Synthesis and Spectroscopic Characterization of Mixed Diamidophosphoric Acid Esters: X-Ray Crystal Structure of $[(CH_3)_2N]$-$[p\text{-}H_3C\text{-}C_6H_4\text{-}O]P(O)X$ (X = $NHC(CH_3)_3$ and $p\text{-}H_3C\text{-}C_6H_4\text{-}NH$)

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Mixed diamidophosphoric acid esters $[(CH_3)_2N][p\text{-}H_3C\text{-}C_6H_4\text{-}O]P(O)X$, where X = $NH(CH_3)$ (**1**), $NHCH(CH_3)_2$ (**2**), $NHC(CH_3)_3$ (**3**) and $p\text{-}H_3C\text{-}C_6H_4\text{-}NH$ (**4**) were synthesized and characterized by ^{31}P, $^{31}P\{^1H\}$, ^{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, β = 99.633(6)°, V = 1492.2(8) Å^3, 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) Å^3, 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 $[(CH_3)_2N][p\text{-}H_3C\text{-}C_6H_4\text{-}O]P(O)X$, where X = $NH(CH_3)$ (**1**), $NHCH(CH_3)_2$ (**2**), $NHC(CH_3)_3$ (**3**) and $p\text{-}H_3C\text{-}C_6H_4\text{-}NH$ (**4**) were synthesized and characterized by ^{31}P, $^{31}P\{^1H\}$, ^{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).

$$(CH_3)_2N[p\text{–}CH_3\text{–}C_6H_4\text{–}O]P(O)Cl + 2\,RNH_2 \rightarrow (CH_3)_2N[p\text{–}CH_3\text{–}C_6H_4\text{–}O]P(O)NHR + RNH_3Cl,\ R{=}CH(CH_3)_2\ (\mathbf{2})\ \text{or}\ C(CH_3)_3\ (\mathbf{3}) \quad (1)$$

NMR study

The ^{31}P chemical shifts ($\delta^{31}P$) in the NMR spectra of the title compounds varied from 6.94 (for compound **4**) to 15.99 ppm (for compound **1**). Comparison of $\delta^{31}P$ values in compounds **1 – 3** demonstrates the electron donating effect of the amine groups in the sequence NH-$C(CH_3)_3$ > NH-$CH(CH_3)_2$ > $NHCH_3$, which causes a decrease of the phosphorus chemical

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Table 1. Fragment relative intensities in the mass spectra of compounds **1** – **4** and reference molecules $[(CH_3)_2N]P(O)X[O\text{-}C_6H_4\text{-}p\text{-}CH_3]$).

X	M^+	$[C_2H_6N]^+$	$[C_7H_7O]^+$	$[C_7H_7]^+$	$[M–C_7H_7O]^+$	$[M–C_7H_7]^+$	$[M–X]^+$	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]
$(C_2H_5)_2N$	10	100	89	4	28	2	8	[6]
$(C_4H_8)NO$	25	100	87	15	48	8	10	[6]
$NH(CH_3)$ (**1**)	14	100	54	12	5	88	–	[c]
NH(*iso*-C_3H_7) (**2**)	3	53	100	25	79	3	–	[b]
NH(*tert*-C_4H_9) (**3**)	1	33	100	–	4	–	42	[c]
p-H_3C-C_6H_4-NH (**4**)	2	100	41	18	33	7	12	[c]

[a] Synthesis and spectroscopic characterization of $[(CH_3)_2N]P(O)Cl[O\text{-}C_6H_4\text{-}p\text{-}CH_3]$ 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 $[(CH_3)_2N]P(O)CN[O\text{-}C_6H_4\text{-}p\text{-}CH_3]$ and $[(CH_3)_2N]P(O)[NH(iso\text{-}C_3H_7)][O\text{-}C_6H_4\text{-}p\text{-}CH_3]$ have not been published elsewhere; X-ray data were reported in refs. [11] and [12], respectively; [c] this work.

shift. In the ^{1}H 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 $N(CH_3)_2$ moieties. Two-bond P–C coupling constants for the carbon atoms of the $N(CH_3)_2$ 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 CH_3 groups in the NH(*iso*-C_3H_7) moiety of compound **2** are diastereotopic and show two doublet peaks in the ^{1}H NMR spectrum (with ^3J(H,H) = 6.5 and 6.4 Hz). Moreover, two doublet peaks appear for the CH_3 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 $[N(CH_3)_2]^+$, $[C_7H_7O]^+$, and $P(O)[N(CH_3)_2]X^+$, where X = $NH(CH_3)$ (**1**), NH(*iso*-C_3H_7) (**2**), NH(*tert*-C_4H_9) (**3**) and *p*-H_3C-C_6H_4-NH (**4**) (Table 1). Moreover, the fragment $P(O)[N(CH_3)_2]$-$[O\text{-}C_6H_4\text{-}p\text{-}CH_3]^+$ 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 $CHCl_3/CH_3CN$ 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 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 2. Crystallography data for compounds **3** and **4**.

	3	**4**
Formula	$C_{13}H_{23}N_2O_2P$	$C_{16}H_{21}N_2O_2P$
M_r	270.30	304.32
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$Pna2_1$
a, Å	9.006(3)	7.0459(14)
b, Å	16.286(5)	20.934(4)
c, Å	10.319(3)	10.436(2)
β, deg	99.633(6)	90
V, Å^3	1492.2(8)	1539.3(5)
Z	4	4
D_{calcd}, g cm^{-3}	1.203	1.313
Absorption coefficient, mm^{-1}	0.182	0.185
F(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	$-10 \le h \le 11$, $-20 \le k \le 20$, $-13 \le l \le 13$	$-8 \le h \le 9$, $-24 \le k \le 27$, $-13 \le l \le 13$
Refl. collected / unique	9737 / 3137	9993 / 3654
R_{int}	0.0965	0.0528
Completeness to θ (%)	96.4	98.6
Observed refls [$I \ge 2\sigma(I)$]	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 (F^2)	0.995	1.005
Final $R1/wR2$ [$I \ge 2\sigma(I)$]	0.0622 / 0.1043	0.0530 / 0.1032
Final $R1/wR2$ (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

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

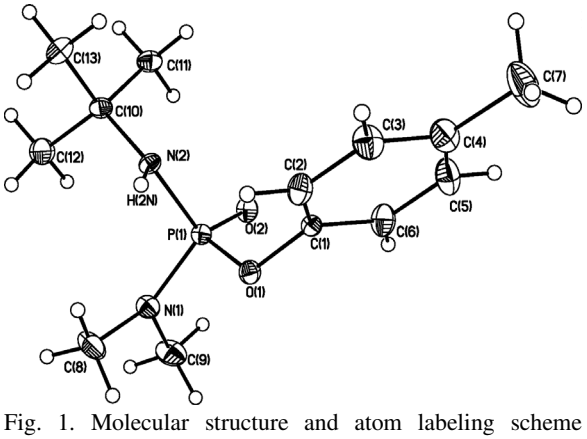

Fig. 1. Molecular structure and atom labeling scheme for [*tert*-C_4H_9NH]P(O)[$(CH_3)_2$N][*p*-O-C_6H_4-CH_3] (**3**) with displacement ellipsoids at the 50 % probability level.

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-C_6H_4-*p*-CH_3 moieties may be ascribed sp^2

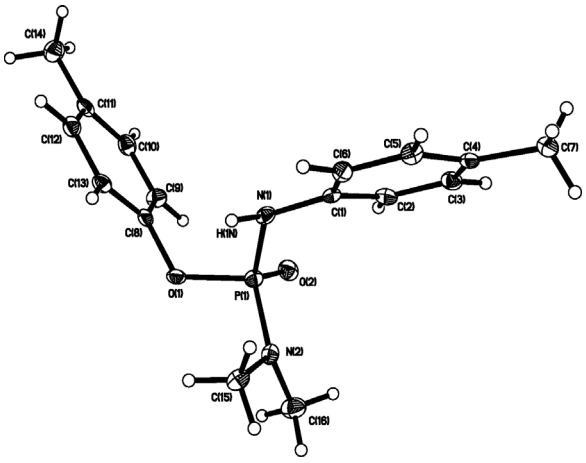

Fig. 2. Molecular structure and atom labeling scheme for [$(CH_3)_2$N]P(O)[*p*-NHC_6H_4-CH_3][*p*-OC_6H_4-CH_3] (**4**) with displacement ellipsoids at the 50 % probability level.

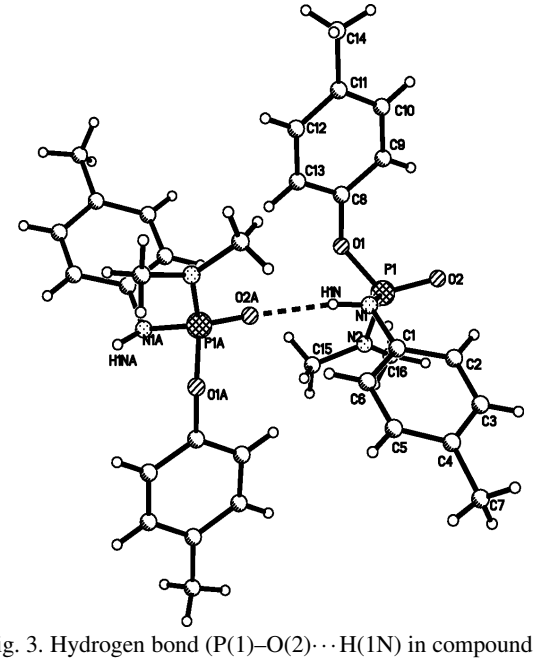

Fig. 3. Hydrogen bond (P(1)–O(2)···H(1N) in compound **4**.

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 $P(O)Cl_3$) [13]. Also, the P–N bond lengths are shorter than the standard P–N single bond length (1.77 Å for $NaHPO_3$-NH_2 [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)°, 114.1(3)° and 120.8(2)°, 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···O=P hydrogen bonds into chains. Fig. 3 shows the N–H···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*-H_3C-C_6H_4-NH moieties. The angle and the distance between mean planes of neighboring moieties is equal to 8.7(1)° 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. $[(CH_3)_2N]P(O)Cl[O\text{-}C_6H_4\text{-}p\text{-}CH_3]$ was synthesized according to the literature [10].

Spectroscopic measurements

^1H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker (Avance DRS) 250 and 500 MHz spectrometers. ^1H, ^{13}C and ^{31}P chemical shifts were obtained in $CDCl_3$ relative to TMS and 85 % H_3PO_4 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, $(CH_3)_2NP(O)[(CH_3)NH][O\text{-}C_6H_4\text{-}p\text{-}CH_3]$ (**1**)*

To a solution of $(CH_3)_2NP(O)Cl[O\text{-}C_6H_4\text{-}p\text{-}CH_3]$ (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, $CDCl_3$, 25 °C, TMS): δ = 2.30 (s, 3H, *p*-CH_3), 2.60 (d, ^3J(P,H) = 12.2 Hz, 3H, methylamine-CH_3), 2.73 (d, ^3J(P,H) = 10.2 Hz, 6H, $N(CH_3)_2$), 3.00 – 3.15 (m, 1H, methylamine-NH), 7.04 – 7.12 (m, 4H, Ar-H). – ^{13}C NMR (62.90 MHz, $CDCl_3$, 25 °C, TMS): δ = 20.69 (s, 1C, *p*-CH_3), 27.02 (s, 1C, methylamine-CH_3), 36.80 (d, ^2J(P,C) = 4.4 Hz, 2C, $N(CH_3)_2$), 120.05 (d, ^3J(P,C) = 4.8 Hz, 2C, C_{ortho}), 130.00 (s, 2C, C_{meta}), 133.70 (s, 1C, C_{para}), 149.05 (d, ^2J(P,C) = 6.3 Hz, 1C, C_{ipso}). – $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, 25 °C, H_3PO_4 external): δ = 15.99 (s). – ^{31}P 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) $[M–C_7H_7]^+$, 121 (5) $[M–C_7H_7O]^+$, 107 (54) $[C_7H_7O]^+$, 91 (12) $[C_7H_7]^+$, 44 (100) $[C_2H_6N]^+$.

*N,N-Dimethyl-N′-iso-propyl-diamidophosphoric acid 4-methyl-phenyl ester, $(CH_3)_2NP(O)[NH(iso\text{-}C_3H_7)][O\text{-}C_6H_4\text{-}p\text{-}CH_3]$ (**2**)*

To a solution of $(CH_3)_2NP(O)Cl[O\text{-}C_6H_4\text{-}p\text{-}CH_3]$ (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, $CDCl_3$, 25 °C, TMS): δ = 1.12 (d, ^3J(H,H) = 6.5 Hz, 3H, *iso*-propylamine-CH_3), 1.15 (d, ^3J(H,H) = 6.4 Hz, 3H, *iso*-propylamine-CH_3), 2.25 (s, 3H, *p*-CH_3), 2.33 (b, 1H, NH), 2.68 (d, ^3J(P,H) = 10.1 Hz, 6H, $N(CH_3)_2$), 3.38 – 3.39 (m, 1H, *iso*-propylamine-CH), 7.03 (m, 4H, Ar-H). – ^{13}C NMR (125.75 MHz, $CDCl_3$, 25 °C, TMS): δ = 20.64 (s, 1C, *p*-CH_3), 25.27 (d, ^3J(P,C) = 5.9 Hz, 1C, *iso*-propylamine-CH_3), 25.52 (d, ^3J(P,C) = 5.3 Hz, 1C, *iso*-propylamine-CH_3), 36.96 (d, ^2J(P,C) = 3.8 Hz, 2C, $N(CH_3)_2$), 43.38 (s, 1C, *iso*-propylamine-CH), 119.92 (d, ^3J(P,C) = 4.8 Hz, 2C, C_{ortho}), 129.96 (s, 2C, C_{meta}), 133.50 (s, 1C, C_{para}), 149.12 (d, ^2J(P,C) = 6.1 Hz, 1C, C_{ipso}). – $^{31}P\{^1H\}$ NMR (202.45 MHz, $CDCl_3$, 25 °C, H_3PO_4 external): δ = 13.70 (s). – ^{31}P 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) $[M–C_7H_7]^+$, 149 (79) $[M–C_7H_7O]^+$, 107 (100) $[C_7H_7O]^+$, 91 (25) $[C_7H_7]^+$, 44 (53) $[C_2H_6N]^+$.

*N,N-Dimethyl-N′-tert-butyl-diamidophosphoric acid 4-methyl-phenyl ester, $[(CH_3)_2N]P(O)[NH(tert\text{-}C_4H_9)][O\text{-}C_6H_4\text{-}p\text{-}CH_3]$ (**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, $CDCl_3$, 25 °C, TMS): δ = 1.32 (s, 9H, *tert*-

butylamine-CH_3), 2.29 (s, 3H, *p*-CH_3), 2.32 (b, 1H, NH), 2.67 (d, ^3J(P,H) = 10.0 Hz, 6H, $N(CH_3)_2$), 7.07 (m, 4H, Ar-H). – ^{13}C NMR (62.90 MHz, $CDCl_3$, 25 °C, TMS): δ = 20.70 (s, 1C, *p*-CH_3), 31.36 (d, ^3J(P,C) = 5.0 Hz, 3C, *tert*-butylamine-CH_3), 36.91 (d, ^2J(P,C) = 3.2 Hz, 2C, $N(CH_3)_2$), 50.80 (s, 1C, *tert*-butylamine-C), 119.90 (d, ^3J(P,C) = 4.8 Hz, 2C, C_{ortho}), 130.00 (s, 2C, C_{meta}), 133.40 (s, 1C, C_{para}), 149.2 (d, ^2J(P,C) = 6.1 Hz, 1C, C_{ipso}). – ^{31}P{^{1}H} NMR (101.25 MHz, $CDCl_3$, 25 °C, H_3PO_4 external): δ = 10.71 (s). – ^{31}P NMR: δ = 10.71 (hept, ^3J(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) $[M–C_4H_{10}N]^+$, 163 (4) $[M–C_7H_7O]^+$, 107 (100) $[C_7H_7O]^+$, 44 (33) $[C_2H_6N]^+$.

*N,N-Dimethyl-N′-paratoluidyl-diamidophosphoric acid 4-methyl-phenyl ester, [(CH$_3$)$_2$N]P(O)[NH-C$_6$H$_4$-p-CH$_3$] [O-C$_6$H$_4$-p-CH$_3$] (**4**)*

Compound **4** was prepared following the procedure described for compound **1** by using *para*-toluidine instead of methylamine hydrochloride. (*para*-toluidine : trietylamine, 1 : 1). Yield: 75 %. M. p. 75 – 79 °C. – ^{1}H NMR (250.13 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.28 (s, 3H, toluidine, *p*-CH_3), 2.30 (s, 3H, tolyl, *p*-CH_3), 2.74 (d, ^3J(P,H) = 10.2 Hz, 6H, $N(CH_3)_2$), 5.09 (d, ^2J(P,H) = 8.2 Hz, 1H, NH), 6.89 – 7.03 (m, 4H, toluidine, Ar-H), 7.08 (m, 4H, tolyl, Ar-H). – ^{13}C NMR (62.90 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.67 (s, 1C, toluidine, *p*-CH_3), 2.80 (s, 1C, tolyl, *p*-CH_3), 36.73 (d, ^2J(P,C) = 4.3 Hz, 2C, $N(CH_3)_2$), 117.90 (d, ^3J(P,C) = 6.7 Hz, 2C, toluidine, C_{ortho}), 120.22 (d, ^3J(P,C) = 4.7 Hz, 2C, tolyl, C_{ortho}), 129.91 (s, 2C, toluidine, C_{meta}), 130.05 (s, 1C, toluidine, C_{para}), 130.23 (s, 2C, tolyl, C_{meta}), 134.20 (s, 1C, tolyl, C_{para}), 138.64 (d, ^2J(P,C) = 1.2 Hz, 1C, toluidine, C_{ipso}), 148.56 (d, ^2J(P,C) = 6.0 Hz, 1C, tolyl, C_{ipso}). – ^{31}P{^{1}H} NMR (101.25 MHz, $CDCl_3$, 25 °C, H_3PO_4 external): δ = 6.94 (s). – ^{31}P 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) $[M–C_7H_7]^+$, 198 (12) $[M–C_7H_7NH]^+$, 197 (33) $[M–C_7H_7O]^+$, 107 (41) $[C_7H_7O]^+$, 91 (18) $[C_7H_7]^+$, 44 (100) $[C_2H_6N]^+$.

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.

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