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The effect of various substituents on the structural parameters of the P(O)[N(CH₃)(CH₂C₆H₅)]₂ moiety. Syntheses and spectroscopic characterization of some new phosphoramidates, crystal structures of P(O)(X)[N(CH₃)(CH₂C₆H₅)]₂, $X = C_6H_5C(O)NH$, Cl and CCl₃C(O)NH

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Abstract

Some new phosphoramidates with the general formula $P(O)(X)[N(CH_3)(CH_2C_6H_5)]_2$, $X = C_6H_5C(O)NH$ (1), Cl (2), $CCl_3C(O)NH$ (3), $N(CH_3)_2$ (4) and 4- NO_2 - C_6H_4NH (5) were prepared and characterized by IR, ¹H, ¹³C, ³¹P NMR spectroscopy and elemental analysis. The structures have been determined for compounds 1–3. Compounds 1 and 3 were obtained in the form of centrosymmetric dimers which were produced by intermolecular $-P=O\cdots H-N-$ hydrogen bonds. In molecules 1–5, containing carbon atoms with two bond distances from the phosphorus atoms, ² $J(P,CH_2) > {}^2J(P,CH_3)$. © 2005 Elsevier Ltd. All rights reserved.

Keywords: X-ray crystallography; NMR spectra; Phosphoramidate; Hydrogen bond

1. Introduction

Phosphoramidates are attractive to study owing to their extensive applications in biochemistry [1,2]. Although many compounds of this series have been reported [3–6], only a few crystal structures, of the formula $P(O)[N(H)R]X_2[7]$, $P(O)[N(H)R]_3[8,9]$, $RC(O)-N(H)P(O)X_2$ [10] and $RC(O)N(H)P(O)[NR^1R^2]_2$ [11–13], are currently known. These compounds were used as O-donor ligands in the reaction with small and hard metal ions [14] and the lithiations of them were discussed [8]. The P–N bond characteristics and its influence on ³¹P

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NMR chemical shifts were considered [15] and also P–C and P–H coupling constants were discussed in order to obtain assignments, conformational and configurational analysis [16,17].

In this study, we report the structures of three new phosphoramidates: *N*-benzoyl, *N'*,*N"*-bis(*N*-benzylmethyl)phosphoric triamide **1**, *N*,*N'*-bis(*N*-benzylmethyl), phosphoramidic chloride **2**, and *N*-trichloroacetyl, *N'*,*N"*-bis(*N*-benzylmethyl)phosphoric triamide **3**. We also considered the structural parameters of several previous reported structures [18–23]. Furthermore, we synthesized two other phosphoramidates: *N*,*N*-dimethyl, *N'*,*N"*-bis(*N*-benzylmethyl)phosphoric triamide **4** and *N*-4-nitrophenyl, *N'*,*N"*-bis(*N*-benzylmethyl)phosphoric triamide **5**. Two bond distance coupling constants, ${}^{2}J(\mathbf{P},\mathbf{C})_{\text{benzylic}}$ of these molecules were compared to ${}^{2}J(\mathbf{P},\mathbf{C})_{\text{methyl}}$.

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2. Experimental

2.1. Materials

Dimethylamine solution (40% in water), 4-nitroaniline (\geq 99%), phosphorus pentachloride (\geq 98%), formic acid (98%), phosphorus oxychloride (\geq 98%) (Fluka) and *N*-benzylmethylamine (\geq 98%), benzamide (\geq 98%), 2,2,2-trichloroacetamide (\geq 98%) (Merck) were used as supplied. In all reactions, low temperature conditions were used.

2.2. X-ray measurements

X-ray data were collected on an Enraf Nonius CAD4 for compound 1 and a Bruker SMART 1000 CCD single crystal diffractometer for compounds 2 and 3 with graphite monochromated Mo K α radiation ($\lambda =$ 0.71073 Å). The structures were refined with SHELXL-97 [24] by full matrix least squares on F^2 . The positions of hydrogen atoms were obtained from the difference Fourier map. Routine Lorentz and polarization corrections were applied and an absorption correction was performed for compounds 2 and 3 using the SADABS program [25].

2.3. Spectroscopic measurements

¹H, ¹³C and ³¹P NMR spectra were recorded on a Bruker Avance DRS 500 spectrometer. ¹H and ¹³C chemical shifts were determined relative to internal TMS, ³¹P chemical shifts relative to 85% H₃PO₄ as external standard. Infrared (IR) spectra were recorded on a Shimadzu model IR-60 spectrometer. Elemental analysis was performed using a Heraeus CHN-O-RA-PID apparatus.

2.4. Syntheses

 $C_6H_5C(O)NHP(O)Cl_2$ and $CCl_3C(O)NHP(O)Cl_2$ were prepared similar to the procedure by Kirsanov et al. [26,27] and Me₂NP(O)Cl₂ and 4-NO₂- $C_6H_4NHP(O)Cl_2$ were prepared similar to the procedure by Keat and Shaw [28] and Johnson et al. [29], respectively.

2.4.1. N-benzoyl, N', N"-bis(N-benzylmethyl)phosphoric triamide (1)

N-benzylmethyl amine (1.21 g, 10 mmol) was added to a solution of *N*-benzoyl phosphoramidic dichloride (0.595 g, 2.5 mmol) in chloroform (40 ml) and stirred at -5 °C. After 4 h, the solvent was removed and the residue that formed was stirred in H₂O. The product was filtered and washed with H₂O and recrystallized from chloroform/*n*-heptane; m.p. 141 °C. *Anal.* Calc. for C₂₃H₂₆N₃O₂P: C, 67.80; H, 6.43; N, 10.31. Found:

C. 67.83; H. 6.40; N. 10.30%. ³¹P NMR (CDCl₃): δ 16.65 (m). ¹³C NMR (CDCl₃): δ 168.95 (s, C=O), 138.04 (d, ${}^{3}J(P,C) = 4.2 \text{ Hz}$), 133.49 (d, ${}^{3}J(P,C) =$ 8.7 Hz), 132.38 (s), 128.64 (s), 128.46 (s), 128.27 (s), 128.12 (s), 127.23 (s), 53.10 (d, ${}^{2}J(P,C) = 5.3$ Hz), 33.82 (d, ${}^{2}J(P,C) = 5.0 \text{ Hz}$). ${}^{1}H$ NMR (CDCl₃): δ 2.72 $(d, {}^{3}J(PNCH) = 10.3 \text{ Hz}, 6H, 2CH_{3}), 4.22 (dd, {}^{3}J (PNCH) = 9.3 \text{ Hz}, {}^{2}J(H,H) = 15.0 \text{ Hz}, 2H, 2CH_{benzylic}),$ 4.37 (dd, ${}^{3}J(\text{PNCH}) = 9.3 \text{ Hz}$, ${}^{2}J(\text{H},\text{H}) = 15.0 \text{ Hz}$, 2H, 2CH_{benzvlic}), 7.22–7.44 (m, 12 Ar–H), 7.50 (t, ${}^{3}J(H,H) = 7.2$ Hz, 1Ar–H), 8.16 (d, ${}^{3}J(H,H) = 7.7$ Hz, 2Ar–H), 9.64 (s, NH, 1H). ${}^{1}H{}^{31}P{}$ NMR (CDCl₃): δ 2.72 (s), 4.22 (d, ${}^{2}J(H,H) = 15.0 \text{ Hz}$), 4.37 (d, $^{2}J(H,H) = 15.0 \text{ Hz}$, 7.21–7.53 (m), 9.64 (s). IR (KBr, cm⁻¹): 3050 (vNH), 1885, 1666 (vC=O), 1446, 1179 (vP=O), 1001, 937, 869 (vP-N), 700 (vP-N).

2.4.2. N,N'-bis(N-benzylmethyl)phosphoramidic chloride (2)

N-benzylmethyl amine (2.41 g, 20 mmol) was added to a solution of phosphoryl chloride (0.76 g, 5 mmol) in acetonitrile (25 ml) and stirred at -5 °C. After 8 h, the precipitate was filtered and the product was obtained from solution by column chromatography [silica gel; hexane:ethyl acetate (4:1)]; m.p. 120 °C. Anal. Calc. for C₁₆H₂₀ClN₂OP: C, 59.54; H, 6.25; N, 8.68. Found: C, 59.51; H, 6.21; N, 8.66%. ³¹P NMR (CDCl₃): δ 34.18 (m). ¹³C NMR (CDCl₃): δ 138.11 (d, ³*J*(P,C) = 5.5 Hz), 129.34 (s), 129.14 (s), 128.34 (s), 53.54 (d, $^{2}J(P,C) = 4.0 \text{ Hz}$, 34.11 (d, $^{2}J(P,C) = 3.5 \text{ Hz}$). ^{1}H NMR (CDCl₃): δ 2.63 (d, ³*J*(PNCH) = 12.6 Hz, 6H, 2CH₃), 4.33 (m, 4H, 2CH₂), 7.29-7.44 (m, 10Ar-H). ${}^{1}H{}^{31}P{NMR}$ (CDCl₃): δ 2.63 (s), 4.33 (m), 7.29–7.44 (m). IR (KBr, cm^{-1}): 3015, 1484, 1442, 1334, 1219, 1190 (vP=O), 1126, 1064, 949, 910, 786 (vPN), 699, 631, 530 (vPCl), 446.

2.4.3. N-trichloroacetyl, N', N"-bis(N-benzylmethyl)phosphoric triamide (3)

N-benzylmethyl amine (0.97 g, 8 mmol) was added to a solution of trichloroacetyl phosphoramidic dichloride (0.56 g, 2 mmol) in acetonitrile (40 ml) and stirred at -5 °C. After 4 h, the solvent was removed and the residue that formed was stirred in H₂O. The product was filtered and washed with H₂O and recrystallized from chloroform/n-heptane; m.p. 153 °C. Anal. Calc. for C₁₈H₂₁Cl₃N₃O₂P: C, 48.18; H, 4.72; N, 9.36. Found: C, 48.16; H, 4.70; N, 9.37%. ³¹P NMR (d₆-DMSO): δ 13.86 (m). ¹³C NMR (d₆-DMSO): δ 163.50 (s, C=O), 139.27 (d, ${}^{3}J(P,C) = 4.8$ Hz), 129.81 (s), 129.48 (s), 128.63 (s), 93.08 (d, ${}^{3}J(P,C) = 9.6$ Hz, CCl₃), 59.63 (s), 51.82 (d, ${}^{2}J(P,C) = 4.9 \text{ Hz}$), 33.23 (d, ${}^{2}J(P,C) = 4.6$ Hz). ¹H NMR (d₆-DMSO): $\delta = 2.49$ $(d, {}^{3}J(PNCH) = 10.2 \text{ Hz}, 6H, 2CH_{3}), 4.16 (d,$ ${}^{3}J(\text{PNCH}) = 9.1 \text{ Hz}, 4\text{H}, 2\text{CH}_{2}), 7.26-7.39 \text{ (m, } 10\text{Ar}-1000 \text{ m})$ H), 10.34 (b, 1H, NH). ${}^{1}H{}^{31}P{}NMR$ (d₆-DMSO): δ 2.49 (s), 4.16 (s), 7.26–7.39 (m), 10.34 (b). IR (KBr, cm⁻¹): 3405 (νNH), 3020, 2915, 2760, 1712 (νC=O), 1452, 1348, 1230, 1198 (νP=O), 1145, 1008, 948, 876 (νPN), 834, 794 (νPN), 695, 669 (νCCl), 588, 491, 453.

2.4.4. N,N-dimethyl, N',N"-bis(N-benzylmethyl)phosphoric triamide (4)

N-benzylmethyl amine (0.81 g, 5 mmol) was added to a solution of N,N-dimethylphosphoramidic dichloride (2.42 g, 20 mmol) in acetonitrile (30 ml) and stirred at -5 °C. After 8 h, the precipitate was filtered and the product was obtained from solution by column chromatography [silica gel; hexane:ethyl acetate (8:1)]. Anal. Calc. for C₁₈H₂₆N₃OP: C, 65.24; H, 7.91; N, 12.61. Found: C, 65.23; H, 7.89; N, 12.63%. ³¹P NMR (CDCl₃): δ 25.48 (m). ¹³C NMR (CDCl₃): δ 138.44 (d, ${}^{3}J(P,C) = 4.5 \text{ Hz}, 130.24 \text{ (s)}, 128.23 \text{ (s)}, 127.13 \text{ (s)},$ 53.18 (d, ${}^{2}J(P,C) = 4.6$ Hz), 37.03 (d, ${}^{2}J(P,C) = 4.0$ Hz), 33.92(d, ${}^{2}J(P,C) = 3.7 \text{ Hz}$). ¹H NMR (CDCl₃): δ 2.54 $(d, {}^{3}J(PNCH) = 9.1 \text{ Hz}, 6 \text{ H}, N(CH_{3})_{2}), 2.69 (d,$ ${}^{3}J(\text{PNCH}) = 9.6 \text{ Hz}, 6\text{H}, 2\text{CH}_{3}, 4.10 \text{ (dd,}$ ³.J- $(PNCH) = 8.3 \text{ Hz}, {}^{2}J(H,H) = 14.8 \text{ Hz}, 2H, 2CH_{benzylic}),$ 4.20 (dd, ${}^{3}J(PNCH) = 8.3$ Hz, ${}^{2}J(H,H) = 14.8$ Hz, 2H, 2CH_{benzylic}), 7.23–7.36 (m, 10Ar–H). ¹H{³¹P}NMR $(CDCl_3)$: δ 2.54 (s), 2.69 (s), 4.10 (d, ²J(H,H) = 14.8 Hz), 4.20 (d, ${}^{2}J(H,H) = 14.8 \text{ Hz}$), 7.23–7.36 (m). IR (KBr, cm⁻¹): 3415, 2920, 2765, 2420, 1724, 1443, 1296, 1204 (vP=O), 998, 946, 778 (vPN), 731 (vPN), 694, 592, 472.

2.4.5. N-4-nitrophenyl, N',N"-bis(N-benzylmethyl)phosphoric triamide (5)

N-benzylmethyl amine (0.97 g, 8 mmol) was added to a mixture of N-4-nitrophenyl phosphoramidic dichloride (0.51 g, 2 mmol) in carbon tetrachloride (30 ml) and stirred at -5 °C. After 6 h, the solvent was removed and the residue that formed was stirred in H₂O. The product was filtered and washed with H₂O; m.p. 115 °C. Anal. Calc. for C22H25N4O3P: C, 62.26; H, 5.94; N, 13.20. Found: C, 62.24; H, 5.95; N, 13.18%. ³¹P NMR (d₆-DMSO): δ 14.79 (m). ¹³C NMR (d₆-DMSO): δ 141.73 (s), 137.17 (d, ${}^{3}J(P,C) = 4.0 \text{ Hz})$, 128.71 (s), 128.34 (s), 128.27 (s), 127.74 (s), 125.55 (s), 117.15 (d, ${}^{2}J(P,C) = 6.5$ Hz), 53.13 (d, ${}^{2}J(P,C) = 4.8$ Hz), 34.04 (d, ${}^{2}J(P,C) = 4.4$ Hz). ¹H NMR (d₆-DMSO): 2.63 $(d, {}^{3}J(PNCH) = 10.0 \text{ Hz}, 6H, 2CH_{3}), 4.25 (dd, {}^{3}J (PNCH) = 7.1 \text{ Hz}, {}^{2}J(H,H) = 14.8 \text{ Hz}, 2H, 2CH_{benzylic}),$ 4.27 (dd, ${}^{3}J(PNCH) = 7.1$ Hz, ${}^{2}J(H,H) = 14.8$ Hz, 2H, $2CH_{benzylic}$), 7.16 (d, ${}^{3}J(H,H) = 9.1$ Hz, 2Ar–H), 7.33 (m, 10Ar–H), 8.07 (d, ${}^{3}J(H,H) = 9.1$ Hz, 2Ar–H), 8.30 $(d, {}^{2}J(PNH) = 9.2 \text{ Hz}, 1\text{ H}, \text{ NH}). {}^{1}H{}^{31}P{}NMR (d_{6}-$ DMSO): δ 2.63 (s), 4.25 (d, ²J(H,H) = 14.8 Hz), 4.27 $(d, {}^{2}J(H,H) = 14.8 \text{ Hz}), 7.16 (d, {}^{3}J(H,H) = 9.1 \text{ Hz}),$ 7.33 (s), 8.07 (d, ${}^{3}J(H,H) = 9.1 \text{ Hz}$), 8.30 (s, 1 H, NH). IR (KBr, cm⁻¹): 3145 (vNH), 2905, 1587 (vNO₂), 1490, 1470, 1327 (vNO₂), 1291, 1247 (vP=O), 1198,

1164, 1103, 969, 902 (vPN), 840, 769, 720 (vPN), 690, 531.

3. Results and discussion

The reaction of *N*-benzylmethylamine with *N*benzoyl phosphoramidic dichloride, trichloroacetyl phosphoramidic dichloride, phosphoryl chloride, *N*, *N*-dimethyl phosphoramidic dichloride and *N*-4-nitrophenyl phosphoramidic dichloride leads to the corresponding phosphoramidates, Scheme 1. The general synthetic methods involve the reactions between the halogen–phosphorus compounds with an amine either alone (in excess) or in the presence of another HCl scavenger (such as triethylamine). The main challenge in these reactions is the separation of the phosphoramidate from the alkylammonium chloride byproduct.

3.1. NMR Study

The molecules 1–5 indicate two various ${}^{2}J(P,C)$ coupling constants for the CH₃ and CH₂ groups in the



Scheme 1. Preparation of compounds 1-5.

No.	Compound	$^{2}J(\mathbf{P},\mathbf{C})_{\mathrm{aliphatic}}$	$^{2}J(P,C)_{benzylic}$	Reference
1	$P(O)(C_6H_5C(O)NH)[N(CH_3)(CH_2C_6H_5)]_2$	5.0	5.3	а
2	$P(O)(Cl)[N(CH_3)(CH_2C_6H_5)]_2$	3.5	4.0	а
3	P(O)(CCl ₃ C(O)NH)[N(CH ₃)(CH ₂ C ₆ H ₅)] ₂	4.6	4.9	а
4	P(O)[N(CH ₃) ₂][N(CH ₃)(CH ₂ C ₆ H ₅)] ₂	3.7, 4.0 [N(CH ₃) ₂]	4.6	а
5	$P(O)(p-NHC_6H_4NO_2)[N(CH_3)(CH_2C_6H_5)]_2$	4.4	4.8	а
6	$(4-CH_3-C_6H_4-O)_2P(O)[N(C_2H_5)(CH_2C_6H_5)]$	3.5	4.9	[21]
7	$(4-CH_3-C_6H_4-O)P(O)(Cl)[N(C_2H_5)(CH_2C_6H_5)]$	3.6	4.6	[21]

Table 1 ${}^{2}J(P,C)_{aliphatic}$ and ${}^{2}J(P,C)_{benzylic}$, Hz in some phosphoramidates

^a This work.

benzylmethylamine moiety, furthermore, compound **4** shows a ${}^{2}J(P,C)$ coupling constant for the CH₃ in the N(CH₃)₂ group. ${}^{2}J(P,C)$ coupling constants in these compounds are in the range of 3.5–5.3 Hz and for each compound ${}^{2}J(P,CH_{2}) > {}^{2}J(P,CH_{3})$, Table 1. The presence of phenyl groups linked to CH₂ causes the deshielding of the CH₂ carbon atoms relative to the CH₃ carbon atoms. Methylene and methyl carbon atoms in compounds **1–5** appear in the range of 51.82–53.54 and 33.23–34.11 ppm in ${}^{13}C$ NMR spectra, respectively. The deshielding of the methylene groups leads to a greater interaction with the corresponding phosphorus atoms. Also, in compounds with the P(O)[N(CH₂CH₃) (CH₂C₆H₅)] moiety [21], Table 1, ${}^{2}J[P,(CH_{2})_{\text{benzylic}}] > {}^{2}J[P,(CH_{2})_{\text{aliphatic}}]$.

The *ipso*-carbon atoms of the phenyl rings related to the amine groups are split into doublet signals by their phosphorus atoms, ${}^{3}J(P,C)$ coupling constant, also mol-

ecules 1 and 3 show a ${}^{3}J(P,C)$ coupling constant for the benzoyl and trichloroacetyl groups of 8.7 and 9.6 Hz, respectively. NH signals of compounds 1 and 3 do not show two bond distance couplings with the P atom, $^{2}J(\text{PNH})$, but in molecule 5, a doublet signal is obtained for NH with ${}^{2}J(PNH) = 9.2$ Hz. The protons of methyl and methylene groups in these compounds indicate ³J(PNCH) coupling constants. Fig. 1 indicates the multiplet structure in the ³¹P NMR spectrum of compound 5 which is produced by the couplings with H atoms of two N(CH₃)(CH₂C₆H₅) groups, the measured ${}^{3}J$ (PNCH) from the ¹H NMR spectrum for this compound are 10 and 7.1 Hz (for the methyl and methylene protons of the $P-N(CH_3)(CH_2C_6H_5)$ moiety). The two benzylic protons are diastereotopic and usually appear with different chemical shifts, but when the rotational energy barrier around the P-N bond is low, these appear with equal chemical shifts on the NMR timescale. Each of



Fig. 1. ³¹P NMR spectrum of compound 5.

the benzylic protons (of compounds 1, 2, 4 and 5) represents the splitting by the phosphorus atom, ${}^{3}J(PNCH)$, followed by ${}^{2}J(H,H)$ splitting. Compound 3 shows only a doublet signal produced by a ${}^{3}J(PNCH)$ coupling constant (the benzylic protons do not have different chemical shifts at 298 K). A similar result was obtained for the benzylic protons of $(CH_3)(C_6H_5CH_2)$ NP(O)(Cl)(4-OC₆H₄CH₃) [30] (a doublet peak at 4.26 ppm) which on lowering the temperature, the protons appear with different chemical shifts.

3.2. X-ray crystallography investigation

Single crystals of compounds 1–3 were obtained from a solution of chloroform and 1-heptane after slow evaporation at room temperature. The crystal data and the details of the X-ray analysis are given in Table 2, selected bond lengths and angles are given in Table 3. Molecular structures of compounds 1–3 are shown in Figs. 2–4.

Both compounds 1 and 3 contain one amidic hydrogen atom and form centrosymmetric dimers, see Fig. 5 for compound 3, that are produced by two equivalent intermolecular $-P=O\cdots H-N-$ hydrogen bonds (Table 4). The earlier studied *N*-benzoyl, phosphoric triamides

Table 2 Crystallographic data for **1**, **2** and **3**

exist either in the form of dimeric aggregates [31] or as polymeric chains [32].

In molecules 1 and 3, the phosphoryl and the carbonyl groups are anti, Figs. 2 and 4. The phosphorus atoms in the structures 1-3 have a slightly distorted tetrahedral configuration. The bond angles around the P(1) atoms in these compounds are in the range of $118.9^{\circ}-102.53^{\circ}$, for the angles O(1)–P(1)–N(2) and N(2)–P(1)–Cl(1) in structure 2. For both compounds 1 and 3, the highest values of the bond angles around phosphorus atoms were obtained for the angles O(1)–P(1)–N(1) in compounds 1 and 3, $105.55(12)^{\circ}$ and $104.81(8)^{\circ}$, are lower than the angles O(1)–P(1)–N(2) and O(1)–P(1)–N(3) ($118.26(13)^{\circ}$, $109.80(13)^{\circ}$ for 1 and $117.53(9)^{\circ}$, $112.05(9)^{\circ}$ for 3).

P(1)–N(2) and P(1)–N(3) bond lengths are 1.630(3) and 1.629(2) Å in compound 1 and 1.6312(17) and 1.6271(17) Å in compound 3. Also, in compound 2 P(1)–N(1) and P(1)–N(2) are 1.610(4) and 1.634(4) Å, respectively. They are significantly shorter than the typical P–N single bond length (1.77 Å) [33]. The shortening of PN bond lengths is likely related to an electrostatic effect (polar bond) which overlaps with P–N σ bond [34]. In compounds 1 and 3, the P(1)–N(1)

	1	2	3
Empirical formula	C ₂₃ H ₂₆ N ₃ O ₂ P	C ₁₆ H ₂₀ ClN ₂ OP	$C_{18}H_{21}Cl_3N_3O_2P$
Formula weight	407.44	322.76	448.70
Temperature (K)	293(2)	116(2)	120(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	orthorhombic	triclinic
Space group	$P\overline{1}$	$P2_{1}2_{1}2_{1}$	$P\overline{1}$
Unit cell dimensions			
a (Å)	9.832(4)	6.939(2)	10.363(2)
b (Å)	10.949(4)	7.176(2)	10.862(2)
<i>c</i> (Å)	11.631(5)	32.447(10)	11.023(2)
$\alpha(^{\circ})$	91.99(3)	90	71.81(3)
β (°)	100.51(3)	90	67.44(3)
γ (°)	115.35(3)	90	63.29(3)
$V(\text{\AA}^3)$	1103.5(8)	1615.8(9)	1008.7(4)
Z, calculated density (Mg m^{-3})	2, 1.226	4, 1.327	2, 1.477
Absorption coefficient (mm ⁻¹)	0.148	0.336	0.553
$F(0\ 0\ 0)$	432	680	464
Crystal size (mm)	$0.6 \times 0.2 \times 0.2$	$0.8 \times 0.6 \times 0.2$	$0.6 \times 0.3 \times 0.2$
θ Range for data collection (°)	1.80-26.97	2.51-24.00	2.03-30.06
Limiting indices	$0 \leqslant h \leqslant 12; -13 \leqslant k \leqslant 12;$	$-7 \leqslant h \leqslant 7; -8 \leqslant k \leqslant 8;$	$-14 \leqslant h \leqslant 14; -14 \leqslant k \leqslant 15;$
	$-14 \leqslant l \leqslant 14$	$-36 \leqslant l \leqslant 37$	$-15 \leqslant l \leqslant 15$
Reflections collected/unique (R_{int})	5063/4774 (0.0255)	10 637/2381 (0.0642)	12 120/5854 (0.0165)
Completeness to θ (%)	99.4	94.5	98.7
Absorption correction	none	semi-empirical from equivalents	semi-empirical from equivalents
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	4774/0/262	2381/0/190	5854/0/244
Goodness-of-fit on F^2	1.009	0.992	0.990
Final R indices	$R_1 = 0.0612; wR_2 = 0.1243$	$R_1 = 0.0647; wR_2 = 0.1219$	$R_1 = 0.0445; wR_2 = 0.0917$
R indices (all data)	$R_1 = 0.0854; wR_2 = 0.1340$	$R_1 = 0.0671; wR_2 = 0.1229$	$R_1 = 0.0498; wR_2 = 0.0937$
Absolute structure parameter		-0.06(17)	
Largest differential peak and hole (e $Å^{-3}$)	0.369 and -0.405	0.657 and -0.342	0.709 and -0.778

Table 3 Selected bond lengths (Å) and angles (°) for compounds $1{-}3$

1		2		3	
Bond lengths					
P(1)–N(1)	1.676(2)	P(1)–O(1)	1.459(4)	P(1)–O(1)	1.4785(15)
P(1)–N(2)	1.630(3)	P(1)–N(1)	1.610(4)	P(1)–N(3)	1.6271(17)
P(1)–N(3)	1.629(2)	N(1)-C(7)	1.463(6)	P(1)–N(2)	1.6312(17)
O(2)–C(1)	1.216(3)	N(1)-C(8)	1.461(6)	P(1)–N(1)	1.7037(16)
N(1)–C(1)	1.372(3)	P(1)–N(2)	1.634(4)	O(2)–C(2)	1.212(2)
P(1)–O(1)	1.476(2)	P(1)–Cl(1)	2.0554(19)	C(1)–C(2)	1.562(3)
N(2)–C(8)	1.452(4)	N(2)–C(9)	1.468(6)	Cl(2)–C(1)	1.763(2)
N(3)-C(16)	1.451(3)	N(2)-C(10)	1.451(6)	Cl(3)–C(1)	1.756(2)
N(2)–C(9)	1.460(4)	C(1)–C(2)	1.390(8)	Cl(1)–C(1)	1.780(2)
N(3)-C(17)	1.466(4)	C(1)–C(6)	1.388(8)	N(1)–C(2)	1.357(2)
C(1)–C(2)	1.491(4)	C(2)–C(3)	1.386(9)	N(2)–C(3)	1.457(2)
C(22)-C(23)	1.371(5)	C(15)-C(16)	1.364(8)	N(2)–C(4)	1.467(2)
Bond angles					
O(1)-P(1)-N(1)	105.55(12)	O(1)–P(1)–N(1)	114.2(2)	O(1)–P(1)–N(3)	112.05(9)
O(1)–P(1)–N(2)	118.26(13)	O(1)–P(1)–N(2)	118.9(2)	O(1)–P(1)–N(2)	117.53(9)
O(1)–P(1)–N(3)	109.80(13)	N(1)-P(1)-N(2)	105.4(2)	N(3)–P(1)–N(2)	106.79(9)
N(2)–P(1)–N(3)	104.49(13)	O(1) - P(1) - Cl(1)	107.70(19)	O(1) - P(1) - N(1)	104.81(8)
N(2)–P(1)–N(1)	106.08(13)	N(1)-P(1)-Cl(1)	106.94(18)	C(3)-N(2)-P(1)	124.81(14)
N(3)–P(1)–N(1)	112.81(13)	N(2)-P(1)-Cl(1)	102.53(16)	C(4)-N(2)-P(1)	120.09(13)
O(2)-C(1)-N(1)	121.4(3)	C(8)–N(1)–C(7)	115.5(4)	C(11)–N(3)–C(12)	115.75(16)
C(1)-N(1)-P(1)	127.6(2)	C(8)-N(1)-P(1)	122.6(3)	C(11)-N(3)-P(1)	122.60(13)
C(8)-N(2)-C(9)	113.6(3)	C(7)-N(1)-P(1)	120.9(4)	N(1)-C(2)-C(1)	113.86(16)
C(8)–N(2)–P(1)	118.2(2)	C(10)–N(2)–C(9)	114.4(4)	N(3)-P(1)-N(1)	110.94(9)
C(16)-N(3)-C(17)	114.8(2)	C(10)-N(2)-P(1)	122.7(3)	N(2)-P(1)-N(1)	104.43(8)
C(16)–N(3)–P(1)	125.8(2)	C(9)-N(2)-P(1)	121.8(3)	C(2)-N(1)-P(1)	127.13(13)
C(9)–N(2)–P(1)	125.5(2)	C(2)-C(1)-C(6)	120.5(5)	C(3)-N(2)-C(4)	114.76(16)
C(17)–N(3)–P(1)	119.41(19)	C(3)-C(2)-C(1)	119.6(6)	C(12)–N(3)–P(1)	121.54(14)
N(1)-C(1)-C(2)	116.6(2)	C(2)-C(3)-C(4)	119.6(5)	N(3)-C(12)-C(13)	113.37(16)
N(3)-C(17)-C(18)	114.1(3)	C(11)-C(16)-C(15)	119.6(5)	O(2)–C(2)–N(1)	126.63(18)
C(3)-C(2)-C(1)	123.6(3)	C(11)-C(16)-C(10)	120.9(5)	O(2)–C(2)–C(1)	119.48(16)
C(23)-C(18)-C(17)	120.4(3)	C(15)-C(16)-C(10)	119.5(5)	N(2)-C(4)-C(5)	114.25(16)



Fig. 2. Molecular structure and atom-labelling scheme for $P(O)(C_6H_5-C(O)NH)[N(CH_3)(CH_2C_6H_5)]_2$, compound 1 (50% probability ellipsoids).

bond lengths (1.676(2) and 1.7037(16) Å, respectively) are longer than the P(1)–N(2) and P(1)–N(3) bond lengths due to the resonance interaction with the C=O system that causes a partial multiple-bond character in N(1)–C(1) (compare N(1)–C(1) in compound 1 and



Fig. 3. Molecular structure and atom-labelling scheme for $P(O)(Cl)[N(CH_3)(CH_2C_6H_5)]_2$, compound **2** (50% probability ellipsoids).



Fig. 4. Molecular structure and atom-labelling scheme for $P(O)(CCl_3-C(O)NH)[N(CH_3)(CH_2C_6H_5)]_2$, compound **3** (50% probability ellipsoids).

N(1)–C(2) in compound **3** with other N–C bond lengths, Table 3). In the previous reported structures, we obtained the P–N bond lengths of (O)P–N(H)–C(O) and P–NR¹R² moieties in the range of 1.678(2)–1.718(3) Å and 1.6032(17)–1.642(2) Å, respectively (Table 5).

The environment of the nitrogen atoms is practically planar. In compound 1, the angles C(8)-N(2)-C(9), C(8)-N(2)-P(1) and C(9)-N(2)-P(1) are 113.6(3)°, 118.2(2)° and 125.5(2)°, respectively, with average 119.1°. Similar results were obtained for the bond angles

C(17) C(16) C(18) C(15) 2(13) C(12) C(14) N(3 0(1) H(1NA) N(1A) N(1) VI2 H(1N) C(9 C(10) O(1A) CI(2) 002121

Fig. 5. Centrosymmetric dimer of compound **3**, produced by hydrogen bonds.

around N(3) atom (average 120°). Also, the sum of the surrounding angles for N(1), N(2) in compound **2** and N(2), N(3) in compound **3** are 359°, 358.9° and 359.7°, 359.9°, respectively. Furthermore, the angles C(1)–N(1)–P(1) in compound **1** and C(2)–N(1)–P(1) in compound **3** are 127.6(2)° and 127.13(13)°. These results confirm the sp² hybridization for the nitrogen atoms,

Table 4 Hydrogen bonds $D-H\cdots A$ for compounds 1 and 3

<i>J</i>	I				
Compound	D–H···A	d(D–H)	$d(\mathbf{H} \cdot \cdot \cdot \mathbf{A})$	∠DHA	$d(\mathbf{D}\cdots\mathbf{A})$
1	N1–H1A···O1' $[-x, -y + 1, -z]$	0.860	1.967	165.87	2.809(3)
3	N1–H1N···O1 $[1-x, -y, -z]$	0.891	1.915	168.13	2.794(2)

Table 5

P=O and P-N bond lengths (Å) in some phosphorus compounds

1 = 0 and $1 = 10$ bond lengths (A) in some pho	osphorus compounds				
Compound	P=O	P–N	P–N	P–N	Reference
$P(O)(C_6H_5C(O)NH)[N(CH_3)(CH_2C_6H_5)]_2$	1.476(2)	1.631(3)	1.631(2)	1.678(2) ^c	а
$P(O)(Cl)[N(CH_3)(CH_2C_6H_5)]_2$	1.471(2)	1.615(2)	1.635(3)		а
$P(O)(CCl_3C(O)NH)[N(CH_3)(CH_2C_6H_5)]_2$	1.4785(15)	1.6271(17)	1.6312(17)	1.7037(16) ^c	а
$P(O)(CCl_3C(O)NH)[NH(tert-C_4H_9)]_2$	1.466(2)	1.608(3)	1.611(4)	$1.718(3)^{c}$	[18]
$P(O)(C_6H_5C(O)NH)[NH(tert-C_4H_9)]_2^b$	1.473(2), 1.476(2)	1.629(2), 1.619(3)	1.629(2), 1.629(2)	$1.711(2)^{\circ}, 1.704(2)$	[18]
$P(O)(C_6H_5C(O)NH)(C_4H_8N)_2$	1.487(3)	1.615(4)	1.618(4)	$1.679(4)^{c}$	[19]
$P(O)[N(CH_3)_2](p-NHC_6H_4CH_3)_2$	1.478(3)	1.626(3), N(CH ₃) ₂	1.642(2)		[22]
$P(O)[N(CH_3)_2](p-OC_6H_4NO_2)_2$	1.4547(14)	1.6032(17)			[23]
$P(O)(p-OC_6H_4CH_3)_2[(C_6H_5)(CH_3)CH-NH]^b$	1.462(3), 1.469(3)	1.610(5), 1.614(5)			[21]

^a This work.

^b These compounds appear as two crystallographically independent molecules.

^c The data are related to P-N of the (O)P-N(H)-C(O) moiety.

although due to repulsion and steric interactions, some angles are greater and others are smaller than 120°.

The P=O bond lengths in molecules 1-3 are 1.476(2), 1.459(4) and 1.478(2) Å, which are larger than the normal P=O bond length (1.45 Å) [33]. The P=O bond lengths in our previously reported structures are in the range of 1.455(1)-1.487(3) Å (Table 5).

4. Supplementary data

Crystallographic data for the structures in this paper have been deposited with Cambridge Crystallographic Data Center as Supplementary Publication Nos. CCDC 240844 ($C_{23}H_{26}N_3O_2P$), 240845 ($C_{16}H_{20}Cl_1N_2OP$) and 240846 ($C_{18}H_{21}Cl_3N_3O_2P$). Copies of the data may be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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