# The effect of various substituents on the structural parameters of the $\mathrm{P}(\mathrm{O})\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)\left(\mathrm{CH}_{2} \mathrm{C}_{6} \mathrm{H}_{5}\right)\right]_{2}$ moiety. Syntheses and spectroscopic characterization of some new phosphoramidates, crystal structures of $\mathrm{P}(\mathrm{O})(\mathrm{X})\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)\left(\mathrm{CH}_{2} \mathrm{C}_{6} \mathrm{H}_{5}\right)\right]_{2}$, $\mathrm{X}=\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{C}(\mathrm{O}) \mathrm{NH}, \mathrm{Cl}$ and $\mathrm{CCl}_{3} \mathrm{C}(\mathrm{O}) \mathrm{NH}$ 

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#### Abstract

Some new phosphoramidates with the general formula $\mathrm{P}(\mathrm{O})(\mathrm{X})\left[\mathrm{N}_{( }\left(\mathrm{CH}_{3}\right)\left(\mathrm{CH}_{2} \mathrm{C}_{6} \mathrm{H}_{5}\right)\right]_{2}, \mathrm{X}=\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{C}(\mathrm{O}) \mathrm{NH}$ (1), Cl (2), $\mathrm{CCl}_{3} \mathrm{C}(\mathrm{O}) \mathrm{NH}(3), \mathrm{N}\left(\mathrm{CH}_{3}\right)_{2}(4)$ and $4-\mathrm{NO}_{2}-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NH}(5)$ were prepared and characterized by IR, ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C},{ }^{31} \mathrm{P}$ NMR spectroscopy and elemental analysis. The structures have been determined for compounds $\mathbf{1}-\mathbf{3}$. Compounds $\mathbf{1}$ and $\mathbf{3}$ were obtained in the form of centrosymmetric dimers which were produced by intermolecular $-\mathrm{P}=\mathrm{O} \cdots \mathrm{H}-\mathrm{N}-$ hydrogen bonds. In molecules $\mathbf{1}-\mathbf{5}$, containing carbon atoms with two bond distances from the phosphorus atoms, ${ }^{2} J\left(\mathrm{P}, \mathrm{CH}_{2}\right)>{ }^{2} J\left(\mathrm{P}, \mathrm{CH}_{3}\right)$. © 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 $\mathrm{P}(\mathrm{O})[\mathrm{N}(\mathrm{H}) \mathrm{R}] \mathrm{X}_{2}$ [7], $\mathrm{P}(\mathrm{O})[\mathrm{N}(\mathrm{H}) \mathrm{R}]_{3}[8,9], \mathrm{RC}(\mathrm{O})$ $\mathrm{N}(\mathrm{H}) \mathrm{P}(\mathrm{O}) \mathrm{X}_{2}$ [10] and $\mathrm{RC}(\mathrm{O}) \mathrm{N}(\mathrm{H}) \mathrm{P}(\mathrm{O})\left[\mathrm{NR}^{1} \mathrm{R}^{2}\right]_{2} \quad[11-$ 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 $\mathrm{P}-\mathrm{N}$ bond characteristics and its influence on ${ }^{31} \mathrm{P}$

[^0]NMR chemical shifts were considered [15] and also P-C and $\mathrm{P}-\mathrm{H}$ 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, $N^{\prime}, N^{\prime \prime}$-bis( $N$-benzylmethyl)phosphoric triamide $\mathbf{1}, N, N^{\prime}$-bis( $N$-benzylmethyl), phosphoramidic chloride $\mathbf{2}$, and $N$-trichloroacetyl, $N^{\prime}, N^{\prime \prime}$-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, $N^{\prime}, N^{\prime \prime}$-bis( $N$-benzylmethyl)phosphoric triamide 4 and $N$-4-nitrophenyl, $N^{\prime}, N^{\prime \prime}$-bis( $N$-benzylmethyl)phosphoric triamide 5. Two bond distance coupling constants, ${ }^{2} J(\mathrm{P}, \mathrm{C})_{\text {benzylic }}$ of these molecules were compared to ${ }^{2} J(\mathrm{P}, \mathrm{C})_{\text {methyl }}$.

## 2. Experimental

### 2.1. Materials

Dimethylamine solution ( $40 \%$ in water), 4-nitroaniline ( $\geqslant 99 \%$ ), phosphorus pentachloride $(\geqslant 98 \%)$, formic acid ( $98 \%$ ), phosphorus oxychloride ( $\geqslant 98 \%$ ) (Fluka) and $N$-benzylmethylamine ( $\geqslant 98 \%$ ), benzamide ( $>98 \%$ ), 2,2,2-trichloroacetamide ( $>98 \%$ ) (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 $\mathbf{3}$ with graphite monochromated Mo $\mathrm{K} \alpha$ radiation $(\lambda=$ $0.71073 \AA$ ). 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 $\mathbf{2}$ and $\mathbf{3}$ using the sadabs program [25].

### 2.3. Spectroscopic measurements

${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ and ${ }^{31} \mathrm{P}$ NMR spectra were recorded on a Bruker Avance DRS 500 spectrometer. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ chemical shifts were determined relative to internal TMS, ${ }^{31} \mathrm{P}$ chemical shifts relative to $85 \% \mathrm{H}_{3} \mathrm{PO}_{4}$ as external standard. Infrared (IR) spectra were recorded on a Shimadzu model IR-60 spectrometer. Elemental analysis was performed using a Heraeus CHN-O-RAPID apparatus.

### 2.4. Syntheses

$\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{C}(\mathrm{O}) \mathrm{NHP}(\mathrm{O}) \mathrm{Cl}_{2}$ and $\mathrm{CCl}_{3} \mathrm{C}(\mathrm{O}) \mathrm{NHP}(\mathrm{O}) \mathrm{Cl}_{2}$ were prepared similar to the procedure by Kirsanov et al. $[26,27]$ and $\mathrm{Me}_{2} \mathrm{NP}(\mathrm{O}) \mathrm{Cl}_{2}$ and $4-\mathrm{NO}_{2}-$ $\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NHP}(\mathrm{O}) \mathrm{Cl}_{2}$ were prepared similar to the procedure by Keat and Shaw [28] and Johnson et al. [29], respectively.

### 2.4.1. $N$-benzoyl, $N^{\prime}, N^{\prime \prime}$-bis( $N$-benzylmethyl)phosphoric

 triamide (1)$N$-benzylmethyl amine ( $1.21 \mathrm{~g}, 10 \mathrm{mmol}$ ) was added to a solution of $N$-benzoyl phosphoramidic dichloride $(0.595 \mathrm{~g}, 2.5 \mathrm{mmol})$ in chloroform $(40 \mathrm{ml})$ and stirred at $-5^{\circ} \mathrm{C}$. After 4 h , the solvent was removed and the residue that formed was stirred in $\mathrm{H}_{2} \mathrm{O}$. The product was filtered and washed with $\mathrm{H}_{2} \mathrm{O}$ and recrystallized from chloroform $/ n$-heptane; m.p. $141^{\circ} \mathrm{C}$. Anal. Calc. for $\mathrm{C}_{23} \mathrm{H}_{26} \mathrm{~N}_{3} \mathrm{O}_{2} \mathrm{P}: \mathrm{C}, 67.80 ; \mathrm{H}, 6.43 ; \mathrm{N}, 10.31$. Found:

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

### 2.4.2. $N, N^{\prime}$-bis( $N$-benzylmethyl)phosphoramidic chloride (2)

$N$-benzylmethyl amine $(2.41 \mathrm{~g}, 20 \mathrm{mmol})$ was added to a solution of phosphoryl chloride $(0.76 \mathrm{~g}, 5 \mathrm{mmol})$ in acetonitrile ( 25 ml ) and stirred at $-5^{\circ} \mathrm{C}$. 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. $120^{\circ} \mathrm{C}$. Anal. Calc. for $\mathrm{C}_{16} \mathrm{H}_{20} \mathrm{ClN}_{2} \mathrm{OP}: \mathrm{C}, 59.54 ; \mathrm{H}, 6.25$; N, 8.68. Found: C, $59.51 ; \mathrm{H}, 6.21 ; \mathrm{N}, 8.66 \% .{ }^{31} \mathrm{P}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 34.18$ (m). ${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 138.11\left(\mathrm{~d},{ }^{3} J(\mathrm{P}, \mathrm{C})=5.5 \mathrm{~Hz}\right)$, 129.34 (s), 129.14 (s), 128.34 (s), 53.54 (d, $\left.{ }^{2} J(\mathrm{P}, \mathrm{C})=4.0 \mathrm{~Hz}\right), \quad 34.11 \quad\left(\mathrm{~d}, \quad{ }^{2} J(\mathrm{P}, \mathrm{C})=3.5 \mathrm{~Hz}\right) . \quad{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 2.63\left(\mathrm{~d},{ }^{3} J(\mathrm{PNCH})=12.6 \mathrm{~Hz}, 6 \mathrm{H}\right.$, $\left.2 \mathrm{CH}_{3}\right), 4.33\left(\mathrm{~m}, 4 \mathrm{H}, 2 \mathrm{CH}_{2}\right), 7.29-7.44(\mathrm{~m}, 10 \mathrm{Ar}-\mathrm{H})$. ${ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 2.63$ (s), $4.33(\mathrm{~m}), 7.29-7.44$ (m). IR (KBr, $\left.\mathrm{cm}^{-1}\right): 3015,1484,1442,1334,1219$, $1190(v \mathrm{P}=\mathrm{O}), 1126,1064,949,910,786(v \mathrm{PN}), 699$, 631, $530(v \mathrm{PCl}), 446$.

### 2.4.3. $N$-trichloroacetyl, $N^{\prime}, N^{\prime \prime}$-bis( $N$-benzylmethyl)phosphoric triamide (3)

$N$-benzylmethyl amine ( $0.97 \mathrm{~g}, 8 \mathrm{mmol}$ ) was added to a solution of trichloroacetyl phosphoramidic dichloride $(0.56 \mathrm{~g}, 2 \mathrm{mmol})$ in acetonitrile $(40 \mathrm{ml})$ and stirred at $-5^{\circ} \mathrm{C}$. After 4 h , the solvent was removed and the residue that formed was stirred in $\mathrm{H}_{2} \mathrm{O}$. The product was filtered and washed with $\mathrm{H}_{2} \mathrm{O}$ and recrystallized from chloroform $/ n$-heptane; m.p. $153^{\circ} \mathrm{C}$. Anal. Calc. for $\mathrm{C}_{18} \mathrm{H}_{21} \mathrm{Cl}_{3} \mathrm{~N}_{3} \mathrm{O}_{2} \mathrm{P}$ : C, 48.18; H, 4.72; $\mathrm{N}, 9.36$. Found: C, 48.16; H, 4.70; N, 9.37\%. ${ }^{31} \mathrm{P}$ NMR ( $\mathrm{d}_{6}-$ DMSO): $\delta \quad 13.86 \quad(\mathrm{~m}) .{ }^{13} \mathrm{C} \quad \mathrm{NMR} \quad\left(\mathrm{d}_{6}\right.$-DMSO): $\delta$ $163.50(\mathrm{~s}, \mathrm{C}=\mathrm{O}), 139.27\left(\mathrm{~d},{ }^{3} J(\mathrm{P}, \mathrm{C})=4.8 \mathrm{~Hz}\right), 129.81$ (s), 129.48 (s), $128.63(\mathrm{~s}), 93.08\left(\mathrm{~d},{ }^{3} J(\mathrm{P}, \mathrm{C})=9.6 \mathrm{~Hz}\right.$, $\left.\mathrm{CCl}_{3}\right), 59.63(\mathrm{~s}), 51.82\left(\mathrm{~d},{ }^{2} J(\mathrm{P}, \mathrm{C})=4.9 \mathrm{~Hz}\right), 33.23$ $\left(\mathrm{d},{ }^{2} J(\mathrm{P}, \mathrm{C})=4.6 \mathrm{~Hz}\right) .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{d}_{6}\right.$-DMSO): $\delta=2.49$ $\left(\mathrm{d}, \quad{ }^{3} J(\mathrm{PNCH})=10.2 \mathrm{~Hz}, \quad 6 \mathrm{H}, \quad 2 \mathrm{CH}_{3}\right), \quad 4.16 \quad(\mathrm{~d}$, $\left.{ }^{3} J(\mathrm{PNCH})=9.1 \mathrm{~Hz}, 4 \mathrm{H}, 2 \mathrm{CH}_{2}\right), 7.26-7.39(\mathrm{~m}, 10 \mathrm{Ar}-$ H), $10.34(\mathrm{~b}, 1 \mathrm{H}, \mathrm{NH}) .{ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\} \mathrm{NMR}\left(\mathrm{d}_{6}\right.$-DMSO):
$\delta 2.49(\mathrm{~s}), 4.16(\mathrm{~s}), 7.26-7.39(\mathrm{~m}), 10.34(\mathrm{~b}) . \mathrm{IR}(\mathrm{KBr}$, $\left.\mathrm{cm}^{-1}\right): 3405(v \mathrm{NH}), 3020,2915,2760,1712(v \mathrm{C}=\mathrm{O})$, 1452, 1348, 1230, $1198(v \mathrm{P}=\mathrm{O}), 1145,1008,948$, $876(\nu \mathrm{PN}), 834,794(\nu \mathrm{PN}), 695,669(\nu \mathrm{CCl}), 588$, 491, 453.

### 2.4.4. $N, N$-dimethyl, $N^{\prime}, N^{\prime \prime}$-bis( $N$-benzylmethyl)-

 phosphoric triamide (4)$N$-benzylmethyl amine ( $0.81 \mathrm{~g}, 5 \mathrm{mmol}$ ) was added to a solution of $N, N$-dimethylphosphoramidic dichloride $(2.42 \mathrm{~g}, 20 \mathrm{mmol})$ in acetonitrile $(30 \mathrm{ml})$ and stirred at $-5^{\circ} \mathrm{C}$. 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 $\mathrm{C}_{18} \mathrm{H}_{26} \mathrm{~N}_{3} \mathrm{OP}: \mathrm{C}, 65.24 ; \mathrm{H}, 7.91 ; \mathrm{N}, 12.61$. Found: C, 65.23; H, 7.89; N, 12.63\%. ${ }^{31} \mathrm{P}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 25.48(\mathrm{~m}) .{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 138.44(\mathrm{~d}$, $\left.{ }^{3} J(\mathrm{P}, \mathrm{C})=4.5 \mathrm{~Hz}\right), 130.24$ (s), 128.23 (s), 127.13 (s), $53.18\left(\mathrm{~d},{ }^{2} J(\mathrm{P}, \mathrm{C})=4.6 \mathrm{~Hz}\right), 37.03\left(\mathrm{~d},{ }^{2} J(\mathrm{P}, \mathrm{C})=4.0 \mathrm{~Hz}\right)$, $33.92\left(\mathrm{~d},{ }^{2} J(\mathrm{P}, \mathrm{C})=3.7 \mathrm{~Hz}\right) .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right): \delta 2.54$ $\left(\mathrm{d},{ }^{3} J(\mathrm{PNCH})=9.1 \mathrm{~Hz}, \quad 6 \mathrm{H}, \quad \mathrm{N}\left(\mathrm{CH}_{3}\right)_{2}\right), \quad 2.69 \quad(\mathrm{~d}$, $\left.{ }^{3} J(\mathrm{PNCH})=9.6 \mathrm{~Hz}, \quad 6 \mathrm{H}, \quad 2 \mathrm{CH}_{3}\right), \quad 4.10 \quad\left(\mathrm{dd}, \quad{ }^{3} J-\right.$ $\left.(\mathrm{PNCH})=8.3 \mathrm{~Hz},{ }^{2} J(\mathrm{H}, \mathrm{H})=14.8 \mathrm{~Hz}, 2 \mathrm{H}, 2 \mathrm{CH}_{\text {benzylic }}\right)$, $4.20\left(\mathrm{dd},{ }^{3} J(\mathrm{PNCH})=8.3 \mathrm{~Hz},{ }^{2} J(\mathrm{H}, \mathrm{H})=14.8 \mathrm{~Hz}, 2 \mathrm{H}\right.$, $\left.2 \mathrm{CH}_{\text {benzylic }}\right)$, $7.23-7.36(\mathrm{~m}, 10 \mathrm{Ar}-\mathrm{H}) .{ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\} \mathrm{NMR}$ $\left(\mathrm{CDCl}_{3}\right): \delta 2.54(\mathrm{~s}), 2.69(\mathrm{~s}), 4.10\left(\mathrm{~d},{ }^{2} J(\mathrm{H}, \mathrm{H})=14.8 \mathrm{~Hz}\right)$, $4.20\left(\mathrm{~d},{ }^{2} J(\mathrm{H}, \mathrm{H})=14.8 \mathrm{~Hz}\right), 7.23-7.36(\mathrm{~m})$. IR (KBr, $\mathrm{cm}^{-1}$ ): 3415, 2920, 2765, 2420, 1724, 1443, 1296, 1204 $(\nu \mathrm{P}=\mathrm{O}), 998,946,778(\nu \mathrm{PN}), 731(\nu \mathrm{PN}), 694,592,472$.

### 2.4.5. $N$-4-nitrophenyl, $N^{\prime}, N^{\prime \prime}$-bis( $N$-benzylmethyl)phosphoric triamide (5)

$N$-benzylmethyl amine ( $0.97 \mathrm{~g}, 8 \mathrm{mmol}$ ) was added to a mixture of $N$-4-nitrophenyl phosphoramidic dichloride $(0.51 \mathrm{~g}, 2 \mathrm{mmol})$ in carbon tetrachloride $(30 \mathrm{ml})$ and stirred at $-5^{\circ} \mathrm{C}$. After 6 h , the solvent was removed and the residue that formed was stirred in $\mathrm{H}_{2} \mathrm{O}$. The product was filtered and washed with $\mathrm{H}_{2} \mathrm{O}$; m.p. $115{ }^{\circ} \mathrm{C}$. Anal. Calc. for $\mathrm{C}_{22} \mathrm{H}_{25} \mathrm{~N}_{4} \mathrm{O}_{3} \mathrm{P}: \mathrm{C}, 62.26 ; \mathrm{H}$, 5.94; N, 13.20. Found: C, 62.24; H, 5.95; N, 13.18\%. ${ }^{31} \mathrm{P}$ NMR ( $\mathrm{d}_{6}$-DMSO): $\delta 14.79$ (m). ${ }^{13} \mathrm{C}$ NMR ( $\mathrm{d}_{6}-$ DMSO): $\delta 141.73$ (s), $137.17\left(\mathrm{~d},{ }^{3} J(\mathrm{P}, \mathrm{C})=4.0 \mathrm{~Hz}\right)$, 128.71 ( s ), 128.34 ( s ), 128.27 ( s , 127.74 ( s$), 125.55$ ( s$)$, $117.15\left(\mathrm{~d},{ }^{2} J(\mathrm{P}, \mathrm{C})=6.5 \mathrm{~Hz}\right), 53.13\left(\mathrm{~d},{ }^{2} J(\mathrm{P}, \mathrm{C})=4.8 \mathrm{~Hz}\right)$, $34.04\left(\mathrm{~d},{ }^{2} J(\mathrm{P}, \mathrm{C})=4.4 \mathrm{~Hz}\right) .{ }^{1} \mathrm{H}$ NMR ( $\mathrm{d}_{6}$-DMSO): 2.63 $\left(\mathrm{d},{ }^{3} J(\mathrm{PNCH})=10.0 \mathrm{~Hz}, 6 \mathrm{H}, 2 \mathrm{CH}_{3}\right), 4.25\left(\mathrm{dd},{ }^{3} J-\right.$ $\left.(\mathrm{PNCH})=7.1 \mathrm{~Hz},{ }^{2} J(\mathrm{H}, \mathrm{H})=14.8 \mathrm{~Hz}, 2 \mathrm{H}, 2 \mathrm{CH}_{\text {benzylic }}\right)$, $4.27\left(\mathrm{dd},{ }^{3} J(\mathrm{PNCH})=7.1 \mathrm{~Hz},{ }^{2} J(\mathrm{H}, \mathrm{H})=14.8 \mathrm{~Hz}, 2 \mathrm{H}\right.$, $\left.2 \mathrm{CH}_{\text {benzylic }}\right), 7.16\left(\mathrm{~d},{ }^{3} J(\mathrm{H}, \mathrm{H})=9.1 \mathrm{~Hz}, 2 \mathrm{Ar}-\mathrm{H}\right), 7.33$ $(\mathrm{m}, 10 \mathrm{Ar}-\mathrm{H}), 8.07\left(\mathrm{~d},{ }^{3} J(\mathrm{H}, \mathrm{H})=9.1 \mathrm{~Hz}, 2 \mathrm{Ar}-\mathrm{H}\right), 8.30$ $\left(\mathrm{d},{ }^{2} J(\mathrm{PNH})=9.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{NH}\right) .{ }^{1} \mathrm{H}\left\{{ }^{\{31} \mathrm{P}\right\} \mathrm{NMR} \quad\left(\mathrm{d}_{6^{-}}\right.$ DMSO): $\delta 2.63$ (s), $4.25\left(\mathrm{~d},{ }^{2} J(\mathrm{H}, \mathrm{H})=14.8 \mathrm{~Hz}\right), 4.27$ $\left(\mathrm{d},{ }^{2} J(\mathrm{H}, \mathrm{H})=14.8 \mathrm{~Hz}\right), 7.16\left(\mathrm{~d},{ }^{3} J(\mathrm{H}, \mathrm{H})=9.1 \mathrm{~Hz}\right)$, $7.33(\mathrm{~s}), 8.07\left(\mathrm{~d},{ }^{3} J(\mathrm{H}, \mathrm{H})=9.1 \mathrm{~Hz}\right), 8.30(\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH})$. IR $\left(\mathrm{KBr}, \mathrm{cm}^{-1}\right): 3145(\nu \mathrm{NH})$, 2905, $1587\left(\nu \mathrm{NO}_{2}\right)$, 1490, 1470, $1327\left(\nu \mathrm{NO}_{2}\right), 1291,1247(\nu \mathrm{P}=\mathrm{O}), 1198$,

1164, 1103, 969, $902(\nu \mathrm{PN}), 840,769,720(\nu \mathrm{PN}), 690$, 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 hal-ogen-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 $\mathbf{1 - 5}$ indicate two various ${ }^{2} J(\mathrm{P}, \mathrm{C})$ coupling constants for the $\mathrm{CH}_{3}$ and $\mathrm{CH}_{2}$ groups in the




Scheme 1. Preparation of compounds 1-5.

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

| No. | Compound | ${ }^{2} J(\mathrm{P}, \mathrm{C})_{\text {aliphatic }}$ | ${ }^{2} J(\mathrm{P}, \mathrm{C})_{\text {benzylic }}$ | Reference |
| :---: | :---: | :---: | :---: | :---: |
| 1 | $\mathrm{P}(\mathrm{O})\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{C}(\mathrm{O}) \mathrm{NH}\right)\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)\left(\mathrm{CH}_{2} \mathrm{C}_{6} \mathrm{H}_{5}\right)\right]_{2}$ | 5.0 | 5.3 | ${ }^{\text {a }}$ |
| 2 | $\mathrm{P}(\mathrm{O})(\mathrm{Cl})\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)\left(\mathrm{CH}_{2} \mathrm{C}_{6} \mathrm{H}_{5}\right)\right]_{2}$ | 3.5 | 4.0 | ${ }^{\text {a }}$ |
| 3 | $\mathrm{P}(\mathrm{O})\left(\mathrm{CCl}_{3} \mathrm{C}(\mathrm{O}) \mathrm{NH}\right)\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)\left(\mathrm{CH}_{2} \mathrm{C}_{6} \mathrm{H}_{5}\right)\right]_{2}$ | 4.6 | 4.9 | a |
| 4 | $\mathrm{P}(\mathrm{O})\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)_{2}\right]\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)\left(\mathrm{CH}_{2} \mathrm{C}_{6} \mathrm{H}_{5}\right)\right]_{2}$ | 3.7, $4.0\left[\mathrm{~N}\left(\mathrm{CH}_{3}\right)_{2}\right]$ | 4.6 | a |
| 5 | $\mathrm{P}(\mathrm{O})\left(p-\mathrm{NHC}_{6} \mathrm{H}_{4} \mathrm{NO}_{2}\right)\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)\left(\mathrm{CH}_{2} \mathrm{C}_{6} \mathrm{H}_{5}\right)\right]_{2}$ | 4.4 | 4.8 | ${ }^{\text {a }}$ |
| 6 | $\left(4-\mathrm{CH}_{3}-\mathrm{C}_{6} \mathrm{H}_{4}-\mathrm{O}\right)_{2} \mathrm{P}(\mathrm{O})\left[\mathrm{N}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)\left(\mathrm{CH}_{2} \mathrm{C}_{6} \mathrm{H}_{5}\right)\right]$ | 3.5 | 4.9 | [21] |
| 7 | $\left(4-\mathrm{CH}_{3}-\mathrm{C}_{6} \mathrm{H}_{4}-\mathrm{O}\right) \mathrm{P}(\mathrm{O})(\mathrm{Cl})\left[\mathrm{N}\left(\mathrm{C}_{2} \mathrm{H}_{5}\right)\left(\mathrm{CH}_{2} \mathrm{C}_{6} \mathrm{H}_{5}\right)\right]$ | 3.6 | 4.6 | [21] |

${ }^{\mathrm{a}}$ This work.
benzylmethylamine moiety, furthermore, compound 4 shows a ${ }^{2} J(\mathrm{P}, \mathrm{C})$ coupling constant for the $\mathrm{CH}_{3}$ in the $\mathrm{N}\left(\mathrm{CH}_{3}\right)_{2}$ group. ${ }^{2} J(\mathrm{P}, \mathrm{C})$ coupling constants in these compounds are in the range of $3.5-5.3 \mathrm{~Hz}$ and for each compound ${ }^{2} J\left(\mathrm{P}_{2} \mathrm{CH}_{2}\right)>{ }^{2} J\left(\mathrm{P}, \mathrm{CH}_{3}\right)$, Table 1. The presence of phenyl groups linked to $\mathrm{CH}_{2}$ causes the deshielding of the $\mathrm{CH}_{2}$ carbon atoms relative to the $\mathrm{CH}_{3}$ carbon atoms. Methylene and methyl carbon atoms in compounds 1-5 appear in the range of 51.82-53.54 and $33.23-34.11 \mathrm{ppm}$ in ${ }^{13} \mathrm{C}$ NMR spectra, respectively. The deshielding of the methylene groups leads to a greater interaction with the corresponding phosphorus atoms. Also, in compounds with the $\mathrm{P}(\mathrm{O})\left[\mathrm{N}\left(\mathrm{CH}_{2} \mathrm{CH}_{3}\right)\right.$ $\left.\left(\mathrm{CH}_{2} \mathrm{C}_{6} \mathrm{H}_{5}\right)\right]$ moiety [21], Table 1, ${ }^{2} J\left[\mathrm{P},\left(\mathrm{CH}_{2}\right)_{\text {benzylic }}\right]>$ ${ }^{2} J\left[\mathrm{P},\left(\mathrm{CH}_{2}\right)_{\text {aliphatic }}\right]$.

The ipso-carbon atoms of the phenyl rings related to the amine groups are split into doublet signals by their phosphorus atoms, ${ }^{3} J(\mathrm{P}, \mathrm{C})$ coupling constant, also mol-
ecules 1 and $\mathbf{3}$ show a ${ }^{3} J(\mathrm{P}, \mathrm{C})$ coupling constant for the benzoyl and trichloroacetyl groups of 8.7 and 9.6 Hz , respectively. NH signals of compounds $\mathbf{1}$ and $\mathbf{3}$ do not show two bond distance couplings with the P atom, ${ }^{2} J(\mathrm{PNH})$, but in molecule 5 , a doublet signal is obtained for NH with ${ }^{2} J(\mathrm{PNH})=9.2 \mathrm{~Hz}$. The protons of methyl and methylene groups in these compounds indicate ${ }^{3} J(\mathrm{PNCH})$ coupling constants. Fig. 1 indicates the multiplet structure in the ${ }^{31} \mathrm{P}$ NMR spectrum of compound 5 which is produced by the couplings with H atoms of two $\mathrm{N}\left(\mathrm{CH}_{3}\right)\left(\mathrm{CH}_{2} \mathrm{C}_{6} \mathrm{H}_{5}\right)$ groups, the measured ${ }^{3} J(\mathrm{PNCH})$ from the ${ }^{1} \mathrm{H}$ NMR spectrum for this compound are 10 and 7.1 Hz (for the methyl and methylene protons of the $\mathrm{P}-\mathrm{N}\left(\mathrm{CH}_{3}\right)\left(\mathrm{CH}_{2} \mathrm{C}_{6} \mathrm{H}_{5}\right)$ moiety). The two benzylic protons are diastereotopic and usually appear with different chemical shifts, but when the rotational energy barrier around the $\mathrm{P}-\mathrm{N}$ bond is low, these appear with equal chemical shifts on the NMR timescale. Each of


Fig. 1. ${ }^{31} \mathrm{P}$ NMR spectrum of compound 5 .
the benzylic protons (of compounds $\mathbf{1 , 2 , 4} 4$ and 5) represents the splitting by the phosphorus atom, ${ }^{3} J(\mathrm{PNCH})$, followed by ${ }^{2} J(\mathrm{H}, \mathrm{H})$ splitting. Compound 3 shows only a doublet signal produced by a ${ }^{3} J(\mathrm{PNCH})$ coupling constant (the benzylic protons do not have different chemical shifts at 298 K ). A similar result was obtained for the benzylic protons of $\left(\mathrm{CH}_{3}\right)\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{2}\right) \quad \mathrm{NP}(\mathrm{O})(\mathrm{Cl})(4-$ $\mathrm{OC}_{6} \mathrm{H}_{4} \mathrm{CH}_{3}$ ) [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 $\mathbf{1}-\mathbf{3}$ 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 $\mathbf{1}$ and $\mathbf{3}$ contain one amidic hydrogen atom and form centrosymmetric dimers, see Fig. 5 for compound 3, that are produced by two equivalent intermolecular $-\mathrm{P}=\mathrm{O} \cdots \mathrm{H}-\mathrm{N}-$ hydrogen bonds (Table 4). The earlier studied $N$-benzoyl, phosphoric triamides
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 $\mathbf{1 - 3}$ have a slightly distorted tetrahedral configuration. The bond angles around the $\mathrm{P}(1)$ atoms in these compounds are in the range of $118.9^{\circ}$ $102.53^{\circ}$, for the angles $\mathrm{O}(1)-\mathrm{P}(1)-\mathrm{N}(2)$ and $\mathrm{N}(2)-\mathrm{P}(1)-$ $\mathrm{Cl}(1)$ in structure $\mathbf{2}$. For both compounds $\mathbf{1}$ and $\mathbf{3}$, the highest values of the bond angles around phosphorus atoms were obtained for the angles $\mathrm{O}(1)-\mathrm{P}(1)-\mathrm{N}(2)$ and $\mathrm{N}(2)-\mathrm{P}(1)-\mathrm{N}(1)$. The angles $\mathrm{O}(1)-\mathrm{P}(1)-\mathrm{N}(1)$ in compounds 1 and $3,105.55(12)^{\circ}$ and $104.81(8)^{\circ}$, are lower than the angles $\mathrm{O}(1)-\mathrm{P}(1)-\mathrm{N}(2)$ and $\mathrm{O}(1)-\mathrm{P}(1)-$ $\mathrm{N}(3)\left(118.26(13)^{\circ}, 109.80(13)^{\circ}\right.$ for 1 and $117.53(9)^{\circ}$, $112.05(9)^{\circ}$ for 3).
$\mathrm{P}(1)-\mathrm{N}(2)$ and $\mathrm{P}(1)-\mathrm{N}(3)$ bond lengths are 1.630(3) and $1.629(2) \AA$ in compound 1 and $1.6312(17)$ and $1.6271(17) \AA$ in compound 3. Also, in compound 2 $\mathrm{P}(1)-\mathrm{N}(1)$ and $\mathrm{P}(1)-\mathrm{N}(2)$ are $1.610(4)$ and $1.634(4) \AA$, respectively. They are significantly shorter than the typical $\mathrm{P}-\mathrm{N}$ single bond length $(1.77 \AA$ ) [33]. The shortening of PN bond lengths is likely related to an electrostatic effect (polar bond) which overlaps with $\mathrm{P}-$ $\mathrm{N} \sigma$ bond [34]. In compounds 1 and $\mathbf{3}$, the $\mathrm{P}(1)-\mathrm{N}(1)$

Table 2
Crystallographic data for 1,2 and $\mathbf{3}$

|  | 1 | 2 | 3 |
| :---: | :---: | :---: | :---: |
| Empirical formula | $\mathrm{C}_{23} \mathrm{H}_{26} \mathrm{~N}_{3} \mathrm{O}_{2} \mathrm{P}$ | $\mathrm{C}_{16} \mathrm{H}_{20} \mathrm{ClN}_{2} \mathrm{OP}$ | $\mathrm{C}_{18} \mathrm{H}_{21} \mathrm{Cl}_{3} \mathrm{~N}_{3} \mathrm{O}_{2} \mathrm{P}$ |
| Formula weight | 407.44 | 322.76 | 448.70 |
| Temperature (K) | 293(2) | 116(2) | 120(2) |
| Wavelength ( A ) | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | triclinic | orthorhombic | triclinic |
| Space group | $P \overline{1}$ | $P 2{ }_{1} 2_{1} 2_{1}$ | $P \overline{1}$ |
| Unit cell dimensions |  |  |  |
| $a(\AA)$ | 9.832(4) | 6.939(2) | 10.363(2) |
| $b(\AA)$ | 10.949(4) | 7.176(2) | 10.862(2) |
| $c(\AA)$ | 11.631(5) | 32.447(10) | 11.023(2) |
| $\alpha\left(^{\circ}\right)$ | 91.99(3) | 90 | 71.81(3) |
| $\beta\left({ }^{\circ}\right)$ | 100.51(3) | 90 | 67.44(3) |
| $\gamma\left({ }^{\circ}\right)$ | $115.35(3)$ | 90 | 63.29(3) |
| $V\left(\AA^{3}\right)$ | 1103.5(8) | 1615.8(9) | 1008.7(4) |
| $Z$, calculated density $\left(\mathrm{Mg} \mathrm{m}^{-3}\right)$ | 2, 1.226 | 4, 1.327 | 2, 1.477 |
| Absorption coefficient ( $\mathrm{mm}^{-1}$ ) | 0.148 | 0.336 | 0.553 |
| $F(000)$ | 432 | 680 | 464 |
| Crystal size (mm) | $0.6 \times 0.2 \times 0.2$ | $0.8 \times 0.6 \times 0.2$ | $0.6 \times 0.3 \times 0.2$ |
| $\theta$ Range for data collection ( ${ }^{\circ}$ ) | 1.80-26.97 | $2.51-24.00$ | $2.03-30.06$ |
| Limiting indices | $\begin{aligned} & 0 \leqslant h \leqslant 12 ;-13 \leqslant k \leqslant 12 ; \\ & -14 \leqslant l \leqslant 14 \end{aligned}$ | $\begin{aligned} & -7 \leqslant h \leqslant 7 ;-8 \leqslant k \leqslant 8 \\ & -36 \leqslant l \leqslant 37 \end{aligned}$ | $\begin{aligned} & -14 \leqslant h \leqslant 14 ;-14 \leqslant k \leqslant 15 ; \\ & -15 \leqslant l \leqslant 15 \end{aligned}$ |
| Reflections collected/unique ( $R_{\text {int }}$ ) | 5063/4774 (0.0255) | 10 637/2381 (0.0642) | 12 120/5854 (0.0165) |
| Completeness to $\theta$ (\%) | 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 | $R_{1}=0.0612 ; w R_{2}=0.1243$ | $R_{1}=0.0647 ; w R_{2}=0.1219$ | $R_{1}=0.0445 ; ~ w R_{2}=0.0917$ |
| $R$ indices (all data) | $R_{1}=0.0854 ; w R_{2}=0.1340$ | $R_{1}=0.0671 ; w R_{2}=0.1229$ | $R_{1}=0.0498 ; w R_{2}=0.0937$ |
| Absolute structure parameter |  | -0.06(17) |  |
| Largest differential peak and hole (e $\AA^{-3}$ ) | 0.369 and -0.405 | 0.657 and -0.342 | 0.709 and -0.778 |

Table 3
Selected bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ for compounds $\mathbf{1}-\mathbf{3}$

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



Fig. 2. Molecular structure and atom-labelling scheme for $\mathrm{P}(\mathrm{O})\left(\mathrm{C}_{6} \mathrm{H}_{5^{-}}\right.$ $\mathrm{C}(\mathrm{O}) \mathrm{NH})\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)\left(\mathrm{CH}_{2} \mathrm{C}_{6} \mathrm{H}_{5}\right)\right]_{2}$, compound $\mathbf{1}(50 \%$ probability ellipsoids).
bond lengths (1.676(2) and $1.7037(16) \AA$, respectively) are longer than the $\mathrm{P}(1)-\mathrm{N}(2)$ and $\mathrm{P}(1)-\mathrm{N}(3)$ bond lengths due to the resonance interaction with the $\mathrm{C}=\mathrm{O}$ system that causes a partial multiple-bond character in $\mathrm{N}(1)-\mathrm{C}(1)$ (compare $\mathrm{N}(1)-\mathrm{C}(1)$ in compound $\mathbf{1}$ and


Fig. 3. Molecular structure and atom-labelling scheme for $\mathrm{P}(\mathrm{O})(\mathrm{Cl})\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)\left(\mathrm{CH}_{2} \mathrm{C}_{6} \mathrm{H}_{5}\right)\right]_{2}$, compound $\mathbf{2}(50 \%$ probability ellipsoids).


Fig. 4. Molecular structure and atom-labelling scheme for $\mathrm{P}(\mathrm{O})\left(\mathrm{CCl}_{3}-\right.$ $\mathrm{C}(\mathrm{O}) \mathrm{NH})\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)\left(\mathrm{CH}_{2} \mathrm{C}_{6} \mathrm{H}_{5}\right)\right]_{2}$, compound $\mathbf{3}(50 \%$ probability ellipsoids).
$\mathrm{N}(1)-\mathrm{C}(2)$ in compound $\mathbf{3}$ with other $\mathrm{N}-\mathrm{C}$ bond lengths, Table 3). In the previous reported structures, we obtained the $\mathrm{P}-\mathrm{N}$ bond lengths of $(\mathrm{O}) \mathrm{P}-\mathrm{N}(\mathrm{H})-\mathrm{C}(\mathrm{O})$ and $\mathrm{P}-\mathrm{NR}^{1} \mathrm{R}^{2}$ moieties in the range of $1.678(2)-1.718(3) \AA$ and $1.6032(17)-1.642(2) \AA$, respectively (Table 5).

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


Fig. 5. Centrosymmetric dimer of compound 3, produced by hydrogen bonds.
around $\mathrm{N}(3)$ atom (average $120^{\circ}$ ). Also, the sum of the surrounding angles for $\mathrm{N}(1), \mathrm{N}(2)$ in compound 2 and $\mathrm{N}(2), \mathrm{N}(3)$ in compound 3 are $359^{\circ}, 358.9^{\circ}$ and $359.7^{\circ}$, $359.9^{\circ}$, respectively. Furthermore, the angles $\mathrm{C}(1)-$ $\mathrm{N}(1)-\mathrm{P}(1)$ in compound 1 and $\mathrm{C}(2)-\mathrm{N}(1)-\mathrm{P}(1)$ in compound 3 are $127.6(2)^{\circ}$ and $127.13(13)^{\circ}$. These results confirm the $\mathrm{sp}^{2}$ hybridization for the nitrogen atoms,

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

| Compound | $\mathrm{D}-\mathrm{H} \cdots \mathrm{A}$ | $d(\mathrm{D}-\mathrm{H})$ | $d(\mathrm{H} \cdots \mathrm{A})$ | $\angle \mathrm{DHA}$ |
| :--- | :--- | :--- | :--- | :--- |
| $\mathbf{1}$ | $\mathrm{N} 1-\mathrm{H} 1 \mathrm{~A} \cdots \mathrm{O}^{\prime}[-x,-y+1,-z]$ | 0.860 | 1.967 | 165.87 |
| $\mathbf{3}$ | N1-H1N $\cdots \mathrm{O} 1[1-x,-y,-z]$ | 0.891 | 1.915 | 168.13 |

Table 5
$\mathrm{P}=\mathrm{O}$ and $\mathrm{P}-\mathrm{N}$ bond lengths $(\AA)$ in some phosphorus compounds

| Compound | $\mathrm{P}=\mathrm{O}$ | $\mathrm{P}-\mathrm{N}$ | $\mathrm{P}-\mathrm{N}$ | $\mathrm{P}-\mathrm{N}$ | Reference |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{P}(\mathrm{O})\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{C}(\mathrm{O}) \mathrm{NH}\right)\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)\left(\mathrm{CH}_{2} \mathrm{C}_{6} \mathrm{H}_{5}\right)\right]_{2}$ | 1.476(2) | 1.631(3) | 1.631(2) | $1.678(2)^{\text {c }}$ | a |
| $\mathrm{P}(\mathrm{O})(\mathrm{Cl})\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)\left(\mathrm{CH}_{2} \mathrm{C}_{6} \mathrm{H}_{5}\right)\right]_{2}$ | 1.471(2) | $1.615(2)$ | 1.635(3) |  | a |
| $\mathrm{P}(\mathrm{O})\left(\mathrm{CCl}_{3} \mathrm{C}(\mathrm{O}) \mathrm{NH}\right)\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)\left(\mathrm{CH}_{2} \mathrm{C}_{6} \mathrm{H}_{5}\right)\right]_{2}$ | $1.4785(15)$ | 1.6271(17) | $1.6312(17)$ | $1.7037(16)^{\text {c }}$ | a |
| $\mathrm{P}(\mathrm{O})\left(\mathrm{CCl}_{3} \mathrm{C}(\mathrm{O}) \mathrm{NH}\right)\left[\mathrm{NH}\left(\text { tert }-\mathrm{C}_{4} \mathrm{H}_{9}\right)\right]_{2}$ | $1.466(2)$ | $1.608(3)$ | 1.611(4) | $1.718(3)^{\text {c }}$ | [18] |
| $\mathrm{P}(\mathrm{O})\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{C}(\mathrm{O}) \mathrm{NH}\right)\left[\mathrm{NH}\left(\text { tert }-\mathrm{C}_{4} \mathrm{H}_{9}\right)\right]_{2}{ }^{\text {b }}$ | 1.473(2), 1.476(2) | 1.629(2), 1.619(3) | 1.629(2), 1.629(2) | $1.711(2)^{\mathrm{c}}, 1.704(2)$ | [18] |
| $\mathrm{P}(\mathrm{O})\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{C}(\mathrm{O}) \mathrm{NH}\right)\left(\mathrm{C}_{4} \mathrm{H}_{8} \mathrm{~N}\right)_{2}$ | $1.487(3)$ | $1.615(4)$ | 1.618(4) | $1.679(4)^{\text {c }}$ | [19] |
| $\mathrm{P}(\mathrm{O})\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)_{2}\right]\left(p-\mathrm{NHC}_{6} \mathrm{H}_{4} \mathrm{CH}_{3}\right)_{2}$ | 1.478 (3) | $1.626(3), \mathrm{N}\left(\mathrm{CH}_{3}\right)_{2}$ | 1.642(2) |  | [22] |
| $\mathrm{P}(\mathrm{O})\left[\mathrm{N}\left(\mathrm{CH}_{3}\right)_{2}\right]\left(p-\mathrm{OC}_{6} \mathrm{H}_{4} \mathrm{NO}_{2}\right)_{2}$ | $1.4547(14)$ | $1.6032(17)$ |  |  | [23] |
| $\mathrm{P}(\mathrm{O})\left(p-\mathrm{OC}_{6} \mathrm{H}_{4} \mathrm{CH}_{3}\right)_{2}\left[\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)\left(\mathrm{CH}_{3}\right) \mathrm{CH}-\mathrm{NH}\right]^{\mathrm{b}}$ | 1.462(3), 1.469(3) | 1.610(5), 1.614(5) |  |  | [21] |

[^1]although due to repulsion and steric interactions, some angles are greater and others are smaller than $120^{\circ}$.

The $\mathrm{P}=\mathrm{O}$ bond lengths in molecules $\mathbf{1 - 3}$ are 1.476(2), $1.459(4)$ and $1.478(2) \AA$, which are larger than the normal $\mathrm{P}=\mathrm{O}$ bond length $(1.45 \AA)$ [33]. The $\mathrm{P}=\mathrm{O}$ bond lengths in our previously reported structures are in the range of $1.455(1)-1.487(3) \AA$ (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 $240844\left(\mathrm{C}_{23} \mathrm{H}_{26} \mathrm{~N}_{3} \mathrm{O}_{2} \mathrm{P}\right), 240845\left(\mathrm{C}_{16} \mathrm{H}_{20} \mathrm{Cl}_{1} \mathrm{~N}_{2} \mathrm{OP}\right)$ and $240846\left(\mathrm{C}_{18} \mathrm{H}_{21} \mathrm{Cl}_{3} \mathrm{~N}_{3} \mathrm{O}_{2} \mathrm{P}\right)$. 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).

## References

[1] D. Barak, A. Ordentlich, D. Kaplan, R. Barak, D. Mizrahi C. Kronman, Y. Segall, B. Velan, A. Shafferman, Biochemistry 39 (2000) 1156.
[2] W.D. Mallender, T. Szegletes, T.L. Rosenberry, Biochemistry 39 (2000) 7753.
[3] A.B. Ouryupin, M.I. Kadyko, P.V. Petrovskii, E.I. Fedin, Tetrahedron Asymm. 6 (1995) 1813.
[4] G. Zon, S.M. Ludeman, W. Egan, J. Am. Chem. Soc. 99 (1977) 5785.
[5] H. Wan, T.A. Modro, Synthesis (1996) 1227.
[6] S. Bauermister, A.M. Modro, T.A. Modro, A. Zwierzak, Can. J. Chem. 69 (1991) 811.
[7] M.P. Du Plessis, T.A. Modro, L.R. Nassimbeni, Acta Crystallogr. B 38 (1982) 1504.
[8] T. Chivers, M. Krahn, G. Schatte, M. Parvez, Inorg. Chem. 42 (2003) 3994.
[9] G.J. Bullen, F.S. Stephens, R.J. Wade, J. Chem. Soc. A (1969) 1804.
[10] P.M. Narula, C.S. Day, B.A. Powers, M.A. Odian, A. Lachgar, W.T. Pennington, R.E. Noftle, Polyhedron 18 (1999) 1751.
[11] K.E. Gubina, V.A. Ovchynnikov, V.M. Amirkhanov, V.V. Skopenko, O.V. Shishkin, Z. Naturforsch. 55b (2000) 495.
[12] K.E. Gubina, V.M. Amirkhanov, Z. Naturforsch. 55b (2000) 1015.
[13] K.E. Gubina, V.A. Ovchynnikov, V.M. Amirkhanov, T.Y.u. Silva, V.V. Skopenko, T. Glowiak, H. Kozowski, Z. Naturforsch. 54b (1999) 1357.
[14] K.E. Gubina, J.A. Shatrava, V.A. Ovchynnikov, V.M. Amirkhanov, Polyhedron 19 (2000) 2203.
[15] S.A. Bourne, X.Y. Mbianda, T.A. Modro, L.R. Nassimbeni H. Wan, J. Chem. Soc., Perkin Trans. 2 (1998) 83.
[16] J.M.A. Al-Rawi, G.Q. Behnam, N. Ayed, R. Kraemer, Magn. Reson. Chem. 23 (1985) 728.
[17] Z. Zalán, T.A. Martinek, L. Lázár, F. Fülöp, Tetrahedron 59 (2003) 9117.
[18] K. Gholivand, M. Pourayoubi, Z. Anorg. Allg. Chem. 630 (2004) 1330.
[19] K. Gholivand, M. Pourayoubi, H. Mostaanzadeh, Anal. Sci. 20 (2004) x-51.
[20] K. Gholivand, M.D. Alavi, M. Pourayoubi, Z. Kristallogr. NCS 219 (2004) 124.
[21] K. Gholivand, Z. Shariatinia, M. Pourayoubi, Z. Naturforsch. 60b (2005) 67.
[22] K. Gholivand, A. Tadjarodi, S.W. Ng, Acta Crystallogr. E57 (2001) 472.
[23] K. Gholivand, A. Tadjarodi, S.W. Ng, Acta Crystallogr. E58 (2002) 200.
[24] G.M. Sheldrick, SHELEX V. 5.10, Structure Determination Software Suit, Bruker AXS, Madison, WI, USA, 1998.
[25] G.M. Sheldrick, in: sadabs V. 2.01, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, WI, USA, 1998.
[26] A.V. Kirsanov, R. Makitra, J. Gen. Chem. 26 (1956) 907.
[27] A.V. Kirsanov, G.I. Derkach, Zhur. Obshchei Khim. 26 (1956) 2082.
[28] R. Keat, R. Shaw, J. Chem. Soc. A (1968) 703.
[29] O. Johnson, M. Murray, G. Woodward, J. Chem. Soc., Dalton Trans. (1989) 821.
[30] K. Gholivand, S. Dehghanpour, G. Gerivani, H.R. Bijanzadeh, Phosphorus Sulfur Silicon 157 (2000) 11.
[31] V. Mizrahi, T.A. Modro, Crystallogr. Struct. Commun. 11 (1982) 627.
[32] O.N. Rebrova, V.N. Biyushkin, T.I. Malinovski, V.M. Ovrutskii, L.D. Protsenko, T.N. Dneprova, M.D. Mazus, Dokl. AN. SSSR (Russia) 324 (1992) 103.
[33] D.E.C. Corbridge, Phosphorus, an Outline of Its Chemistry, Biochemistry and Technology, 5th ed., Elsevier, The Netherlands, 1995.
[34] D.G. Gilheany, Chem. Rev. 94 (1994) 1339.


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[^1]:    ${ }^{\text {a }}$ This work.
    ${ }^{\mathrm{b}}$ These compounds appear as two crystallographically independent molecules.
    ${ }^{c}$ The data are related to $\mathrm{P}-\mathrm{N}$ of the $(\mathrm{O}) \mathrm{P}-\mathrm{N}(\mathrm{H})-\mathrm{C}(\mathrm{O})$ moiety.

