

Synthesis and Spectroscopic Characterization of Mixed Diamidophosphoric Acid Esters: X-Ray Crystal Structure of $[(\text{CH}_3)_2\text{N}][p\text{-H}_3\text{C-C}_6\text{H}_4\text{-O}]\text{P}(\text{O})\text{X}$ ($\text{X} = \text{NHC}(\text{CH}_3)_3$ and $p\text{-H}_3\text{C-C}_6\text{H}_4\text{-NH}$)

Saied Ghadimi^a, Mehrdad Pourayoubi^b, and Ali Asghar Ebrahimi Valmoozi^a

^a Department of Chemistry, Imam Hossein University, Tehran, Iran

^b Department of Chemistry, Ferdowsi University of Mashhad, Mashhad, Iran

Reprint requests to Dr. Saied Ghadimi. E-mail: ghadimi_saied@yahoo.com

Z. Naturforsch. **2009**, *64b*, 565–569; received December 10, 2008

Mixed diamidophosphoric acid esters $[(\text{CH}_3)_2\text{N}][p\text{-H}_3\text{C-C}_6\text{H}_4\text{-O}]\text{P}(\text{O})\text{X}$, where $\text{X} = \text{NH}(\text{CH}_3)$ (**1**), $\text{NHCH}(\text{CH}_3)_2$ (**2**), $\text{NHC}(\text{CH}_3)_3$ (**3**) and $p\text{-H}_3\text{C-C}_6\text{H}_4\text{-NH}$ (**4**) were synthesized and characterized by ^{31}P , $^{31}\text{P}\{^1\text{H}\}$, ^{13}C , ^1H NMR, and IR spectroscopy and mass spectrometry, and single crystal X-ray diffraction analysis for the compounds **3** and **4**. Compound **3** crystallizes in the monoclinic, space group $P2_1/c$ with unit cell parameters $a = 9.006(3)$, $b = 16.286(5)$, $c = 10.319(3)$ Å, $\beta = 99.633(6)^\circ$, $V = 1492.2(8)$ Å³, $Z = 4$. The final R value is 0.0622 for 2074 reflections [$I \geq 2\sigma(I)$]. Compound **4** crystallizes in the orthorhombic, space group $Pna2_1$ with unit cell parameters $a = 7.0459(14)$, $b = 20.934(4)$, $c = 10.436(2)$ Å, $V = 1539.3(5)$ Å³, $Z = 4$. The final R value is 0.0530 for 3025 reflections [$I \geq 2\sigma(I)$].

Key words: Mixed Diamidophosphoric Acid Ester, Spectroscopic Characterization, X-Ray Crystal Structure

Introduction

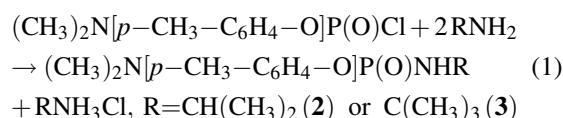
The extensive studies on the biochemical properties of phosphoramidate derivatives revealed various possibilities for their application in agrochemistry and medicine as insecticides, pesticides, and drugs [1–3]. Gerhard Schrader discovered the insecticide properties of amidophosphoric acid esters [4], which exert their toxicity by the inhibition of the acetylcholinesterase (AChE), the enzyme responsible for the degradation of the cholinergic neurotransmitter acetylcholine [5].

To the best of our knowledge, little attention has been given to the crystal structure and spectroscopic properties of these compounds [6–8]. Herein, mixed diamidophosphoric acid esters of the formula $[(\text{CH}_3)_2\text{N}][p\text{-H}_3\text{C-C}_6\text{H}_4\text{-O}]\text{P}(\text{O})\text{X}$, where $\text{X} = \text{NH}(\text{CH}_3)$ (**1**), $\text{NHCH}(\text{CH}_3)_2$ (**2**), $\text{NHC}(\text{CH}_3)_3$ (**3**) and $p\text{-H}_3\text{C-C}_6\text{H}_4\text{-NH}$ (**4**) were synthesized and characterized by ^{31}P , $^{31}\text{P}\{^1\text{H}\}$, ^{13}C , ^1H NMR, and IR spectroscopy and mass spectrometry, and the crystal structures of compounds **3** and **4** were determined by single crystal X-ray diffraction analysis.

Results and Discussion

General preparation of compounds 1–4

Compounds **1–4** were synthesized from the reaction of *N,N*-dimethylamido(chloro)phosphoric acid 4-methyl-phenyl ester and the corresponding amine (or the hydrochloride salt of the amine for compound **1**) in the presence of triethylamine as an HCl scavenger (for compounds **1** and **4**) or an excess of amine (for compounds **2** and **3**, Eq. 1).



NMR study

The ^{31}P chemical shifts ($\delta^{31}\text{P}$) in the NMR spectra of the title compounds varied from 6.94 (for compound **4**) to 15.99 ppm (for compound **1**). Comparison of $\delta^{31}\text{P}$ values in compounds **1–3** demonstrates the electron donating effect of the amine groups in the sequence $\text{NH-C}(\text{CH}_3)_3 > \text{NH-CH}(\text{CH}_3)_2 > \text{NHCH}_3$, which causes a decrease of the phosphorus chemical

Table 1. Fragment relative intensities in the mass spectra of compounds **1–4** and reference molecules [(CH₃)₂N]P(O)X[O-C₆H₄-*p*-CH₃].

| X | M ⁺ | [C ₂ H ₆ N] ⁺ | [C ₇ H ₇ O] ⁺ | [C ₇ H ₇] ⁺ | [M-C ₇ H ₇ O] ⁺ | [M-C ₇ H ₇] ⁺ | [M-X] ⁺ | Ref. |
|---|----------------|--|--|---|--|---|--------------------|--------------|
| Cl ³⁵ | 100 | 53 | 91 | 29 | 62 | 4 | 16 | ^a |
| CN | 71 | 100 | 35 | 78 | 48 | 2 | 3 | ^b |
| OCH ₃ | 64 | 100 | 67 | 10 | 69 | 71 | 16 | [6] |
| (C ₂ H ₅) ₂ N | 10 | 100 | 89 | 4 | 28 | 2 | 8 | [6] |
| (C ₄ H ₈)NO | 25 | 100 | 87 | 15 | 48 | 8 | 10 | [6] |
| NH(CH ₃) (1) | 14 | 100 | 54 | 12 | 5 | 88 | – | ^c |
| NH(<i>iso</i> -C ₃ H ₇) (2) | 3 | 53 | 100 | 25 | 79 | 3 | – | ^b |
| NH(<i>tert</i> -C ₄ H ₉) (3) | 1 | 33 | 100 | – | 4 | – | 42 | ^c |
| <i>p</i> -H ₃ C-C ₆ H ₄ -NH (4) | 2 | 100 | 41 | 18 | 33 | 7 | 12 | ^c |

^a Synthesis and spectroscopic characterization of [(CH₃)₂N]P(O)Cl[O-C₆H₄-*p*-CH₃] have been reported in ref. [9] and the modified strategy for the synthesis and the X-ray crystallography data in ref. [10]; the intensities reported in Table 1 were determined by the authors; ^b MS data of [(CH₃)₂N]P(O)CN[O-C₆H₄-*p*-CH₃] and [(CH₃)₂N]P(O)[NH(*iso*-C₃H₇)] [O-C₆H₄-*p*-CH₃] have not been published elsewhere; X-ray data were reported in refs. [11] and [12], respectively; ^c this work.

shift. In the ¹H NMR spectra of compounds **1–4** doublet peaks with ³J(P,H) in the range of 10.0 Hz (for compound **3**) to 10.2 Hz (for compounds **1** and **4**) appear for the N(CH₃)₂ moieties. Two-bond P–C coupling constants for the carbon atoms of the N(CH₃)₂ moiety with ²J(P,C) are in the range of 3.2 Hz (for compound **3**) to 4.4 Hz (for compound **1**). The data of the NMR spectra show ³J(P,H) (**1**) > ³J(P,H) (**2**) > ³J(P,H) (**3**) and ²J(P,C) (**1**) > ²J(P,C) (**2**) > ²J(P,C) (**3**). The CH₃ groups in the NH(*iso*-C₃H₇) moiety of compound **2** are diastereotopic and show two doublet peaks in the ¹H NMR spectrum (with ³J(H,H) = 6.5 and 6.4 Hz). Moreover, two doublet peaks appear for the CH₃ carbon atoms with ³J(P,C) = 5.9 and 5.3 Hz.

Mass spectrometry investigation

Mass spectra of the compounds indicate the presence of the fragments [N(CH₃)₂]⁺, [C₇H₇O]⁺, and P(O)[N(CH₃)₂]⁺X⁺, where X = NH(CH₃) (**1**), NH(*iso*-C₃H₇) (**2**), NH(*tert*-C₄H₉) (**3**) and *p*-H₃C-C₆H₄-NH (**4**) (Table 1). Moreover, the fragment P(O)[N(CH₃)₂]-[O-C₆H₄-*p*-CH₃]⁺ is observed in the mass spectra of compounds **3** and **4**.

X-Ray crystallography

The crystal structure of compound **2** was reported in reference [12]. Single crystals of compounds **3** and **4** were obtained from CHCl₃/CH₃CN at r. t. The crystallographic data and the details of the X-ray analysis are presented in Table 2, selected bond lengths and angles for compounds **3** and **4** are given in Table 3. Hydrogen bonding data are listed in Table 4. The molecular structures of **3** and **4** are shown in Figs. 1 and 2, respectively. The phosphorus atoms have a distorted

Table 2. Crystallography data for compounds **3** and **4**.

| | 3 | 4 |
|--|---|---|
| Formula | C ₁₃ H ₂₃ N ₂ O ₂ P | C ₁₆ H ₂₁ N ₂ O ₂ P |
| <i>M</i> _r | 270.30 | 304.32 |
| Temperature (K) | 100(2) | 100(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | monoclinic | orthorhombic |
| Space group | <i>P</i> 2 ₁ / <i>c</i> | <i>Pna</i> 2 ₁ |
| <i>a</i> , Å | 9.006(3) | 7.0459(14) |
| <i>b</i> , Å | 16.286(5) | 20.934(4) |
| <i>c</i> , Å | 10.319(3) | 10.436(2) |
| β, deg | 99.633(6) | 90 |
| <i>V</i> , Å ³ | 1492.2(8) | 1539.3(5) |
| <i>Z</i> | 4 | 4 |
| <i>D</i> _{calcd.} , g cm ⁻³ | 1.203 | 1.313 |
| Absorption coefficient, mm ⁻¹ | 0.182 | 0.185 |
| <i>F</i> (000), e | 584 | 648 |
| Cryst. size, mm ³ | 0.35 × 0.20 × 0.15 | 0.25 × 0.15 × 0.08 |
| θ range for data collection, deg | 2.29–27.00 | 1.95–28.00 |
| Limiting indices | –10 ≤ <i>h</i> ≤ 11, –20 ≤ <i>k</i> ≤ 20, –13 ≤ <i>l</i> ≤ 13 | –8 ≤ <i>h</i> ≤ 9, –24 ≤ <i>k</i> ≤ 27, –13 ≤ <i>l</i> ≤ 13 |
| Refl. collected / unique | 9737 / 3137 | 9993 / 3654 |
| <i>R</i> _{int} | 0.0965 | 0.0528 |
| Completeness to θ (%) | 96.4 | 98.6 |
| Observed refls [<i>I</i> ≥ 2σ(<i>I</i>)] | 2074 | 3025 |
| Absorption correction | none | semi-empirical from equivalents |
| Max. / min. transmission | – | 0.9854 / 0.9552 |
| Data / restraints / parameters | 3137 / 0 / 169 | 3654 / 1 / 194 |
| GoF (<i>F</i> ²) | 0.995 | 1.005 |
| Final <i>R</i> 1/ <i>wR</i> 2 [<i>I</i> ≥ 2σ(<i>I</i>)] | 0.0622 / 0.1043 | 0.0530 / 0.1032 |
| Final <i>R</i> 1/ <i>wR</i> 2 (all data) | 0.1068 / 0.1192 | 0.0695 / 0.1099 |
| Largest diff. peak/hole, e Å ⁻³ | 0.368 / –0.339 | 0.655 / –0.410 |

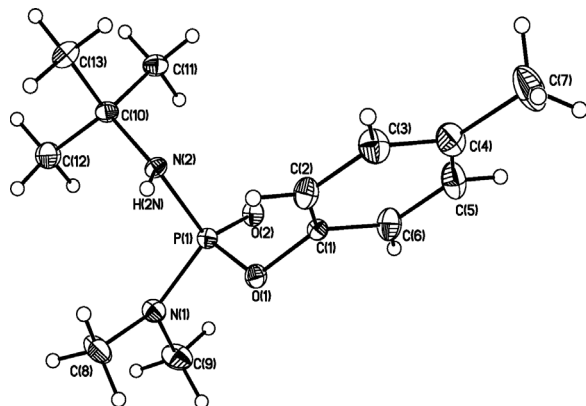
tetrahedral configuration. The bond angles around the phosphorus atom are in the range of 102.76(14)° [∠O(2)–P(1)–N(2)] to 114.77(14)° [∠O(1)–P(1)–N(2)] in compound **2**, 102.32(11)° [∠O(1)–P(1)–N(2)] to 115.58(12)° [∠O(2)–P(1)–N(2)] in compound **3**

Table 3. Selected bond lengths (Å) and bond angles (deg) for compounds **3** and **4**.

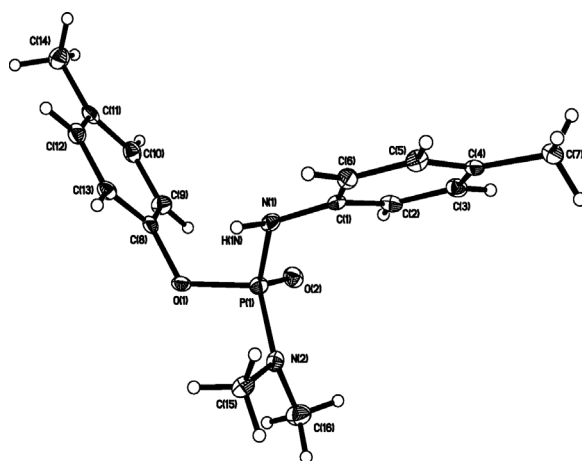
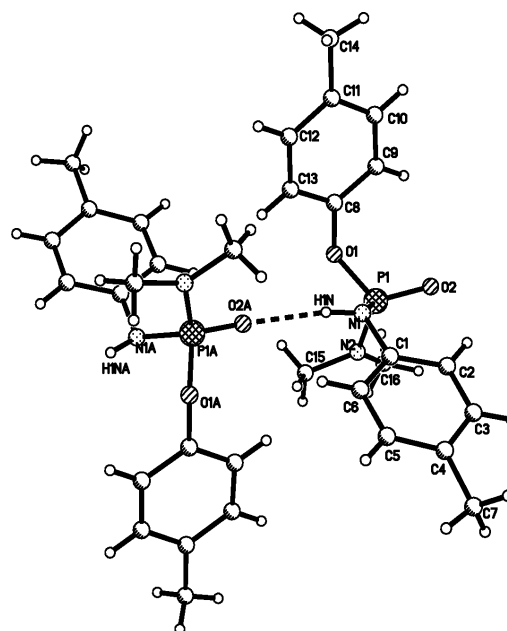
| 3 | | 4 | |
|-----------------|------------|-----------------|------------|
| P(1)–O(2) | 1.462(2) | P(1)–O(2) | 1.474(2) |
| P(1)–O(1) | 1.608(2) | P(1)–O(1) | 1.604(2) |
| P(1)–N(2) | 1.631(2) | P(1)–N(2) | 1.633(3) |
| P(1)–N(1) | 1.641(2) | P(1)–N(1) | 1.648(3) |
| O(1)–C(1) | 1.409(3) | O(1)–C(8) | 1.421(3) |
| N(1)–C(9) | 1.452(4) | N(1)–C(1) | 1.430(4) |
| N(1)–C(8) | 1.458(4) | N(2)–C(16) | 1.441(4) |
| N(2)–C(10) | 1.486(3) | N(2)–C(15) | 1.458(4) |
| C(1)–C(6) | 1.373(4) | C(1)–C(6) | 1.389(4) |
| O(2)–P(1)–O(1) | 114.19(11) | O(2)–P(1)–O(1) | 114.82(13) |
| O(2)–P(1)–N(2) | 115.58(12) | O(2)–P(1)–N(2) | 110.64(12) |
| O(1)–P(1)–N(2) | 102.32(11) | O(1)–P(1)–N(2) | 105.10(12) |
| O(2)–P(1)–N(1) | 110.06(12) | O(2)–P(1)–N(1) | 114.64(13) |
| O(1)–P(1)–N(1) | 102.94(12) | O(1)–P(1)–N(1) | 100.51(12) |
| N(2)–P(1)–N(1) | 110.85(12) | N(2)–P(1)–N(1) | 110.37(13) |
| C(1)–O(1)–P(1) | 120.41(17) | C(8)–O(1)–P(1) | 120.81(17) |
| C(9)–N(1)–C(8) | 114.4(2) | C(1)–N(1)–P(1) | 123.1(2) |
| C(6)–C(1)–C(2) | 121.3(3) | C(6)–C(1)–C(2) | 119.1(3) |
| C(6)–C(1)–O(1) | 119.7(2) | C(6)–C(1)–N(1) | 119.6(3) |
| C(2)–C(1)–O(1) | 118.7(2) | C(2)–C(1)–N(1) | 121.2(3) |
| C(1)–C(2)–C(3) | 119.0(3) | C(3)–C(2)–C(1) | 119.6(3) |
| C(4)–C(3)–C(2) | 121.5(3) | C(4)–C(3)–C(2) | 121.7(3) |
| C(10)–N(2)–P(1) | 126.10(18) | C(15)–N(2)–P(1) | 120.8(2) |

Table 4. Hydrogen bond parameters for compounds **3** and **4** (Å, deg).

| D–H...A | <i>d</i> (D–H) | <i>d</i> (H...A) | <i>d</i> (D...A) | ∠DHA |
|--|----------------|------------------|------------------|------|
| 3 : N(2)–H(2N)···O(2) | 0.880 | 2.022 | 2.869(3) | 161 |
| [<i>x</i> , – <i>y</i> + 1/2, <i>z</i> + 1/2] | | | | |
| 4 : N(1)–H(1N)···O(2) | 0.90 | 2.07 | 2.957(4) | 170 |
| [– <i>x</i> + 1, – <i>y</i> , <i>z</i> + 1/2] | | | | |

Fig. 1. Molecular structure and atom labeling scheme for [*tert*-C₄H₉NH]P(O)[(CH₃)₂N][*p*-O-C₆H₄-CH₃] (**3**) with displacement ellipsoids at the 50% probability level.

and 100.51(12)° [∠O(1)–P(1)–N(1)] to 114.82(13)° [∠O(2)–P(1)–O(1)] in compound **4**. The oxygen atoms of the O-C₆H₄-*p*-CH₃ moieties may be ascribed *sp*²

Fig. 2. Molecular structure and atom labeling scheme for [(CH₃)₂N]P(O)[*p*-NHC₆H₄-CH₃][*p*-OC₆H₄-CH₃] (**4**) with displacement ellipsoids at the 50% probability level.Fig. 3. Hydrogen bond (P(1)–O(2)···H(1N)) in compound **4**.

character, P–O–C: 120.30(2)° (**2**), 120.41(17)° (**3**) and 120.81(17)° (**4**). Their P–O bond lengths (1.607(2), 1.608(2) and 1.604(2) Å) are shorter than a standard P–O single bond (1.64 Å [13]). The P=O bond lengths in molecules **2**, **3** and **4** are 1.473(2), 1.462(2) and 1.474(2) Å, respectively, and thus longer than the normal P=O bond length (1.45 Å for P(O)Cl₃) [13]. Also, the P–N bond lengths are shorter than the standard P–N single bond length (1.77 Å for NaHPO₃-NH₂ [13]). The nitrogen atoms of the aliphatic amine

groups in the title compounds indicate sp^2 hybridization. For example, in compound **4**, the angles P(1)–N(2)–C(16), C(16)–N(2)–C(15) and C(15)–N(2)–P(1) are $121.4(2)^\circ$, $114.1(3)^\circ$ and $120.8(2)^\circ$, respectively. The sum of the angles around the N2 and N1 atoms are 354.9° and 355.8° for compound **3**. The deviation from the ideal value of 360° may be caused by steric effects. Molecules of compounds **2–4** are linked *via* N–H \cdots O=P hydrogen bonds into chains. Fig. 3 shows the N–H \cdots O=P hydrogen bond in crystals of compound **4**. H-bonded chains spreading along the crystallographic *c* axis in the crystal of compound **4** are connected into ribbons through π stacking between *p*-H₃C–C₆H₄–NH moieties. The angle and the distance between mean planes of neighboring moieties is equal to $8.7(1)^\circ$ and $3.26(1)$ Å, respectively. The shortest distances between the center of the phenylene ring and the H atom of a neighboring methyl group is equal to $2.682(3)$ Å.

Experimental Section

Materials

Acetonitrile (99%), *iso*-propylamine (99%), *tert*-butylamine (99%), methylamine (46% aqueous solution), triethylamine (98%), and chloroform (99%) (Merck) were used as supplied. $[(\text{CH}_3)_2\text{N}]P(\text{O})\text{Cl}[\text{O}-\text{C}_6\text{H}_4-p\text{-CH}_3]$ was synthesized according to the literature [10].

Spectroscopic measurements

¹H, ¹³C and ³¹P NMR spectra were recorded on Bruker (Avance DRS) 250 and 500 MHz spectrometers. ¹H, ¹³C and ³¹P chemical shifts were obtained in CDCl₃ relative to TMS and 85% H₃PO₄ as external standards, respectively. IR spectra were obtained using KBr pellets on a Perkin Elmer 783 model spectrometer. A Varian Star 3400 CX mass spectrometer was used for mass spectrometry investigation. Melting points were obtained with an Electrothermal instrument.

N,N-Dimethyl-*N'*-methyl-diamidophosphoric acid 4-methyl-phenyl ester, $(\text{CH}_3)_2\text{NP}(\text{O})[(\text{CH}_3)\text{NH}][\text{O}-\text{C}_6\text{H}_4-p\text{-CH}_3]$ (**1**)

To a solution of $(\text{CH}_3)_2\text{NP}(\text{O})\text{Cl}[\text{O}-\text{C}_6\text{H}_4-p\text{-CH}_3]$ (0.82 g, 3.5 mmol) in 30 mL of dry acetonitrile, methylamine hydrochloride (0.24 g, 3.5 mmol) and triethylamine (0.71 g, 7 mmol) were added at 0 °C. After 12 h stirring, the solvent was evaporated *in vacuo*. Then, the flash gradient chromatography method was used for the purification of the product (silicagel, hexane-ethyl acetate 9:1). The solvent was evaporated *in vacuo* to afford the product as a colorless liquid. Yield: 68%. – ¹H NMR (250.13 MHz, CDCl₃, 25 °C, TMS): δ = 2.30 (s, 3H, *p*-CH₃), 2.60 (d, ³*J*(P,H) = 12.2 Hz, 3H, methylamine-CH₃), 2.73 (d, ³*J*(P,H) = 10.2 Hz,

6H, N(CH₃)₂), 3.00–3.15 (m, 1H, methylamine-NH), 7.04–7.12 (m, 4H, Ar-H). – ¹³C NMR (62.90 MHz, CDCl₃, 25 °C, TMS): δ = 20.69 (s, 1C, *p*-CH₃), 27.02 (s, 1C, methylamine-CH₃), 36.80 (d, ²*J*(P,C) = 4.4 Hz, 2C, N(CH₃)₂), 120.05 (d, ³*J*(P,C) = 4.8 Hz, 2C, *C*_{ortho}), 130.00 (s, 2C, *C*_{meta}), 133.70 (s, 1C, *C*_{para}), 149.05 (d, ²*J*(P,C) = 6.3 Hz, 1C, *C*_{ipso}). – ³¹P{¹H} NMR (101.25 MHz, CDCl₃, 25 °C, H₃PO₄ external): δ = 15.99 (s). – ³¹P NMR: δ = 15.99 (m). – IR (KBr): ν = 3220 (NH), 3010, 2920, 2800, 1600, 1580, 1505, 1300, 1225 (P=O), 1170, 1118, 1070, 988 (P–O), 920, 810, 715 (P–N), 645 cm^{–1}. – MS (20 eV, EI): *m/z* (%) = 228 (14) [M]⁺, 137 (88) [M–C₇H₇]⁺, 121 (5) [M–C₇H₇O]⁺, 107 (54) [C₇H₇O]⁺, 91 (12) [C₇H₇]⁺, 44 (100) [C₂H₆N]⁺.

N,N-Dimethyl-*N'*-*iso*-propyl-diamidophosphoric acid 4-methyl-phenyl ester, $(\text{CH}_3)_2\text{NP}(\text{O})[\text{NH}(\text{iso}-\text{C}_3\text{H}_7)][\text{O}-\text{C}_6\text{H}_4-p\text{-CH}_3]$ (**2**)

To a solution of $(\text{CH}_3)_2\text{NP}(\text{O})\text{Cl}[\text{O}-\text{C}_6\text{H}_4-p\text{-CH}_3]$ (0.82 g, 3.5 mmol) in 30 mL of dry chloroform, *iso*-propylamine (0.42 g, 7.1 mmol) was slowly added and the mixture stirred at 0 °C for 12 h. The solvent was evaporated *in vacuo*. Single crystals of the product were obtained from a solution in chloroform-acetonitrile (4:1) after slow evaporation at r.t. Yield: 73%. M. p. 61–64 °C. – ¹H NMR (500.13 MHz, CDCl₃, 25 °C, TMS): δ = 1.12 (d, ³*J*(H,H) = 6.5 Hz, 3H, *iso*-propylamine-CH₃), 1.15 (d, ³*J*(H,H) = 6.4 Hz, 3H, *iso*-propylamine-CH₃), 2.25 (s, 3H, *p*-CH₃), 2.33 (b, 1H, NH), 2.68 (d, ³*J*(P,H) = 10.1 Hz, 6H, N(CH₃)₂), 3.38–3.39 (m, 1H, *iso*-propylamine-CH), 7.03 (m, 4H, Ar-H). – ¹³C NMR (125.75 MHz, CDCl₃, 25 °C, TMS): δ = 20.64 (s, 1C, *p*-CH₃), 25.27 (d, ³*J*(P,C) = 5.9 Hz, 1C, *iso*-propylamine-CH₃), 25.52 (d, ³*J*(P,C) = 5.3 Hz, 1C, *iso*-propylamine-CH₃), 36.96 (d, ²*J*(P,C) = 3.8 Hz, 2C, N(CH₃)₂), 43.38 (s, 1C, *iso*-propylamine-CH), 119.92 (d, ³*J*(P,C) = 4.8 Hz, 2C, *C*_{ortho}), 129.96 (s, 2C, *C*_{meta}), 133.50 (s, 1C, *C*_{para}), 149.12 (d, ²*J*(P,C) = 6.1 Hz, 1C, *C*_{ipso}). – ³¹P{¹H} NMR (202.45 MHz, CDCl₃, 25 °C, H₃PO₄ external): δ = 13.70 (s). – ³¹P NMR: δ = 13.70 (m). – IR (KBr): ν = 3210 (NH), 2949, 2940, 1599, 1499, 1455, 1297, 1227 (P=O), 1198, 1162, 1040, 985 (P–O), 906, 816, 794, 705 cm^{–1} (P–N). – MS (20 eV, EI): *m/z* (%) = 257 (30) [M+1]⁺, 256 (3) [M]⁺, 165 (3) [M–C₇H₇]⁺, 149 (79) [M–C₇H₇O]⁺, 107 (100) [C₇H₇O]⁺, 91 (25) [C₇H₇]⁺, 44 (53) [C₂H₆N]⁺.

N,N-Dimethyl-*N'*-*tert*-butyl-diamidophosphoric acid 4-methyl-phenyl ester, $[(\text{CH}_3)_2\text{N}]P(\text{O})[\text{NH}(\text{tert}-\text{C}_4\text{H}_9)]-\text{O}-\text{C}_6\text{H}_4-p\text{-CH}_3]$ (**3**)

Compound **3** was prepared following the procedure described for compound **2** by using *tert*-butylamine instead of *iso*-propylamine. Yield: 82%. M. p. 83–86 °C. – ¹H NMR (250.13 MHz, CDCl₃, 25 °C, TMS): δ = 1.32 (s, 9H, *tert*-

butylamine-CH₃), 2.29 (s, 3H, *p*-CH₃), 2.32 (b, 1H, NH), 2.67 (d, ³*J*(P,H) = 10.0 Hz, 6H, N(CH₃)₂), 7.07 (m, 4H, Ar-H). – ¹³C NMR (62.90 MHz, CDCl₃, 25 °C, TMS): δ = 20.70 (s, 1C, *p*-CH₃), 31.36 (d, ³*J*(P,C) = 5.0 Hz, 3C, *tert*-butylamine-CH₃), 36.91 (d, ²*J*(P,C) = 3.2 Hz, 2C, N(CH₃)₂), 50.80 (s, 1C, *tert*-butylamine-C), 119.90 (d, ³*J*(P,C) = 4.8 Hz, 2C, *C*_{ortho}), 130.00 (s, 2C, *C*_{meta}), 133.40 (s, 1C, *C*_{para}), 149.2 (d, ²*J*(P,C) = 6.1 Hz, 1C, *C*_{ipso}). – ³¹P{¹H} NMR (101.25 MHz, CDCl₃, 25 °C, H₃PO₄ external): δ = 10.71 (s). – ³¹P NMR: δ = 10.71 (hept, ³*J*(P,H) = 10.0 Hz). – IR (KBr): ν = 3180 (NH), 2923, 2880, 1580, 1565, 1485, 1450, 1290, 1230 (P=O), 1190, 1158, 1015, 978 (P–O), 910, 813, 750 (P–N), 708 cm^{–1}. – MS (20 eV, EI): *m/z* (%) = 271 (35) [M+1]⁺, 270 (1) [M]⁺, 198 (42) [M–C₄H₁₀N]⁺, 163 (4) [M–C₇H₇O]⁺, 107 (100) [C₇H₇O]⁺, 44 (33) [C₂H₆N]⁺.

N,N-Dimethyl-*N'*-paratoluidyl-diamidophosphoric acid 4-methyl-phenyl ester; [(CH₃)₂N]P(O)[NH–C₆H₄-*p*-CH₃][O–C₆H₄-*p*-CH₃] (**4**)

Compound **4** was prepared following the procedure described for compound **1** by using *para*-toluidine instead of methylamine hydrochloride. (*para*-toluidine : triethylamine, 1 : 1). Yield: 75%. M. p. 75–79 °C. – ¹H NMR (250.13 MHz, CDCl₃, 25 °C, TMS): δ = 2.28 (s, 3H, toluide, *p*-CH₃), 2.30 (s, 3H, tolyl, *p*-CH₃), 2.74 (d, ³*J*(P,H) = 10.2 Hz, 6H, N(CH₃)₂), 5.09 (d, ²*J*(P,H) = 8.2 Hz, 1H, NH), 6.89–7.03 (m, 4H, toluide, Ar-H), 7.08 (m, 4H, tolyl, Ar-H). – ¹³C NMR (62.90 MHz, CDCl₃, 25 °C, TMS): δ = 2.67 (s, 1C, toluide, *p*-CH₃), 2.80 (s, 1C, tolyl, *p*-CH₃), 36.73 (d, ²*J*(P,C) = 4.3 Hz, 2C, N(CH₃)₂), 117.90 (d, ³*J*(P,C) = 6.7 Hz, 2C, toluide, *C*_{ortho}), 120.22 (d,

³*J*(P,C) = 4.7 Hz, 2C, tolyl, *C*_{ortho}), 129.91 (s, 2C, toluide, *C*_{meta}), 130.05 (s, 1C, toluide, *C*_{para}), 130.23 (s, 2C, tolyl, *C*_{meta}), 134.20 (s, 1C, tolyl, *C*_{para}), 138.64 (d, ²*J*(P,C) = 1.2 Hz, 1C, toluide, *C*_{ipso}), 148.56 (d, ²*J*(P,C) = 6.0 Hz, 1C, tolyl, *C*_{ipso}). – ³¹P{¹H} NMR (101.25 MHz, CDCl₃, 25 °C, H₃PO₄ external): δ = 6.94 (s). – ³¹P NMR: δ = 6.98 (m). – IR (KBr): ν = 3215 (NH), 2955, 2930, 1600, 1500, 1445, 1305, 1235 (P=O), 1190, 1155, 1025, 970 (P–O), 915, 710 cm^{–1} (P–N). – MS (20 eV, EI): *m/z* (%) = 305 (29) [M+1]⁺, 304 (2) [M]⁺, 213 (7) [M–C₇H₇]⁺, 198 (12) [M–C₇H₇NH]⁺, 197 (33) [M–C₇H₇O]⁺, 107 (41) [C₇H₇O]⁺, 91 (18) [C₇H₇]⁺, 44 (100) [C₂H₆N]⁺.

X-Ray structure determinations

X-Ray data of compounds **3** and **4** were collected on a Bruker SMART 1000 CCD single crystal diffractometer with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) [14]. Routine Lorentz and polarization corrections were applied, and an absorption correction was performed using the program SADABS [15]. The structures were refined with SHELXL-97 by full-matrix least-squares procedures on *F*² [16]. The positions of hydrogen atoms were obtained from a difference Fourier map.

CCDC 693076 (**3**) and CCDC 393077 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

Support of this work by Imam Hossein University is gratefully acknowledged.

- [1] W. Mallender, T. Szegletes, T. Rosenberry, *Biochemistry* **2000**, *39*, 7753.
- [2] A. Baldwin, Z. Huang, Y. Jounaidi, D. Waxman, *Arch. Biochem. Biophys.* **2003**, *409*, 197.
- [3] Y. Pang, T. Kollmeyer, F. Hong, J. Lee, P. Hammond, S. Haugabouk, S. Brimijoin, *Biochem. Biol.* **2003**, *10*, 491.
- [4] L. Costa, *Clinic. Chim. Acta* **2006**, *366*, 1, and refs. therein.
- [5] K. Kamil, B. Jirl, C. Jirl, K. Jirl, *Bioorg. Medic. Chem. Lett.* **2003**, *13*, 3545.
- [6] S. Ghadimi, A. A. Ebrahimi Valmoozi, M. Pourayoubi, K. A. Samani, *J. Enzy. Inhibit. Medic. Chem.* **2008**, *23*, 556.
- [7] K. Gubina, J. Shatrava, V. Ovchynnikov, V. Amir-khanov, *Polyhedron* **2000**, *19*, 2203.
- [8] K. Gholivand, Z. Shariatinia, M. Pourayoubi, *Z. Naturforsch.* **2005**, *60b*, 67.
- [9] K. Gholivand, A. Mahmoudkhani, M. Khosravi, *Phosphorus Sulfur and Silicon* **1995**, *106*, 173.
- [10] S. Ghadimi, A. A. Ebrahimi Valmoozi, M. Pourayoubi, *Z. Kristallogr. NCS* **2007**, *222*, 339.
- [11] S. Ghadimi, A. A. Ebrahimi Valmoozi, M. Pourayoubi, *Acta. Crystallogr.* **2007**, *E63*, o3260.
- [12] M. Pourayoubi, S. Ghadimi, A. A. Ebrahimi Valmoozi, *Acta. Crystallogr.* **2007**, *E63*, o4093.
- [13] D. E. C. Corbridge, *Phosphorus, an Outline of its Chemistry, Biochemistry and Technology*, Elsevier, Amsterdam **1995**.
- [14] Bruker, SMART (version 5.059), Bruker Molecular Analysis Research Tool, Bruker AXS, Madison, WI (USA) **1998**.
- [15] G. M. Sheldrick, SADABS (version 2.01), Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, WI (USA) **1998**.
- [16] G. M. Sheldrick, SHELXTL (version 5.10), Structure Determination Software Suit, Bruker AXS, Madison, WI (USA) **1998**.