogen bonding interactions, electronic distribution, presence of electron-withdrawing groups) parameters [32]. The equilibrium can be expected to be shifted towards the imide form when electron accepting substituents are bonded to the thiazole ring or to the exocyclic nitrogen, e.g., 2-*p*-tosyl-aminothiazole [33].

The more relevant ^{13}C NMR data of **1** are listed in Table 1. The two thiazole rings appear equivalent in the NMR spectra, and C1 and C4 present resonances at higher frequency (δ = 165.3 ppm) due to their location between sulfur and nitrogen atoms. Regarding the configuration of the geometric isomers around the *exo* C—N bond, two forms can be expected with the phosphorus atom in *cis* or *trans* position with respect to the endocyclic C—S bond. As

Table 1
^{13}C NMR chemical shift (in ppm) and coupling constant ($^nJ_{C,P}$ in Hz) for the title compound dissolved in DMSO-d_6.

Atom[a]	C1, C4	C2, C5	C3, C6	C7	C8, C12	C9, C11	C10
Chemical shift	165.3	109.0	131.7	133.4	131.0	127.9	131.1
$^nJ_{C,P}$				162.3 (n = 1)	9.7 (n = 2)	13.8 (n = 3)	2.1 (n = 4)

[a] For atom numbering see Fig. 1.

suggested by Contreras and coworkers [34] in the study of 2-aminobenzothiazole phosphorus amides, the geometric isomerism can be determined by the observation of the long range W-coupling constants in the ^{13}C NMR spectrum [34]. Thus, a detailed analysis of the $^4J_{C,P}$ coupling at C2 and C5 base of the sulfur (δ = 109.0 ppm) was performed. There is no visible phosphorus coupling with these carbons, which indicates that P is on the same side of endocyclic sulfur atom.

The ^{1}H NMR spectrum in DMSO-d_6 shows a characteristic broad signal at δ = 10.7 ppm for N—H. By analyzing the signals for the protons of the —HC=CH— group in the thiazole rings and some protons of phenyl group, two series of signals with different intensities (97:3%) were observed at room temperature (Table 2). From their relative chemical shifts and coupling constants measured for these signals, the presence of both amine/imine tautomers could be determined for the title compound. The equilibrium composition was determined by integration of the proper signals in the ^{1}H NMR spectrum. Comparison with the reported chemical shift values for 2-aminothiazole and 2-iminothiazoline indicates a composition ratio of 97:3% for the amine with respect to the imine form, respectively. As was early reported by Barone et al. [35] it is expected that the ring protons in 2-iminothiazolines should appear shifted to higher fields than those of 2-aminothiazoles. It was suggested that the identification of tautomers of 2-aminobenzothiazole in solution could be done by evaluating the chemical shift of the carbon atom bonded to the endocyclic nitrogen in the ^{13}C NMR spectrum [36]. In the present case C3 and C6 absorb at δ = 131.7 ppm, originating a broad signal precluding a further analysis of the tautomeric equilibrium. The overall analysis of ^{1}H and ^{13}C NMR spectra indicates the presence of the amine tautomer with minor, but clearly detectable, amounts of the imine form in DMSO solution at room temperature.

Table 2
^{1}H NMR data for tautomeric forms of compound **1** (DMSO-d_6). Chemical shift are given in ppm and coupling constant in Hz.

Atom[a]	H—C2, H—C5	H—C3, H—C6	H—C8, H—C12
Amine form	δ = 6.7 (d) $^3J_{H,H}$ = 3.9	δ = 7.1 (d) $^3J_{H,H}$ = 4.1	δ = 7.8 (dd) $^3J_{H,H}$ = 6.9, $^3J_{P,H}$ = 13.0
Imine form	δ = 6.5 (d) $^3J_{H,H}$ = 3.7	δ = 6.9 (d) $^3J_{H,H}$ = 3.7	δ = 7.7 (dd) $^3J_{H,H}$ = 6.9 Hz, $^3J_{P,H}$ = 13.0

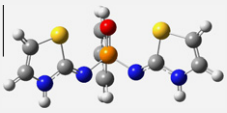
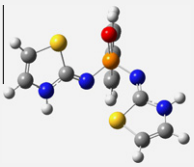
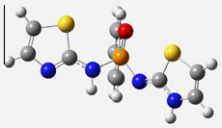
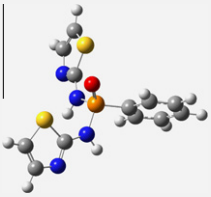
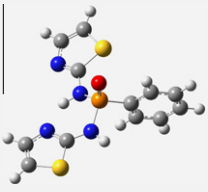
[a] For atom numbering see Fig. 1.

3.2. Vibrational spectra and quantum chemical calculations

The infrared spectrum of the title compound (solid in KBr pellets) is given as Supplementary material. Harmonic vibrational frequencies were obtained for the fully optimized geometries of both tautormers as well as for several plausible conformers of the title compound and compared with the experimental spectrum. The vibrational analysis enables the characterization of a given molecular structure as a true minimum on the molecular potential energy surface. The calculated harmonic frequencies are also useful for the assignment of the experimental vibrational data. The computed relative energy values for structures that result to be minima at B3LYP and MP2 methods are listed in Table 3. The B3LYP method computes a mixed structure with non-equivalent thiazole rings – in which one of endocyclic nitrogen atom in the thiazole ring is protonated, while the other thiazole group is deprotonated – as the most stable form for the gas phase (vacuum isolated) molecule. The two conformations (named as A and B in the molecular structures showed in Table 3) of the amine and imine tautomers are computed to be also stable forms, located at 1.09 (amine_A) and 2.44 kcal/mol (imine_A) higher in energy than the imine/amine form, respectively, at the B3LYP/CBSB7 level. As observed in Table 3, the order of the computed stability exhibits little effect on the basis sets. However, a different description is obtained by applying the MP2 method: a drastic change is obtained in the relative stability values. In this case the most stable tautomer corresponds to the amine, lying the imine form much higher in energy (11.6 kcal/mol for the imine_A form at the MP2/CBSB7 level). The structure with only one thiazole ring protonated has intermediate energy values, i.e. ca. 4.6 kcal/mol at the same level of calculation.

The computed vibrational frequencies for both tautomers are quite similar, precluding the unambiguous identification of each form based on the sole comparison of computed and experimental infrared spectra. Thus, a tentative assignment of the most prominent bands observed in the infrared spectrum was carried out by comparison with relevant data reported in the literature for related carbacylamidophosphates [24,37–44] and thiazolyl derivative species [45]. The infrared spectrum is dominated by very intense and broad absorptions at 1565 and 1528 cm^{-1}, assigned to the coupled symmetric and antisymmetric stretching of the exocyclic C=N bonds in the imine tautomer. Intense absorptions observed at 1179 and 962 cm^{-1} can be assigned with confidence to the characteristic P=O and P—N stretching modes, respectively. The high wavenumbers region of the infrared spectrum shows the presence of a strong absorption centered at 2750 cm^{-1} associated with the ν(C—H) modes on the thiazolyl ring. The ν(N—H) stretching modes, presumably due to the symmetric and antisymmetric group motions of the endocyclic N—H groups, appears at 3020 and 2990 cm^{-1}, respectively. A weak signal shifted at higher frequencies (at 3407 cm^{-1}) suggests that minor quantities of the amine form are also present in the solid. In effect, it is expected that the

Table 3
Relative energies (kcal/mol) calculated at the B3LYP and MP2 methods for plausible tautomers of *N,N′* bis(2-thiazolyl) phenylphosphonic diamide in different conformations.

Form	Molecular structure	B3LYP			MP2	
		6-31+G*	6-311++G**	CBSB7	6-311++G**	CBSB7
Imine_A		3.11	2.87	2.44	13.10	11.58
Imine_B		4.89	4.62	4.55	14.98	12.62
Imine/amine		0.00	0.00	0.00	5.11	4.57
Amine_A		0.58	0.68	1.09	0.00	0.00
Amine_B		1.12	0.92	1.49	2.00	1.42

ν(N—H) stretching mode for the exocyclic N—H group appear at higher frequency values than that of the endocyclic one.

3.3. Crystal structure

The title compound crystallizes from dried methanol at room temperature to give brown crystals. In order to unambiguously determine the tautomeric form present in the solid state, a single crystal X-ray diffraction structure determination was performed. The ORTEP of the final refined structure of **1** is shown in Fig. 1 and crystallographic data are given in Table 4. Selected bond lengths and bond angles found in this compound are listed in Table 5. The X-ray analysis of the orthorhombic crystals shows the tautomer with the N—H protons at the endocyclic nitrogen atoms and the conjugate system C=N—P=O. One of the sulfur atom and oxygen of the phosphoryl group are coplanar and close to each other (3.081 Å), and thus, an intramolecular S···O interaction is anticipated ($\sum r_{vdw}$ = 3.32 Å). The intermolecular non-bonded distances are shown in Fig. 2. The torsional angle S1—C1—N1—P1 [5.5(2)°] indicates that the phosphorus is nearly located on the same plane formed by the thiazolyl ring. The preferred conformation in the solid state of the studied molecule shows the phosphoryl group and both thiazolyl rings adopting a mutual synclinal orientation, with dihedral angles around the P—N1 and P—N3 bonds of 59.39(15) and −42.10(16) degrees, respectively. The P—N bond lengths (P1—N2 and P1—N3) are 1.6404(14) and 1.6406(14) Å, which falls between a single- (ca. 1.77 Å) and a double- (ca. 1.56 Å), nitrogen–phosphorous bond [46]. This intermediate bond distance indicates some degree of electronic delocalization, that is consistent with the corresponding distances found in previous reported phosphonic diamides [47]. Bond angles around phosphorus are characteristic of a distorted tetrahedral geometry. The P(1)—O(1) bond length (1.498(2) Å) are slightly longer than the P=O double bond length (1.45 Å) [46]. Bond lengths N4—C4 1.348(2) Å, N2—C1 1.352(2) Å, N3—C4 1.314(2) Å and N1—C1 1.298(2) Å show that the exocyclic N—C bonds present a strong double bond character, as expected for the imine tautomer. The C1—S1 [1.7767(16) Å] and C4—S2 [1.7545(17) Å] bond lengths are slightly longer than a single C—S bond (1.75 Å).

Table 4
Crystal data and structure refinement parameters of *N,N′* bis(2-thiazolyl) phenylphosphonic diamide.

Crystal data	
Chemical formula	$C_{12}H_{11}N_4OPS_2$
M_r	322.34
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, *Pbca*
a, *b*, *c* (Å)	8.2866(6), 11.4253(9), 29.314(2)
V (Å^3)	2775.4(4)
Z	8
Density (mg/m^3)	1.543
Absorption coefficient (mm^{-1})	0.499
F(0 0 0)	1328
Crystal size (mm^3)	0.6 × 0.4 × 0.08
Refinement method	Full-matrix least squares on F^2
Reflections collected	14,196
Data collection	
Data/restraints/parameters	3035/0/181
Goodness-of-fit on F^2	1.034
Final *R* indices [for 2699 refl. with $I > 2\text{sigma}(I)$]	R_1 = 0.0298, wR_2 = 0.0781
R indices (all data)	R_1 = 0.0347, wR_2 = 0.0816
Largest diff. peak and hole (e Å^{-3})	0.440 and −0.318
Theta range for data collection (°)	2.78–27.00
Index ranges	$-10 \leqslant h \leqslant 8$, $-14 \leqslant k \leqslant 14$, $-37 \leqslant l \leqslant 37$

For comparison purposes, calculated geometrical parameters at the B3LYP method using the extended 6-311++G(3df,2p) basis set are also included in Table 5. It is worthy to notice, that the most stable conformer of the imine tautomer, the imine_A form in Table 3, calculated for the vacuum isolated molecule at this level of approximation belongs to the point group of symmetry C_S, with the phenyl ring lying in the symmetry plane. In this conformation, both thiazolyl groups are equivalent with both C—S bonds eclipsing the P=O bond, with synperiplanar orientation around the C=N_{exo} bonds (see molecular structure displayed in Table 3). Thus, intermolecular interactions can play a major role not only in determining the tautomeric species present in the solid-phase but also affecting the conformational behavior.

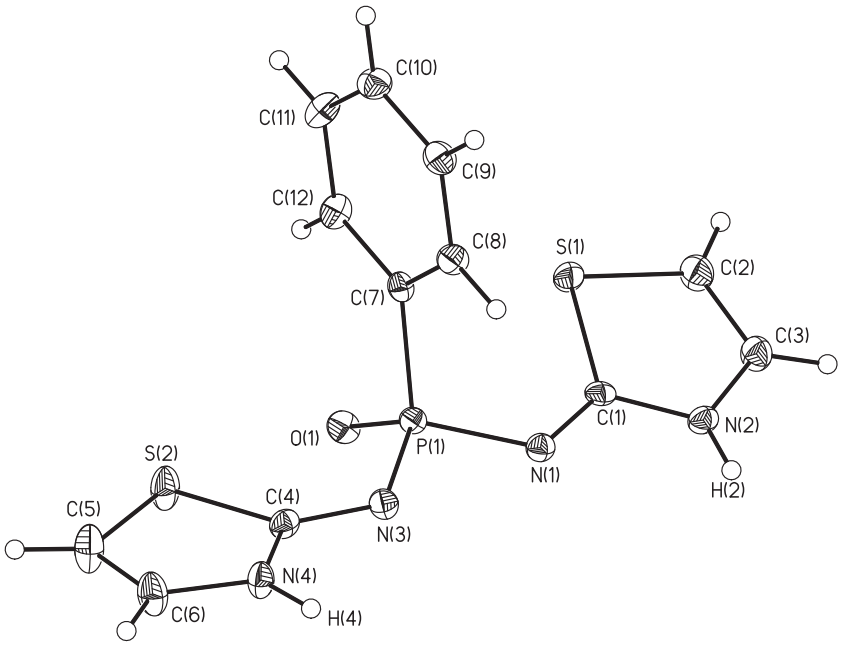


Fig. 1. Ortep view of compound **1** with atom numbering scheme, showing 50% probability ellipsoids.

Table 5
Experimental (X-ray) and calculated[a] [B3LYP/6-311++G(3df,2p)] selected bond lengths (Å) and angles (degrees) for *N,N′* bis(2-thiazolyl) phenylphosphonic diamide.

	Experimental	Calculated		Experimental	Calculated
Bond lengths					
P(1)—N(3)	1.6404(14)	1.656	N(3)—C(4)	1.314(2)	1.280
P(1)—N(1)	1.6406(14)		N(1)—C(1)	1.298(2)	
P(1)—C(7)	1.8111(17)	1.812	N(4)—C(4)	1.348(2)	1.371
S(2)—C(4)	1.7545(17)	1.789	N(2)—C(1)	1.352(2)	
S(1)—C(1)	1.7767(16)		N(4)—C(6)	1.383(2)	1.383
S(2)—C(5)	1.7435(19)	1.752	N(2)—C(3)	1.380(2)	
S(1)—C(2)	1.7402(18)		C(5)—C(6)	1.338(3)	1.338
P(1)—O(1)	1.4980(12)	1.491	C(2)—C(3)	1.337(2)	
Bond angles					
O(1)—P(1)—N(3)	115.87(7)	115.2	C(1)—N(2)—C(3)	116.09(14)	116.9
O(1)—P(1)—N(1)	116.07(7)		C(4)—N(4)—C(6)	115.73(14)	
O(1)—P(1)—C(7)	108.32(7)	112.2	N(1)—C(1)—N(2)	123.28(14)	122.3
N(3)—P(1)—C(7)	106.54(7)	104.6	N(3)—C(4)—N(4)	122.48(15)	
N(1)—P(1)—C(7)	108.80(7)		N(2)—C(1)—S(1)	107.76(11)	107.2
C(2)—S(1)—C(1)	91.47(8)	91.0	N(4)—C(4)—S(2)	108.79(12)	
C(5)—S(2)—C(4)	91.21(8)		C(2)—C(3)—N(2)	114.03(15)	113.0
C(1)—N(1)—P(1)	122.61(12)	123.7	C(5)—C(6)—N(4)	113.41(16)	
C(4)—N(3)—P(1)	122.32(12)		N(1)—C(1)—S(1)	128.96(13)	130.5
C(6)—C(5)—S(2)	110.84(14)	111.9	N(3)—C(4)—S(2)	128.73(13)	
C(3)—C(2)—S(1)	110.65(13)		N(3)—P(1)—N(1)	100.62(7)	103.9

[a] The most stable conformer in the imine form belongs to the point group of symmetry C_S.

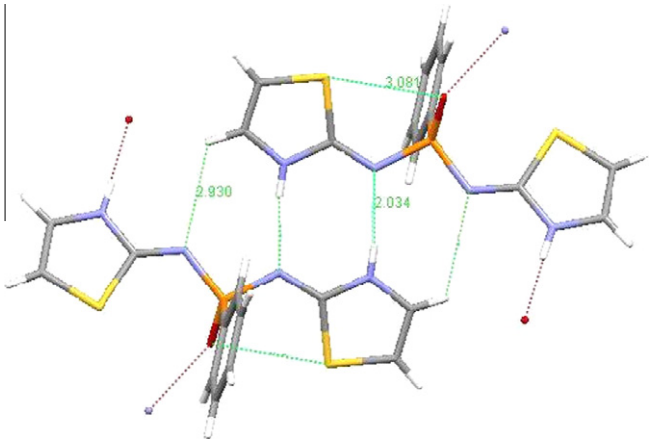


Fig. 2. Molecular structure of **1** showing hydrogen bonds interactions in ADAD–DADA arrangements.

It has been recognized that related 2-aminobenzothiazole derivatives are at the same time a base and a very reactive acid [48]. Interestingly the formation of ADAD–DADA type (A, acceptor site; D, donor site) centro-symmetric dimers is observed in the crystalline state. This cyclic eight-member motif is formed through NH···N3 (2.034 Å) and CH···N1 (2.930 Å) interactions, which are shorter than the corresponding sum of the van der Waals radii ($\sum r_{vdw}$ = 3.00 Å) (Fig. 2). It is also observed another intermolecular hydrogen bond through N2—H2N···O1—P1 (1.87 Å) interactions involving the phosphoryl group. Thus, the whole packing structure results in the two-dimensional polymeric chain showed in Fig. 3.

4. Conclusion

N,N′ bis(2-thiazolyl) phenylphosphonic diamide was prepared in good yield and purity by treating chloroform solutions of 2-aminothiazole and phenylphosphonic dichloride using a 2:1 M ratio in the presence of triethylamine as a Lewis base catalyst. The novel species was characterized by elemental analysis and mass-spectrometry and confirmed by UV, multinuclear (^{1}H, ^{13}C and ^{31}P) NMR and IR spectroscopy techniques. Structural properties were determined by using experimental techniques which include vibrational spectroscopy as well as X-ray diffraction analysis. The prominence of the amine tautomer was determined in DMSO

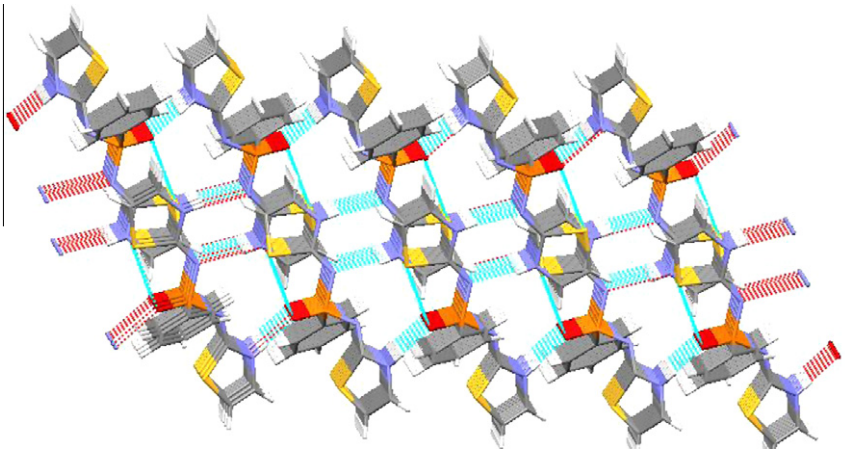


Fig. 3. A two-dimensional polymer obtained from intermolecular hydrogen bonds in the crystalline network of **1**.

solution at room temperature, with minor contribution of the imine form (3%). On the other hand, the crystalline solid consist of the imine tautomer – with the tautomeric proton attached to the endocyclic nitrogen atom –, and a preferred cisoid conformation – the dihedral angles around the N_{exo}—C bonds amount 5.5(2) and 10.9(2) degrees – with the phosphorous on the same side of the endocyclic sulfur atoms.

5. Supplementary data

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge crystallographic data center as supplementary publication No. CCDC-709116 ($C_{12}H_{11}N_4OPS_2$). Copies of the data can be obtained free of charge on application to CCDC.12 Union Road Cambridge CB2 1EZ UK (fax: C441223 336033; e-mail: deposit@ccdc.cam.ac.uk). ^1H, ^{13}C and ^{31}P NMR spectra for the title compound are given in Figs. S1–S8. Infrared and mass spectra are showed in Figs. S9–S11. The crystallographic data, condition and some feature of the structure are listed in Table S1 (Supporting information). Atomic coordinates, equivalent isotropic displacement coefficients, and anisotropic displacement parameters are given in Tables S1–S4. Hydrogen coordinates and the whole geometrical parameters derived from the X-ray analysis are given in table format (Tables S5–S7).

References

[1] H. Beyer, Organic Chemistry, Verlag Harry Deutsch, Frankfurt-um-Main and Zürich, 1963, pp. 609.
[2] A.-C. Gaumont, M. Gulea, J. Levillain, Chem. Rev. 109 (2009) 1371.
[3] U.G. Ibatullin, T.F. Petrushina, L.Y. Leitis, I.Z. Minibaev, B.O. Logvin, Khim. Geterotsitl. Soedin. (1993) 715.
[4] A. Göblyös, S.N. Santiago, D. Pietra, T. Mulder-Krieger, J. von Frijtag Drabbe Künzel, J. Brussee, A.P. Ijzerman, Bioorg. Med. Chem. 13 (2005) 2079.
[5] N.J. Datta, R.C. Khunt, A.R. Parikh, Indian J. Chem. B Org. Chem. Med. Chem. B 41 (2002) 433.
[6] P.C. Hang, J.F. Honek, Bioorg. Med. Chem. Lett. 15 (2005) 1471.
[7] P. Beuchet, M. Varache-Lembège, A. Neveu, J.-M. Léger, J. Vercauteren, S. Larrouture, G. Deffieux, A. Nuhrich, Eur. J. Med. Chem. 34 (1999) 773.
[8] A. Geronikaki, G. Theophilidis, Eur. J. Med. Chem. 27 (1992) 709.
[9] A. Geronikaki, P. Vicini, N. Dabarakis, A. Lagunin, V. Poroikov, J. Dearden, H. Modarresi, M. Hewitt, G. Theophilidis, Eur. J. Med. Chem. 44 (2009) 473.
[10] C. Papadopoulou, A. Geronikaki, D. Hadjipavlou-Litina, Farmaco 60 (2005) 969.
[11] A. Kreutzberger, H. Schimmelpfennig, Arch. Pharm. 314 (1981) 385.
[12] A.A. Mohamed, A.W. El-Harby, J. Mol. Struct. (THEOCHEM) 849 (2008) 52.
[13] J. Chouteau, G. Davidovics, J. Metzger, A. Bonzom, Spectrochim. Acta 22 (1966) 19.
[14] C.L. Angyal, R.L. Werner, J. Chem. Soc. (1952) 2911.
[15] W. Wilson, R. Woodger, J. Chem. Soc. (1955) 2943.
[16] D. Suciu, Z. Györfi, Rev. Roum. Chim. 18 (1973) 1777.
[17] M. Sélim, G. Martin, M. Sélim, Bull. Soc. Chim. Fr. (1968) 3268.
[18] L. Forlani, P.D. Maria, Chem. Soc. Perkin Trans. 2 (1982) 535.
[19] Y. Zeng, Y. Ren, Int. J. Quantum Chem. 107 (2007) 247.
[20] T.A. Mohamed, A.M. Mustafa, W.M. Zoghaib, M.S. Afifi, R.S. Farag, Y. Badr, J. Mol. Struct. (THEOCHEM) 868 (2008) 27.
[21] N.N. Melnikov, A.F. Grapov, L.V. Razvodovskaya, P.V. Popov, A.S. Sedykh, G.K. Shapovalova, G.M. Abelentseva, T.A. Siforova, T.A. Nikolaeva, V.V. Galitsina, L.D. Stonov, L.A. Bakumenko, US Patent 4188382, Vsesojuzny Nauchno, Moscow 6, USSR, 1980, pp. 8.
[22] H.L. Milton, M.V. Wheatley, A.M.Z. Slawin, J.D. Woollins, Inorg. Chim. Acta 358 (2005) 1393.
[23] K. Gholivand, H. Mostaanzadeh, T. Koval, M. Dusek, M.F. Erben, C.O. Della Védova, Acta Crystallogr. B 65 (2009) 502.
[24] K. Gholivand, Z. Shariatinia, S.M. Mashhadi, F. Daeepour, N. Farshidnasab, H.R. Mahzouni, N. Taheri, S. Amiri, S. Ansar, Polyhedron 28 (2009) 307.
[25] K. Gholivand, Z. Shariatinia, S. Ansar, S.M. Mashhadi, F. Daeepour, Struct. Chem. 20 (2009) 481.
[26] G. Sheldrick, Acta Crystallogr. A A64 (2008) 112.
[27] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Revision B.04 ed., Gaussian, Inc., Pittsburgh, PA, 2003.
[28] A.C. Scheiner, J. Baker, J.W. Andzelm, J. Comput. Chem. 18 (1997) 775.
[29] J.J.A. Montgomery, M.J. Frisch, J.W. Ochterski, G.A. Petersson, J. Chem. Phys. 110 (1999) 2822.
[30] A.C. Larry, R. Krishnan, W.T. Gary, A.P. John, J. Chem. Phys. 94 (1991) 7221.
[31] D. Glossman-Mitnik, A. Márquez-Lucero, J. Mol. Struct. (THEOCHEM) 548 (2001) 153.
[32] L. Forlani, E. Mezzina, C. Boga, M. Forconi, Eur. J. Org. Chem. 2001 (2001) 2779.
[33] L. Forlani, Gazz. Chim. Ital. 111 (1981) 159.
[34] Z. García-Hernández, A. Flores-Parra, J.M. Grevy, Á. Ramos-Organillo, R. Contreras, Polyhedron 25 (2006) 1662.
[35] R. Barone, M. Chanon, R. Gallo, Aminothiazoles and their Derivatives in the Chemistry of Heterocyclic Compounds, vol. 34, Part 2, Wiley, New York, 1979.
[36] E.C.-G. Agueda, R.-O. Angel, H.-D. Julio, N.-M. Jonathan, C. Rosalinda, E.C.-B. Silvia, Heteroatom Chem. 11 (2000) 392.
[37] K. Gholivand, C.O. Della Védova, A. Anaraki Firooz, A. Madani Alizadehgan, M.C. Michelini, R. Pis Diez, J. Mol. Struct. 750 (2005) 64.
[38] K. Gholivand, A.M. Alizadehgan, S. Arshadi, A.A. Firooz, J. Mol. Struct. 791 (2006) 193.
[39] K. Gholivand, C.O. Della Védova, M.F. Erben, F. Mojahed, A.M. Alizadehgan, J. Mol. Struct. 840 (2007) 66.
[40] K. Gholivand, C.O. Della Védova, M.F. Erben, H.R. Mahzouni, Z. Shariatinia, S. Amiri, J. Mol. Struct. 874 (2008) 178.
[41] A.G. Iriarte, M.F. Erben, K. Gholivand, J.L. Jios, S.E. Ulic, C.O. Della Védova, J. Mol. Struct. 886 (2008) 66.
[42] K. Gholivand, A. Madani Alizadehgan, F. Mojahed, P. Soleimani, Polyhedron 27 (2008) 1639.
[43] K. Gholivand, M. Pourayoubi, Z. Shariatinia, H. Mostaanzadeh, Polyhedron 24 (2005) 655.
[44] K. Gholivand, M. Pourayoubi, Z. Anorg. Allg. Chem. 630 (2004) 1330.
[45] R. Yoda, Y. Matsushima, Heterocycles 26 (1987) 2887.
[46] D.E.C. Corbridge, Phosphorus: An Outline of Its Chemistry, Biochemistry and Technology, fifth ed., Elsevier, Amsterdam, 1995.
[47] R. Murugavel, R. Pothiraja, New J. Chem. 27 (2003) 968.
[48] E.V. Bakhmutova, H. Nöth, R. Contreras, B. Wrackmeyer, Z. Anorg. Allg. Chem. 627 (2001) 1846.