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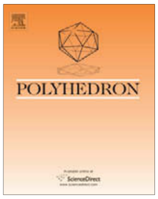

The influence of the substituent [PhNHNH– and EtN(NH_2)–] on the *N*-thiophosphorylated thiosemicarbazides RC(S)NHP(S)(O*i*Pr)$_2$ crystal design

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ABSTRACT

Two *N*-thiophosphorylated thiosemicarbazides of the common formula RC(S)NHP(S)(O*i*Pr)$_2$ [R = PhNHNH- (**1**); EtN(NH_2)- (**2**)] have been synthesized and characterized by IR, ^{1}H and ^{31}P spectroscopy, and the single crystal X-ray diffraction method. Single crystal X-ray diffraction studies showed the thiosemicarbazides form both intra- and intermolecular hydrogen bonds, which in turn lead to polymeric chain formation. Moreover, according to the X-ray data of the phenylsubstituted thiosemicarbazide, the formation of intermolecular H···η^6-phenyl interactions were established.

1. Introduction

N-(Thio)phosphorylated (thio)amides RC(X)NHP(Y)R′$_2$ and (thio)ureas RR′NC(X)NHP(Y)R″$_2$ (X = O, S) have been intensively studied [1,2]. The interest is caused not only from the fact that these compounds show a wide variety of complexes with various metal cations but also from the potential of these amidophosphates as agents for extraction and transporting different cations, anions and organic molecules [3], and as ligands in metal complexes used as single source precursors for thin films, nanocrystals and semiconductors [4].

On the other hand, thiosemicarbazides and their derivatives are very attractive compounds among NS donor compounds because of the large number useful biological properties, particularly their antitumor activity [5,6]. Since 4,4′,4″-phosphinylidynetrisemicarbazide showed the confirmed activity in Walker carcinosarcoma [7] the preparation of additional hydrazine compounds as potential antitumor agents, particularly (thio)phosphorylated derivatives, was encouraged [8–10]. Both compounds reported, herein, are structurally related to agents possessing antimicrobial and anticancer activities [8,10].

Herein, we report two *N*-thiophosphorylated thiosemicarbazides PhNHNHC(S)NHP(S)(O*i*Pr)$_2$ (**1**) and EtN(NH_2)C(S)NHP(S)(O*i*Pr)$_2$ (**2**). Compound **1** was described by us earlier [11] and in this work we present the X-ray structure investigation of it in comparison with **2**.

2. Experimental

2.1. Synthesis

Thiosemicarbazide **1** was synthesized according to the previously described method [9]. Compound **2** was synthesized similarly to **1**: a solution of ethylhydrazine (5 mmol, 0.30 g) in anhydrous CH_2Cl_2 (15 mL) was treated under vigorous stirring with a solution of (*i*PrO)$_2$P(S)NCS (5.5 mmol, 1.31 g) in the same solvent. The mixture was stirred for 2 h. The solvent was removed in a vacuum, and the product was purified by recrystallization from a 1:5 (v/v) mixture of methylene chloride and *n*-hexane.

Compound **1**: ^{1}H NMR ($CDCl_3$): $\delta = 1.35–1.40$ (m, 12H, CH_3), 4.92 (d. sept, $^3J_{POCH} = 10.6$ Hz, $^3J_{H,H} = 6.2$ Hz, 2H, OCH), 6.34 (s, 1H, PhNH), 6.84–6.92 (m, 2H, *o*-H, Ph), 6.96–7.05 (m, 1H, *p*-H, Ph), 7.24–7.32 (m, overlapped with the solvent signal, *m*-H, Ph), 8.00 (s, 1H, C(S)NHN), 8.23 (d, 1H, $^2J_{PNH} = 13.9$ Hz, P(S)NH), 9.44 (d, $^4J_{PNH} = 5.6$ Hz, C(S)NHN, minor form) ppm. ^{31}P NMR ($CDCl_3$): $\delta = 53.5$ (br t, $^3J_{POCH} = 9.8$ Hz, 1P), 58.5 (q, $^2J_{PNH} = {}^3J_{POCH} = 12.2$ Hz, 1.9P) ppm. IR: $\nu = 624$ (P=S), 1000, 1010 (POC), 1528 (S=C–N), 3224, 3288 (NH) cm^{-1}.

Compound **2**: Yield: 1.27 g (85%). M.p. 97 °C. ^{1}H NMR ($CDCl_3$): $\delta = 1.25$ (t, $^3J_{H,H} = 7.2$ Hz, 3H, CH_3, Et), 1.37 (d, $^3J_{H,H} = 6.2$ Hz, 12H, CH_3, O*i*Pr), 3.91 (br s, 2H, NH_2), 4.16 (q, $^3J_{H,H} = 7.1$ Hz, 2H, CH_2, Et), 4.94 (d. sept, $^3J_{POCH} = {}^3J_{H,H} = 6.2$ Hz, 2H, OCH), 8.98 (br s, 1H, P(S)NH) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 54.1$ (1P), 59.3 (3.5P) ppm. IR: $\nu = 653$ (P=S), 981, 998, 1020 (POC), 1488 (S=C–N), 1627, 3106, 3173, 3208, 3247, 3323 (NH + NH_2) cm^{-1}. *Anal.* Calc. for $C_9H_{22}N_3O_2PS_2$ (299.39): C, 36.11; H, 7.41; N, 14.04. Found: C, 36.18; H, 7.34; N, 14.10%.

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2.2. Physical measurements

Infrared spectra (Nujol) were recorded with a Specord M-80 spectrometer in the range 400–3600 cm^{-1}. NMR spectra were obtained on a Varian Unity-300 NMR spectrometer at 25 °C. ^{1}H and ^{31}P NMR spectra were recorded at 299.948 and 121.420 MHz, respectively. Chemical shifts are reported with reference to $SiMe_4$ (^{1}H) and H_3PO_4 (^{31}P). Elemental analyses were performed on a Perkin–Elmer 2400 CHN microanalyser.

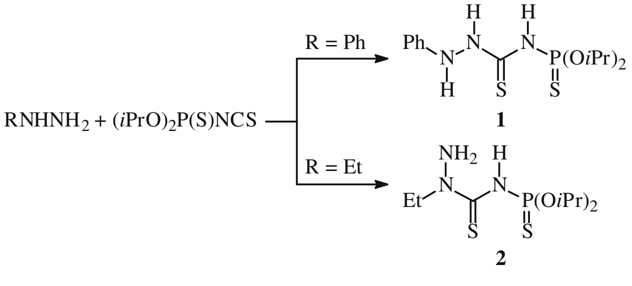
2.3. Crystal structure determination and refinement

The X-ray data were collected on a STOE IPDS-II diffractometer with graphite-monochromatized Mo Kα radiation generated by a fine-focus X-ray tube operated at 50 kV and 40 mA. The images were indexed, integrated and scaled using the X-Area data reduction package [12]. Data were corrected for absorption using the PLATON program [13]. The structure was solved by direct methods using the SHELXS-97 program [14] and refined first isotropically and then anisotropically using SHELXL-97 [14]. Hydrogen atoms were revealed from $\Delta\rho$ maps and those bonded to C were refined using a riding model. H atoms bonded to N were freely refined.

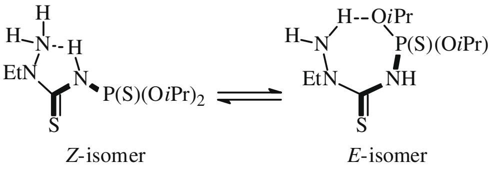
3. Results and discussion

Thiosemicarbazide **1** was synthesized according to the previously described method [9]. Compound **2** was synthesized similar to **1** by treatment of ethylhydrazine isothiocyanate $(iPrO)_2P(S)NCS$ (Scheme 1). Their compositions were successfully proved by microanalysis data. Condensations of isocyanates with arylsubstituted hydrazines are reported to yield 1-substituted semicarbazides [15]. The reaction between monoalkylhydrazines and isocyanates, however, gives 2-substituted alkyl semicarbazides [16] due to the greater nucleophilic character of the secondary amine groups.

There are absorption bands for the NH_2 group in the IR spectrum of **2**. This confirms the isothiocyanate addition to the substituted nitrogen atom of the parent hydrazine. The $^{31}P\{^{1}H\}$ NMR spectrum of **2** contains two signals at 54.1 and 59.3 ppm. The ratio of the integrated intensities at 25 °C is ~1:3.5. When the crystalline material is dissolved in $CDCl_3$ two lines in the $^{31}P\{^{1}H\}$ NMR spectrum indicate that the equilibrium reaction shown in Scheme 2 is slow on the NMR timescale. We suppose that in a solution of **2** both



Scheme 1. Preparation of **1** and **2**.



Scheme 2.

Table 1
Crystal data, data collection and refinement details for **1** and **2**.

	1	**2**
Empirical formula	$C_{13}H_{22}N_3O_2PS_2$	$C_9H_{22}N_3O_2PS_2$
Formula weight	347.43	299.39
Temperature (K)	173(2)	173(2)
Radiation Mo Kα (Å)	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$
a (Å)	6.1221(6)	22.7946(16)
b (Å)	8.0835(8)	10.1656(5)
c (Å)	17.8130(18)	14.7330(10)
α (°)	99.261(8)	90
β (°)	91.141(8)	113.301(5)
γ (°)	94.760(8)	90
V (Å^3)	866.54(15)	3135.5(3)
Z	2	8
D_{calc} (Mg m^{-3})	1.332	1.268
Absorption correction, μ (cm^{-1})	4.06	4.38
$F(000)$	368	1280
Crystal size (mm^3)	0.34 × 0.19 × 0.09	0.27 × 0.26 × 0.24
Recording range, θ_{max} (°)	3.34–25.65	2.46–25.93
Number of recorded reflections	10372	17948
Number of recorded independent reflections [R_{int}]	3246 [0.0476]	3049 [0.0377]
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0308, wR_2 = 0.0779	R_1 = 0.0261, wR_2 = 0.0682
R indices (all data)	R_1 = 0.0373, wR_2 = 0.0802	R_1 = 0.0284, wR_2 = 0.0694
S	1.015	1.026

Table 2
Selected bond lengths (Å), and bond and torsion angles (°) for **1**.

Bond lengths			
P(1)–O(1)	1.5844(12)	S(1)–C(1)	1.6848(16)
P(1)–O(2)	1.5805(12)	N(1)–C(1)	1.369(2)
P(1)–N(1)	1.6917(15)	N(2)–C(1)	1.346(2)
P(1)–S(2)	1.9249(6)	N(2)–N(3)	1.401(2)
Bond angles			
O(2)–P(1)–O(1)	103.80(6)	C(1)–N(1)–P(1)	126.79(12)
O(2)–P(1)–N(1)	106.39(7)	C(1)–N(2)–N(3)	120.84(14)
O(1)–P(1)–N(1)	94.32(7)	N(2)–C(1)–N(1)	115.04(14)
O(2)–P(1)–S(2)	116.17(5)	N(2)–C(1)–S(1)	120.35(12)
O(1)–P(1)–S(2)	116.67(5)	N(1)–C(1)–S(1)	124.58(13)
N(1)–P(1)–S(2)	116.65(6)		
Torsion angles			
O(2)–P(1)–N(1)–C(1)	71.73(15)	N(3)–N(2)–C(1)–S(1)	178.56(12)
O(1)–P(1)–N(1)–C(1)	177.49(14)	P(1)–N(1)–C(1)–N(2)	163.61(12)
S(2)–P(1)–N(1)–C(1)	−59.71(15)	P(1)–N(1)–C(1)–S(1)	−18.3(2)
N(3)–N(2)–C(1)–N(1)	−3.3(2)		

Table 3
Selected bond lengths (Å), and bond and torsion angles (°) for **2**.

Bond lengths			
P(1)–O(1)	1.5754(9)	S(2)–C(1)	1.6750(14)
P(1)–O(2)	1.5772(10)	N(1)–C(1)	1.3694(18)
P(1)–N(1)	1.6716(11)	N(2)–C(1)	1.3512(17)
P(1)–S(1)	1.9329(5)	N(2)–N(3)	1.4187(17)
Bond angles			
O(1)–P(1)–O(2)	105.29(5)	C(1)–N(1)–P(1)	127.86(10)
O(1)–P(1)–N(1)	105.55(6)	C(1)–N(2)–N(3)	117.29(11)
O(2)–P(1)–N(1)	93.85(6)	N(2)–C(1)–N(1)	113.88(12)
O(1)–P(1)–S(1)	115.52(4)	N(2)–C(1)–S(2)	123.83(10)
O(2)–P(1)–S(1)	115.79(4)	N(1)–C(1)–S(2)	122.29(10)
N(1)–P(1)–S(1)	118.08(5)		
Torsion angles			
O(1)–P(1)–N(1)–C(1)	68.99(13)	N(3)–N(2)–C(1)–S(2)	174.79(10)
O(2)–P(1)–N(1)–C(1)	−176.03(12)	P(1)–N(1)–C(1)–N(2)	−172.63(10)
S(1)–P(1)–N(1)–C(1)	61.95(13)	P(1)–N(1)–C(1)–S(2)	7.31(18)
N(3)–N(2)–C(1)–N(1)	−5.27(18)		