

## Synthesis and spectroscopic study of two new phosphorus compounds: (2-Cl-C<sub>6</sub>H<sub>4</sub>O)(2-Cl-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NH)<sub>2</sub>P(O) and (C<sub>6</sub>H<sub>5</sub>)(4-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>NH)<sub>2</sub>P(O)

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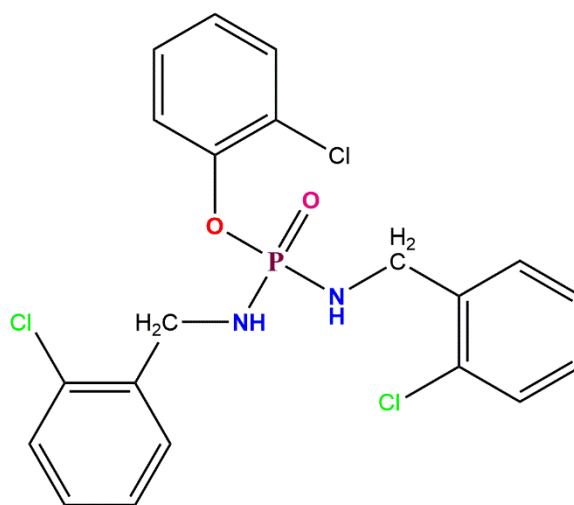
**Abstract** – The phosphorus signals of (2-Cl-C<sub>6</sub>H<sub>4</sub>O)(2-Cl-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NH)<sub>2</sub>P(O) diamidophosphoester (**I**), and (C<sub>6</sub>H<sub>5</sub>)(4-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>NH)<sub>2</sub>P(O) phosphonicamide (**II**) appear at 13.30 and 8.62 ppm, respectively. The NH protons of (**I**) reveal a doublet of triplets with apparent coupling constants of 7.3 and 14.6 Hz (due to vicinal hydrogen-hydrogen and geminal phosphorus-hydrogen couplings). The phosphorus-carbon coupling constants <sup>n</sup>J<sub>PC</sub> (n = 2 and 3) in (**I**) and <sup>m</sup>J<sub>PC</sub> (m = 1, 2, 3 and 4) in (**II**) were evaluated.

**Keywords:** Diamidophosphoester, Phosphonicamide, Phosphorus-carbon coupling constant, Phosphorus-hydrogen coupling constant

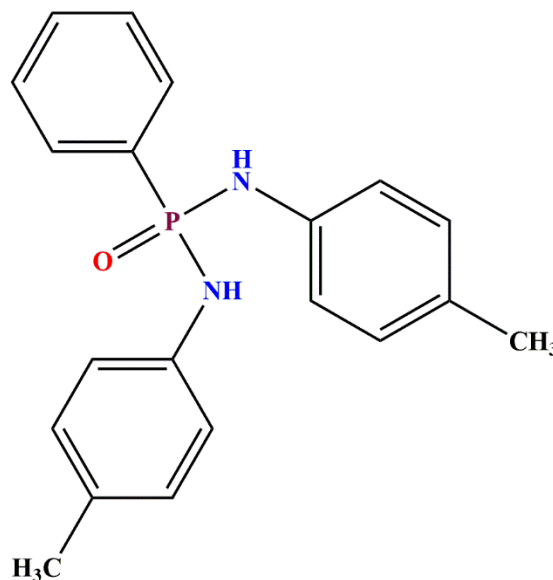
### 1. Introduction

The phosphorus-nitrogen compounds, typically amidophosphoesters/phosphonicamides, are well-known for different applications in flame retardants, and manufacturing of drugs [1–3]. Nuclear magnetic resonance (NMR) is a beneficial technique to study of these compounds, due to the existence of NMR-active nuclei (<sup>31</sup>P, <sup>1</sup>H, <sup>13</sup>C). Moreover, NMR spin-spin coupling constants are used to prove the assignment of signals, and analysis related to conformation/configuration [4].

In this work, the synthesis and spectroscopic characterization of two new phosphorus compounds, belonging to diamidophosphoester and phosphonicamide families are investigated. These compounds are (2-Cl-C<sub>6</sub>H<sub>4</sub>O)(2-Cl-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NH)<sub>2</sub>P(O) (Scheme 1), and (C<sub>6</sub>H<sub>5</sub>)(4-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>NH)<sub>2</sub>P(O) (Scheme 2). Some topics related to the phosphorus-hydrogen and phosphorus-carbon coupling constants were issued.



Scheme 1. Chemical structure of (2-Cl-C<sub>6</sub>H<sub>4</sub>O)(2-Cl-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NH)<sub>2</sub>P(O).



Scheme 2. Chemical structure of (C<sub>6</sub>H<sub>5</sub>)(4-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>NH)<sub>2</sub>P(O).

### 2. Experimental

#### 2.1. Synthesis and Identification:

### Synthesis of (2-Cl-C<sub>6</sub>H<sub>4</sub>O)(2-Cl-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NH)<sub>2</sub>P(O) (I):

To a solution of (2-Cl-C<sub>6</sub>H<sub>4</sub>O)Cl<sub>2</sub>P(O) in dry CHCl<sub>3</sub>, a solution of 2-chlorobenzylamine and triethylamine in the same solvent (1:2:2 mole ratio) was added dropwise and stirred for 4 hours. Initial temperature is 0 °C (ice-bath) to start the reaction, which warms to room temperature during the reaction time. After removing the solvent (under a vacuum), the resulting solid was washed with distilled water to separate the [(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NH]Cl salt. The product was dried in air, and the solid substance was recrystallized in a mixture of chloroform and normal hexane.

<sup>31</sup>P{<sup>1</sup>H}-NMR (121.78 MHz, DMSO-*d*<sub>6</sub>, 295.6 K): δ = 13.30 (s) (Fig. 1). <sup>13</sup>C{<sup>1</sup>H}-NMR (75.65 MHz, DMSO-*d*<sub>6</sub>, 296.2 K, TMS): δ = 42.42 (s), 122.32 (d, *J* = 3.0 Hz), 125.07 (d, *J* = 6.8 Hz), 125.43 (s), 127.38 (s), 128.43 (s), 128.70 (s), 129.19 (s), 129.22 (s), 130.58 (s), 132.01 (s), 138.17 (d, *J* = 6.0 Hz), 148.01 (d, *J* = 5.9 Hz) (Fig. 2). <sup>1</sup>H-NMR (300.81 MHz, DMSO-*d*<sub>6</sub>, 295.5 K, TMS): δ = 4.26 (dd, *J* = 11.7 Hz, 7.2 Hz, 4H, CH<sub>2</sub>), 5.80 (dt, *J* = 14.6 Hz, 7.3 Hz, 2H, NH), 7.40 (m, 12H) (Fig. 3). IR (KBr, cm<sup>-1</sup>): 3273, 3161, 3068, 3005, 2919, 1586, 1481, 1437, 1246, 1200, 1122, 1043, 1011, 932, 817, 748, 687 (Fig. 4).

### Synthesis of (C<sub>6</sub>H<sub>5</sub>)(4-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>NH)<sub>2</sub>P(O) (II):

To a solution of (C<sub>6</sub>H<sub>5</sub>)Cl<sub>2</sub>P(O) in dry CHCl<sub>3</sub>, a solution of *p*-toluidine in the same solvent (1:4 mole ratio) was added dropwise and stirred for 4 hours. Initial temperature to start the reaction is 0 °C (ice-bath), which warms to room temperature during the reaction time. After removing the solvent (under a vacuum), the resulting solid was washed with distilled water to separate the [4-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>NH<sub>3</sub>]Cl salt. The product was dried in air, and the solid substance was recrystallized in a mixture of chloroform and normal hexane.

<sup>31</sup>P{<sup>1</sup>H}-NMR (121.78 MHz, DMSO-*d*<sub>6</sub>, 295.5 K): δ = 8.62 (s) (Fig. 5). <sup>13</sup>C{<sup>1</sup>H}-NMR (75.65 MHz, DMSO-*d*<sub>6</sub>, 296.1 K, TMS): δ = 20.67 (s), 118.28 (d, *J* = 6.7 Hz), 128.81 (d, *J* = 13.5 Hz), 129.33 (s), 129.61 (s), 132.07 (d, *J* = 10.2 Hz), 132.10 (d, *J* ≈ 1.9 Hz, overlapped), 133.56 (d, *J* = 152.7 Hz), 140.05 (s) (Fig. 6). <sup>1</sup>H-NMR (300.81 MHz, DMSO-*d*<sub>6</sub>, 295.3 K, TMS): δ = 2.18 (s, 3H, CH<sub>3</sub>), 6.95 (d, *J* = 8.4 Hz, 4H), 7.08 (d, *J* = 8.4 Hz, 4H), 7.47–7.59 (m, 3H), 7.80–7.87 (m, 4H, CH & NH) (Fig. 7). IR (KBr, cm<sup>-1</sup>): 3241, 3179, 3001, 2615, 1616, 1579, 1515, 1443, 1385, 1282, 1235, 1174, 1125, 1029, 932, 811, 747, 697 (Fig. 8).

## 3. Results and discussion

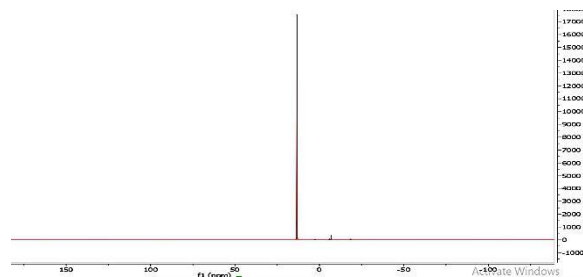
### 3.1. NMR spectroscopy:

The phosphorus signals (<sup>31</sup>P{<sup>1</sup>H}-NMR) appear at 13.30 and 8.62 ppm for **I** and **II**, respectively.

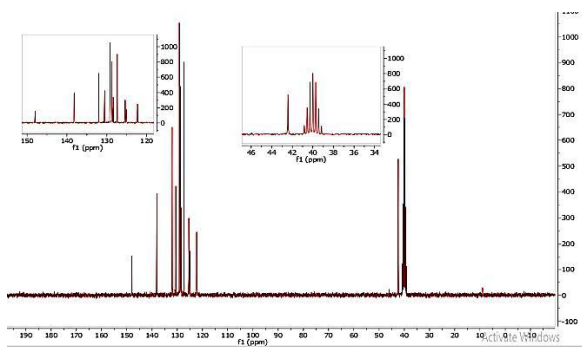
In the <sup>1</sup>H-NMR spectrum of **I**, the NH proton appears at 5.80 ppm with a *dt* (doublet of triplets) fine structure, due to geminal (<sup>2</sup>*J*) phosphorus-hydrogen and vicinal hydrogen-hydrogen (<sup>3</sup>*J*) couplings (14.6 and 7.3 Hz). The signal at 4.26 ppm (doublet of doublets) associates to the CH<sub>2</sub> protons with apparent *J* values of 11.7 and 7.2 Hz. These values associate to the couplings with phosphorus nucleus and the NH proton, respectively. For **II**, the peak of NH proton is mixed with the peak of two aromatic protons (belonging to the phenyl group directly attached to phosphorus).

The *ipso*-carbon atom of 2-Cl-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub> moiety and the *ipso/ortho*-carbon atoms of 2-Cl-C<sub>6</sub>H<sub>4</sub>O group show couplings with phosphorus. These carbon atoms, respectively with a three and two/three bonds separation from phosphorus reveal doublets in the <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum. Typically, the doublet at 148.01 ppm (<sup>2</sup>*J*<sub>PC</sub> = 5.9 Hz) associates to the *ipso*-carbon atom of the 2-Cl-C<sub>6</sub>H<sub>4</sub>O moiety. This coupling constant is comparable with the one observed for an analogous compound (C<sub>6</sub>H<sub>5</sub>O)<sub>2</sub>(4-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-R-(+)CH(CH<sub>3</sub>)NH)P(O) with the calculated values of 6.5 Hz for both signals at 151.10 and 151.23 ppm. The reason for the observation of two signals in literature compound is the presence of chiral fragment and observation of two sets of carbon signals related to two diastereotopic C<sub>6</sub>H<sub>5</sub>O groups [5].

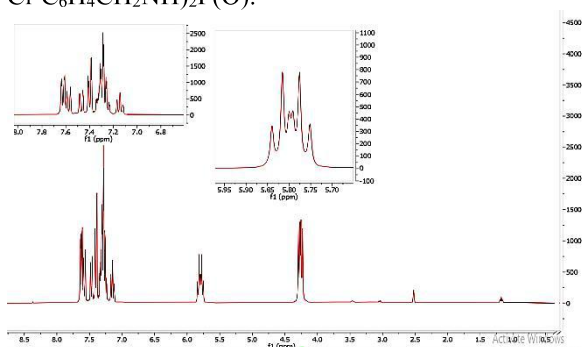
All carbon atoms of phenyl group directly attached to phosphorus in compound **II** show couplings with phosphorus (<sup>1</sup>*J*, <sup>2</sup>*J*, <sup>3</sup>*J* and <sup>4</sup>*J*). The doublet centred at 133.56 (<sup>1</sup>*J* = 152.7 Hz) is related to the *ipso*-carbon atom. The signal of *para*-carbon atom (about 132.10 ppm) is mixed with the neighboring signal, and from the shapes of these two overlapped signals the <sup>4</sup>*J* value is estimated to be about 1.9 Hz. The doublets at 132.07 and 128.81 ppm (*J* = 10.2 and 13.5 Hz) are assigned to the *ortho*- and *meta*-carbon atoms.



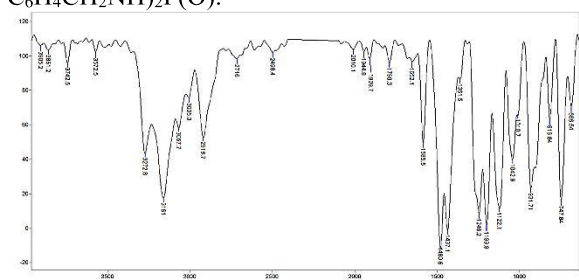
**Fig. 1.** <sup>31</sup>P{<sup>1</sup>H}-NMR spectrum of (2-Cl-C<sub>6</sub>H<sub>4</sub>O)(2-Cl-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NH)<sub>2</sub>P(O).



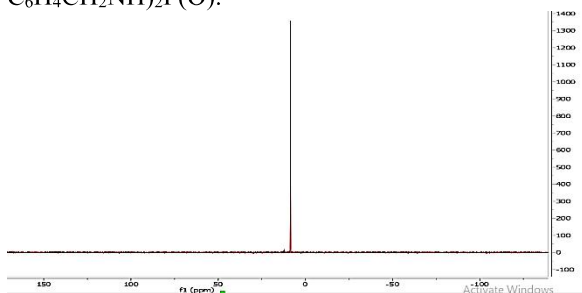
**Fig. 2.**  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of  $(2\text{-Cl-C}_6\text{H}_4\text{O})(2\text{-Cl-C}_6\text{H}_4\text{CH}_2\text{NH})_2\text{P(O)}$ .



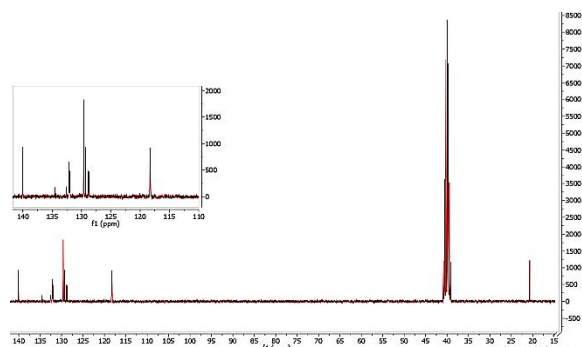
**Fig. 3.**  $^1\text{H}$ -NMR spectrum of  $(2\text{-Cl-C}_6\text{H}_4\text{O})(2\text{-Cl-C}_6\text{H}_4\text{CH}_2\text{NH})_2\text{P(O)}$ .



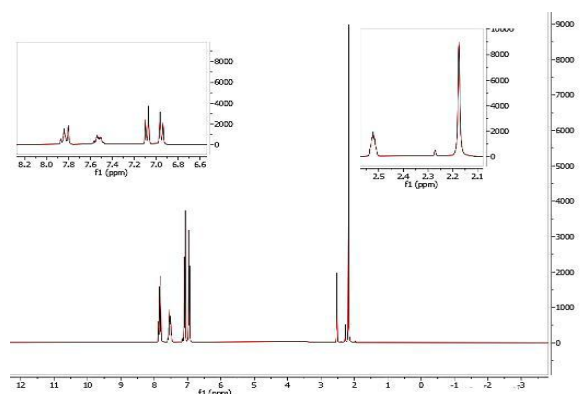
**Fig. 4.** IR spectrum of  $(2\text{-Cl-C}_6\text{H}_4\text{O})(2\text{-Cl-C}_6\text{H}_4\text{CH}_2\text{NH})_2\text{P(O)}$ .



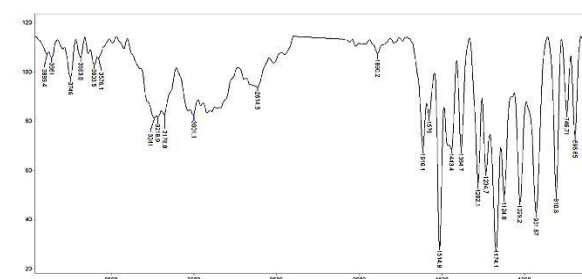
**Fig. 5.**  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of  $(\text{C}_6\text{H}_5)(4\text{-CH}_3\text{-C}_6\text{H}_4\text{NH})_2\text{P(O)}$ .



**Fig. 6.**  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of  $(\text{C}_6\text{H}_5)(4\text{-CH}_3\text{-C}_6\text{H}_4\text{NH})_2\text{P(O)}$ .



**Fig. 7.**  $^1\text{H}$ -NMR spectrum of  $(\text{C}_6\text{H}_5)(4\text{-CH}_3\text{-C}_6\text{H}_4\text{NH})_2\text{P(O)}$ .



**Fig. 8.** IR spectrum of  $(\text{C}_6\text{H}_5)(4\text{-CH}_3\text{-C}_6\text{H}_4\text{NH})_2\text{P(O)}$ .

#### 4. References

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