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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 ($CDCl_3$): δ = 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 ($CDCl_3$): δ = 53.5 (br t, $^3J_{POCH}$ = 9.8 Hz, 1P), 58.5 (q, $^2J_{PNH}$ = $^3J_{POCH}$ = 12.2 Hz, 1.9P) ppm. IR: ν = 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 ($CDCl_3$): δ = 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 ($CDCl_3$): δ = 54.1 (1P), 59.3 (3.5P) ppm. IR: ν = 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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