# organic compounds

# Two new $X$P(O)[NHC(CH$_3$)$_3$]$_2$ phosphoramidates, with $X$ = (CH$_3$)$_2$N and [(CH$_3$)$_3$CNH]$_2$P(O)(O)

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In $N,N'$-di-*tert*-butyl-$N'',N''$-dimethylphosphoric triamide, C$_{10}$H$_{26}$N$_3$OP, (I), and $N,N',N'',N'''$-tetra-*tert*-butoxybis(phosphonic diamide), C$_{16}$H$_{40}$N$_4$O$_3$P$_2$, (II), the extended structures are mediated by P(O)$\cdots$(H—N)$_2$ interactions. The asymmetric unit of (I) consists of six independent molecules which aggregate through P(O)$\cdots$(H—N)$_2$ hydrogen bonds, giving $R_2^1(6)$ loops and forming two independent chains parallel to the $a$ axis. Of the 12 independent *tert*-butyl groups, five are disordered over two different positions with occupancies ranging from $\frac{1}{6}$ to $\frac{5}{6}$. In the structure of (II), the asymmetric unit contains one molecule. P(O)$\cdots$(H—N)$_2$ hydrogen bonds give $S(6)$ and $R_2^2(8)$ rings, and the molecules form extended chains parallel to the $c$ axis. The structures of (I) and (II), along with similar structures having (N)P(O)(NH)$_2$ and (NH)$_2$P(O)(O)-P(O)(NH)$_2$ skeletons extracted from the Cambridge Structural Database, are used to compare hydrogen-bond patterns in these families of phosphoramidates. The strengths of P(O)[$\cdots$H—N]$_x$ ($x$ = 1, 2 or 3) hydrogen bonds are also analysed, using these compounds and previously reported structures with (N)$_2$P(O)(NH) and P(O)(NH)$_3$ fragments.

## Comment

The strengths of PO$\cdots$H—N hydrogen bonds were investigated recently in compounds having C(O)NHP(O)[NH]$_2$ and C(O)NHP(O)[N]$_2$ skeletons (Pourayoubi, Tarahhomi *et al.*, 2011). In another recent report by our group, the double hydrogen-bond acceptor capability of the P(O) unit in phosphoramidates, and the formation of the PO$\cdots$[H—N]-[H—N] grouping, were discussed (Pourayoubi *et al.*, 2012).

We report here a study of the hydrogen-bond patterns in new compounds having (N)P(O)(NH)$_2$ and (NH)$_2$P(O)(O)-P(O)(NH)$_2$ fragments (with $n$ H-atom acceptors and $2n$ H-atom donor centres, with $n$ = 1 and 2), with a double

hydrogen-bond acceptor capability at the P(O) group. The observed hydrogen-bond patterns are compared with those of analogous structures. Moreover, for comparison, the strengths of the PO$\cdots$[H—N]$_x$ ($x$ = 1, 2 or 3) hydrogen bonds are analysed for the new structures, for previously reported analogous compounds and also for compounds with (N)$_2$P(O)-(NH) and P(O)(NH)$_3$ skeletons.
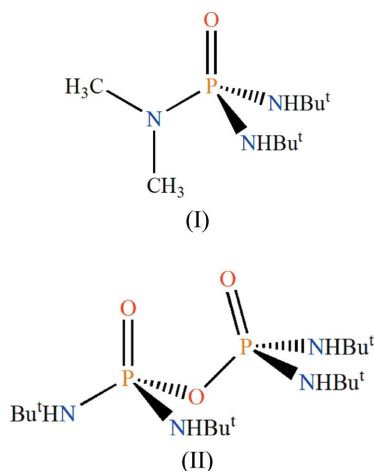


A search of the Cambridge Structural Database (CSD, Version 5.32, May 2011 update; Allen, 2002; CSD refcodes will be given in capitals followed by the primary reference) shows that the N atom of the P(O)N group in phosphoramidate compounds does not usually act as a hydrogen-bond acceptor because of its weak Lewis base character.
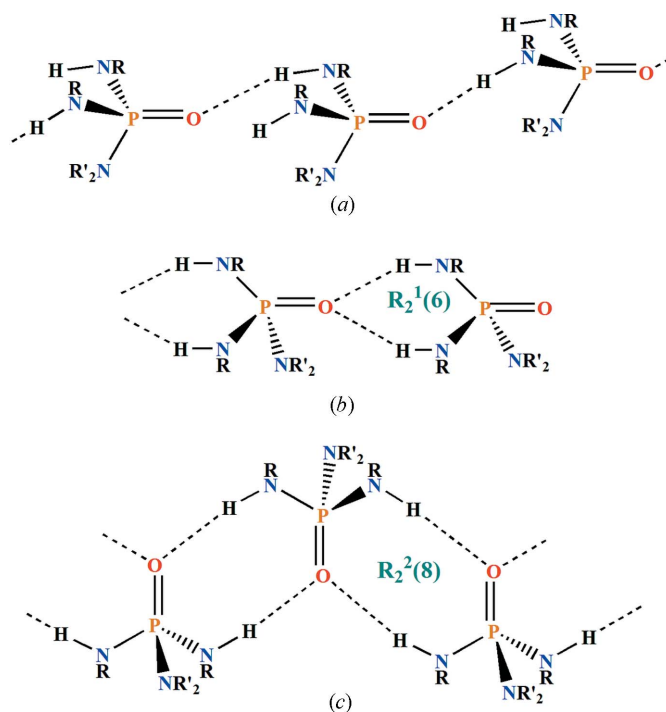


**Figure 1**
Three different types of linear arrangement in compounds having an (N)P(O)(NH)$_2$ skeleton (dashed lines indicate hydrogen bonds): (a) through P(O)$\cdots$H—N hydrogen bonds, (b) *via* a PO$\cdots$(H—N)(H—N) grouping, building $R_2^1(6)$ rings and (c) *via* a PO$\cdots$(H—N)(H—N) group, building $R_2^2(8)$ rings.
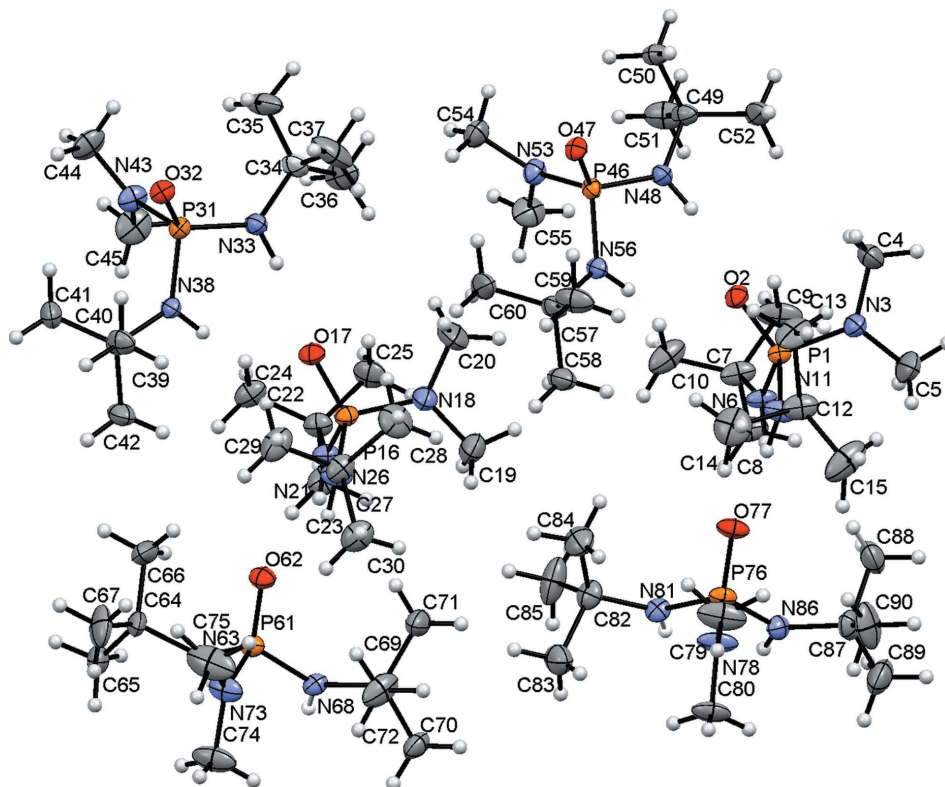
**Figure 2**
The asymmetric unit of (I), showing six independent molecules and the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The minor disordered components are not shown.

In compounds having an (N)P(O)(NH)$_2$ skeleton (six structures), three different linear arrangements were observed: (i) formed through PO···H—N hydrogen bonds, with one N—H unit not involved in hydrogen bonding (Fig. 1a) (NUVROL; Bourne *et al.*, 1998); (ii) with molecules linked by an $R_2^1(6)$ ring (Fig. 1b) (MIFYIJ; Gholivand *et al.*, 2002); (iii) formed *via* an $R_2^2(8)$ ring (Fig. 1c) (IKASAP; Sabbaghi *et al.*, 2011) [see Bernstein *et al.* (1995) for nomenclature of hydrogen-bond motifs]. In the two latter cases, with PO···(H—N)(H—N) groups, the phosphoryl O atom acts as a double hydrogen-bond acceptor.

In a compound with an (N)P(O)(NH)$_2$ skeleton, but with one additional hydrogen-bond acceptor present (nitrogen) in the substituent (pyridine) linked to the amide N atom (HIVLII; Gholivand *et al.*, 2008), the PO···H—N hydrogen bond also mediates a linear arrangement, although an intra-molecular N—H···N hydrogen bond is also found in the structure.

The molecular structure of (I), with an (N)P(O)(NH)$_2$ skeleton, is shown in Fig. 2. The asymmetric unit of (I) is composed of six independent molecules. The P atom exhibits a distorted tetrahedral environment which is reflected in its bond lengths and angles (Table 1), as has been noted for other phosphoramide derivatives (Pourayoubi, Tarahhomi *et al.*, 2011). The P=O and P—N bond lengths are comparable with those in similar compounds (IKASAP; Sabbaghi *et al.*, 2011). In the (CH$_3$)$_2$NP(O) unit, the O—P—N—C torsion angles, which reflect the orientations of the methyl groups with

respect to the phosphoryl group, are in the ranges −177.7 (4) to −168.1 (3)° and −9.5 (4) to 4.9 (4)°. Two independent one-dimensional chains are present in the extended structure, each chain containing three independent molecules. In each chain,
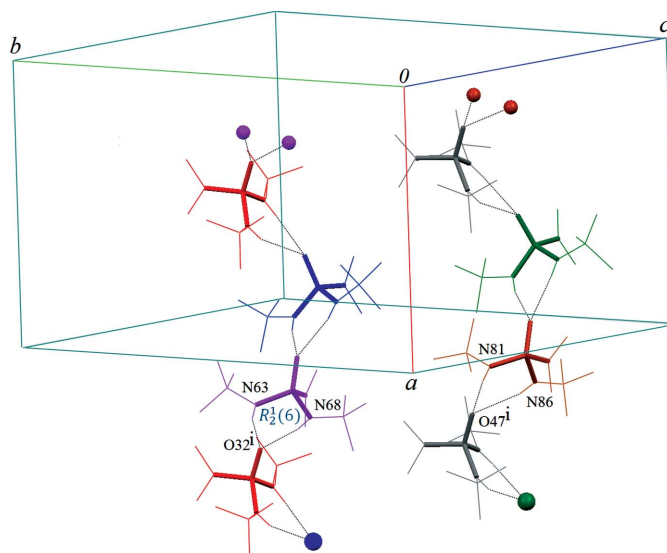


**Figure 3**
The packing in (I), showing two independent one-dimensional aggregates *via* PO···(H—N)(H—N) hydrogen bonds (dotted lines) building $R_2^1(6)$ rings. Only H atoms involved in hydrogen bonds are shown. The P(O)(N)$_3$ moieties are shown as capped sticks and the chains are extended at the sides indicated as balls. [Symmetry code: (i) $x + 1$, $y$, $z$.]
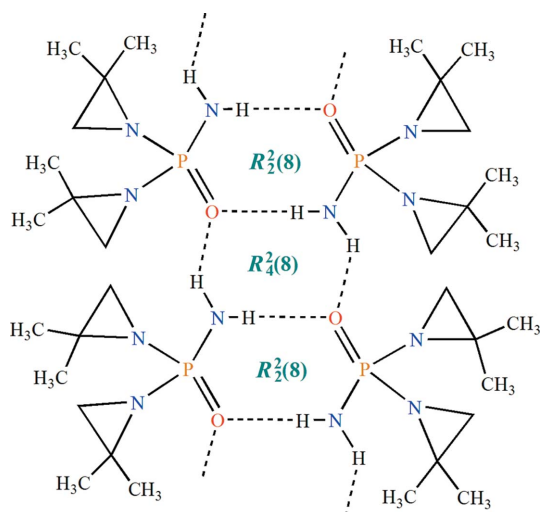
**Figure 4**
The one-dimensional ladder arrangement containing alternating $R_2^2(8)$ and $R_4^2(8)$ rings in the structure of P(O)[NH$_2$][NC$_4$H$_8$]$_2$ (Hempel *et al.*, 1999). Dashed lines indicate hydrogen bonds.

adjacent molecules are linked *via* PO···[H—N]$_2$ groups (Table 2), building $R_2^1(6)$ rings in a linear arrangement parallel to [100] (Fig. 3). In each of the independent molecules, the phosphoryl O atom acts as a double hydrogen-bond acceptor.

The hydrogen-bond pattern of a previously published structure, [CH$_3$NH]P(O)[N$_2$C$_4$H$_6$O$_2$] (DIYMED; Hutton *et al.*, 1986), is very similar to that of (I). The asymmetric unit contains four independent molecules which form two one-dimensional chains, each composed of two independent molecules.

Among the six independent molecules in the asymmetric unit of (I), five *tert*-butyl groups (of a total of 12) were found to be disordered. The relative site occupancies were refined to values in the range 0.16–0.84. Disorder in the *tert*-butyl groups was observed in some similar structures reported previously, even at low temperature (Chivers *et al.*, 2003; Gholivand, Pourayoubi *et al.*, 2005; Gholivand *et al.*, 2009).

There are two previous examples of compounds having an (N)$_2$P(O)(NH$_2$) skeleton [BIXFOE (Kattuboina & Li, 2008) and GOMDOB (Hempel *et al.*, 1999)], with hydrogen bonding mediating the formation of a one-dimensional chain for BIXFOE and a one-dimensional ladder with alternating $R_2^2(8)$ and $R_4^2(8)$ rings for GOMDOB. In the latter, the phosphoryl O atom acts as a double hydrogen-bond acceptor (Fig. 4).

The molecular structure of (II) is shown in Fig. 5. As in (I), the P atoms exhibit a distorted tetrahedral environment, with bond angles at P1 in the range 100.28 (8)–116.84 (7)°. The P=O and P—N bond lengths in (II) are as expected (Table 3). The two [(CH$_3$)$_3$CNH]$_2$P(O) units are bridged *via* an O atom [P—O—P = 126.85 (8)°]. The P1—O1 and P2—O1 bond lengths [mean value 1.619 (2) Å] are standard for the P—O—P moiety (Pourayoubi *et al.*, 2010). The bridging O atom of the P—O—P fragment does not take part in hydrogen bonding. The $R_2^2(8)$ hydrogen-bond motif of this compound, which contains an (NH$_2$)$_2$P(=O)OP(=O)(NH$_2$)$_2$ skeleton, is similar to that found for some compounds with an (N)P(=O)(NH$_2$)$_2$

core. Only one neutral molecular structure with this skeleton has been reported so far: {P(O)[NHC$_6$H$_4$(2-CH$_3$)]$_2$}$_2$O [OXPOTU (Cameron *et al.*, 1978) and OXPOTU01 (Pourayoubi, Padělková *et al.*, 2011)]. In the structure of (II), each of the phosphoryl O atoms acts as a double hydrogen-bond acceptor, but in this case it participates in one intra- and one intermolecular N—H···O hydrogen bond (Table 4), building $S(6)$ and $R_2^2(8)$ rings which are further linked into an extended chain parallel to the $c$ axis (Fig. 6). This hydrogen-bond pattern has also been observed in {P(O)[NHC$_6$H$_4$(2-CH$_3$)]$_2$}$_2$O (OXPOTU and OXPOTU01). Compounds containing an (NH$_2$)$_2$P(=O)OP(=O)(NH$_2$)$_2$ group, when crystallized as salts, show a diversity of hydrogen-bond patterns, as in the case of the hydrated salt C$_{48}$H$_{100}$N$_{14}$O$_3$P$_6{}^{2+}$·2Cl$^-$·0.5HCl·-3.5H$_2$O (GAHGAZ; Ledger *et al.*, 2010), which has a complicated hydrogen-bond pattern, because H$_2$O and Cl$^-$ are also involved.

In order to gauge the strengths of the hydrogen bonds in this family of compounds, we have examined 59 previously reported neutral molecular structures (one unavailable CIF was excluded) with the skeletons discussed in this work, and
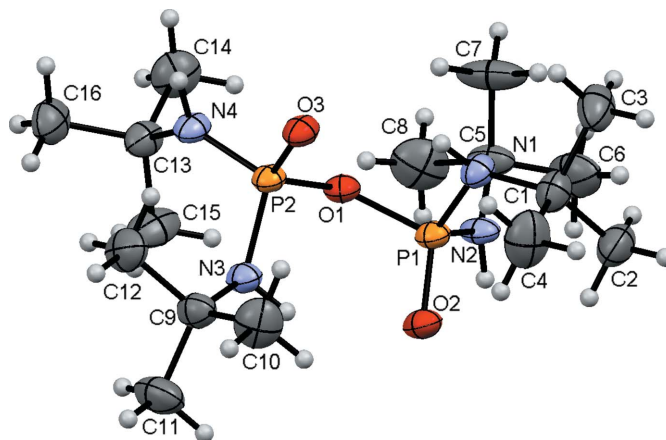


**Figure 5**
The asymmetric unit of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.
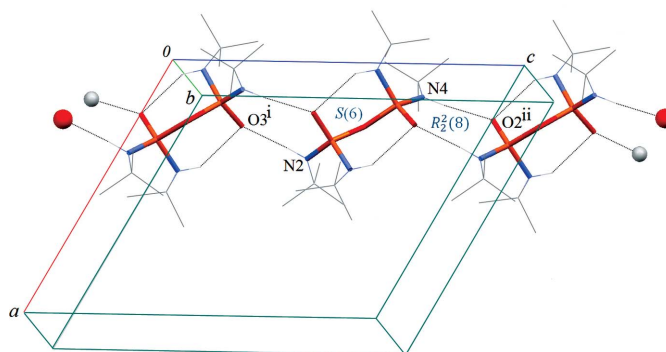


**Figure 6**
The packing in (II), with hydrogen bonds shown as dotted lines. Only H atoms involved in hydrogen bonds are shown. The (N)$_2$P(O)OP(O)(N)$_2$ moieties are shown as capped sticks and the structure is extended at the sides indicated as balls. [Symmetry codes: (i) $x$, $-y + \frac{1}{2}$, $z - \frac{1}{2}$; (ii) $x$, $-y + \frac{1}{2}$, $z + \frac{1}{2}$.]
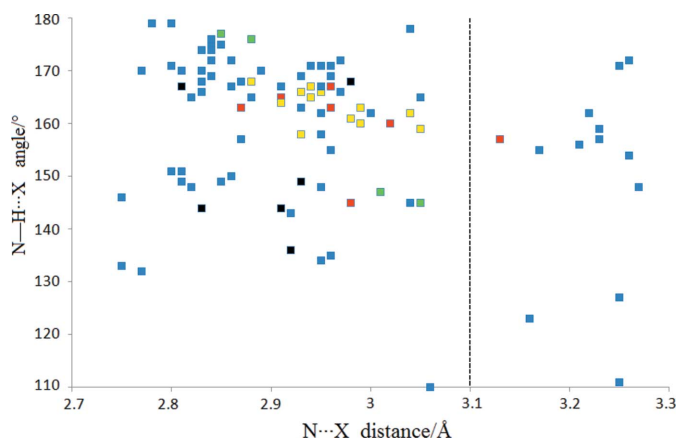
**Figure 7**
A scatter plot of N—H$\cdots X$ angles *versus* N$\cdots X$ distances ($X$ = O, N) in phosphoramides with a P(O)(NH)$_m$(N)$_{3-m}$ ($m$ = 1, 2 or 3) or (NH)$_2$-P(=O)OP(=O)(NH)$_2$ skeleton. [In the electronic version of the paper, the yellow and green squares are data from compounds (I) and (II), respectively. The other squares denote compounds with (N)P(O)(NH)$_2$ (red), (NH)$_2$P(=O)OP(=O)(NH)$_2$ (black), and P(O)(NH)$_3$ and (N)$_2$P(O)(NH) (blue) skeletons.]

also compounds containing (N)$_2$P(O)(NH) and P(O)(NH)$_3$ skeletons for comparison. A scatter plot of N—H$\cdots X$ angles *versus* N$\cdots X$ distances ($X$ = O, N) for 104 N—H$\cdots$O and N—H$\cdots$N hydrogen bonds in these compounds is shown in Fig. 7. Contacts with $D$—H$\cdots A$ angles smaller than 110° and $D\cdots A$ distances greater than 3.3 Å were not included in Fig. 7. Cocrystals and solvates were also excluded.

Double hydrogen-bond acceptor capability is also found in the structures of compounds having a P(O)(NH)$_3$ skeleton {for example, in P(O)[NHC$_6$H$_4$(4-OCH$_3$)]$_3$ (WAWNIS; Li *et al.*, 2005) and P(O)[NHCH$_2$C$_6$H$_5$]$_3$ (TOKXIB; Gholivand *et al.*, 2006)}. A four-centred P(O)$\cdots$[H—N]$_3$ unit {for example, in P(O)[NHCH$_3$]$_3$ (KABVAL; Chivers *et al.*, 2003)} has also been reported.

The data reveal weak hydrogen bonding for P(O)[NHCH$_3$]$_3$ [KABVAL (Chivers *et al.*, 2003); N$\cdots$O and N—H$\cdots$O are 2.970 (2) Å/172 (2)°, 2.961 (2) Å/155 (2)° and 3.253 (2) Å/171 (3)°]. For P(O)[NHC(CH$_3$)$_3$]$_3$ (KABVEP; Chivers *et al.*, 2003), three weak N—H$\cdots$O hydrogen bonds, in a P(O)$\cdots$[H—N]$_3$ grouping, were found: 3.255 (4) Å/111.1 (2)°, 3.159 (4) Å/123.0 (2)° and 3.294 (4) Å/93.4 (2)°; the last of these, with a low N—H$\cdots$O angle and marginal character, is not included in Fig. 7.

All data to the right of the dashed vertical line in Fig. 7 ($D\cdots A$ > 3.1 Å) are from N—H$\cdots$N and PO$\cdots$[H—N]$_x$ ($x$ = 2 or 3) assemblies. However, these types of hydrogen bonds are also found on the left-hand side of the line.

The maximum population of the distribution is found for hydrogen bonds in the region with $D\cdots A$ = 2.80–3.05 Å and $D$—H$\cdots A$ = 144–179°.

The shortest N$\cdots$O distances are found in two hydrogen bonds of [(CH$_3$)$_2$N]P(O)$Y$, where $Y$ = NHCH(C$_6$H$_5$)CH-(C$_6$H$_5$)N(C$_{10}$H$_7$) (both $D\cdots A$ = 2.75 Å), with different angles (XAVXEY; Alcock *et al.*, 2005). Also, a short distance with a relatively linear angle [2.770 (2) Å and 169.8 (1)°] occurs in

the N—H$\cdots$OP hydrogen bond of P(O)[NHC$_6$H$_4$(4-NO$_2$)]-[NC$_5$H$_9$(4-CH$_3$)]$_2$ (WALQUW; Gholivand, Shariatinia & Pourayoubi, 2005).

Interestingly, a long donor–acceptor distance [3.477 (2) Å] is observed with a nearly linear angle [171 (2)°] for the N—H$\cdots$O—(CH$_3$) hydrogen bond in P(O)[NHC$_6$H$_4$(4-OCH$_3$)]$_3$ (WAWNIS; Li *et al.*, 2005), which is not included in Fig. 7.

## Experimental

[(CH$_3$)$_2$N]P(O)Cl$_2$ was prepared according to the literature method of Gholivand *et al.* (2002).

For the preparation of (I), a solution of *tert*-butylamine (2.7 g, 37.04 mmol) in chloroform (10 ml) was added at 273 K to a solution of [(CH$_3$)$_2$N]P(O)Cl$_2$ (1.5 g, 9.26 mmol) in dry chloroform (15 ml). After stirring for 4 h, the solvent was removed in vacuo, and the product was washed with deionized water and recrystallized from chloroform–methanol (4:1 *v/v*) at room temperature.

For the preparation of (II), *tert*-butylamine (3.4 g, 46.8 mmol) was added to a solution of P(O)Cl$_3$ (1.2 g, 7.8 mmol) in dry chloroform (30 ml) at 273 K. After stirring for 4 h, the solvent was evaporated in vacuo and the product was washed with distilled water. Single crystals of (II) were obtained fortuitously from a reaction between (II), Zn(CH$_3$COO)$_2$·2H$_2$O and piperazine in CH$_3$OH under reflux, followed by slow evaporation of the filtered solution at room temperature.

### Compound (I)

*Crystal data*

| | |
|---|---|
| C$_{10}$H$_{26}$N$_3$OP | $V$ = 4406.5 (3) Å$^3$ |
| $M_r$ = 235.31 | $Z$ = 12 |
| Monoclinic, $P2_1$ | Mo $K\alpha$ radiation |
| $a$ = 12.0615 (4) Å | $\mu$ = 0.17 mm$^{-1}$ |
| $b$ = 21.2567 (7) Å | $T$ = 150 K |
| $c$ = 17.1877 (6) Å | 0.40 × 0.25 × 0.22 mm |
| $\beta$ = 90.529 (3)° | |

*Data collection*

| | |
|---|---|
| Agilent Gemini-S diffractometer with Sapphire3 detector | 29385 measured reflections |
| Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2010) | 17386 independent reflections |
| | 11821 reflections with $I$ > 2$\sigma$($I$) |
| $T_{min}$ = 0.558, $T_{max}$ = 1.000 | $R_{int}$ = 0.051 |

*Refinement*

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.061 | H-atom parameters constrained |
| $wR(F^2)$ = 0.161 | $\Delta\rho_{max}$ = 0.53 e Å$^{-3}$ |
| $S$ = 0.92 | $\Delta\rho_{min}$ = −0.57 e Å$^{-3}$ |
| 17382 reflections | Absolute structure: Flack (1983), |
| 947 parameters | with 6936 Friedel pairs |
| 207 restraints | Flack parameter: 0.00 (8) |

### Compound (II)

*Crystal data*

| | |
|---|---|
| C$_{16}$H$_{40}$N$_4$O$_3$P$_2$ | $V$ = 2412.51 (18) Å$^3$ |
| $M_r$ = 398.5 | $Z$ = 4 |
| Monoclinic, $P2_1/c$ | Cu $K\alpha$ radiation |
| $a$ = 11.3715 (4) Å | $\mu$ = 1.80 mm$^{-1}$ |
| $b$ = 17.7755 (7) Å | $T$ = 150 K |
| $c$ = 13.6956 (5) Å | 0.37 × 0.22 × 0.09 mm |
| $\beta$ = 119.371 (4)° | |

# organic compounds

## Table 1
Selected geometric parameters (Å, °) for (I).

| | | | |
|---|---|---|---|
| P1—O2 | 1.481 (3) | P46—O47 | 1.474 (3) |
| P1—N3 | 1.646 (4) | P46—N48 | 1.631 (4) |
| P1—N6 | 1.639 (3) | P46—N53 | 1.651 (4) |
| P1—N11 | 1.629 (3) | P46—N56 | 1.645 (4) |
| P16—O17 | 1.472 (3) | P61—O62 | 1.484 (3) |
| P16—N18 | 1.635 (4) | P61—N63 | 1.644 (4) |
| P16—N21 | 1.641 (3) | P61—N68 | 1.624 (3) |
| P16—N26 | 1.645 (3) | P61—N73 | 1.650 (4) |
| P31—O32 | 1.481 (3) | P76—O77 | 1.484 (3) |
| P31—N33 | 1.636 (3) | P76—N78 | 1.652 (4) |
| P31—N38 | 1.642 (3) | P76—N81 | 1.612 (3) |
| P31—N43 | 1.640 (4) | P76—N86 | 1.630 (4) |
| | | | |
| O2—P1—N3 | 106.67 (17) | O47—P46—N48 | 117.44 (17) |
| O2—P1—N6 | 115.95 (18) | O47—P46—N53 | 106.71 (17) |
| N3—P1—N6 | 110.01 (19) | N48—P46—N53 | 106.44 (19) |
| O2—P1—N11 | 117.89 (18) | O47—P46—N56 | 116.76 (18) |
| N3—P1—N11 | 106.8 (2) | N48—P46—N56 | 99.03 (17) |
| N6—P1—N11 | 99.08 (17) | N53—P46—N56 | 109.93 (19) |
| O17—P16—N18 | 106.97 (18) | O62—P61—N63 | 117.21 (18) |
| O17—P16—N21 | 117.46 (19) | O62—P61—N68 | 118.09 (18) |
| N18—P16—N21 | 108.2 (2) | N63—P61—N68 | 99.12 (17) |
| O17—P16—N26 | 116.42 (19) | O62—P61—N73 | 107.09 (19) |
| N18—P16—N26 | 107.7 (2) | N63—P61—N73 | 107.6 (2) |
| N21—P16—N26 | 99.50 (17) | N68—P61—N73 | 107.0 (2) |
| O32—P31—N33 | 116.98 (17) | O77—P76—N78 | 106.81 (17) |
| O32—P31—N38 | 117.15 (17) | O77—P76—N81 | 116.69 (18) |
| N33—P31—N38 | 99.41 (17) | N78—P76—N81 | 107.4 (2) |
| O32—P31—N43 | 105.90 (18) | O77—P76—N86 | 116.79 (18) |
| N33—P31—N43 | 108.7 (2) | N78—P76—N86 | 108.8 (2) |
| N38—P31—N43 | 108.34 (19) | N81—P76—N86 | 99.87 (16) |
| | | | |
| O77—P76—N78—C79 | 0.2 (5) | O32—P31—N43—C45 | −175.5 (4) |
| O77—P76—N78—C80 | −176.8 (4) | O32—P31—N43—C44 | 4.9 (4) |
| O2—P1—N3—C4 | −7.1 (5) | O47—P46—N53—C54 | −9.5 (4) |
| O2—P1—N3—C5 | −171.3 (5) | O47—P46—N53—C55 | −168.1 (3) |
| O17—P16—N18—C20 | 4.2 (6) | O62—P61—N73—C74 | −177.7 (4) |
| O17—P16—N18—C19 | −176.8 (4) | O62—P61—N73—C75 | 3.9 (5) |

## Table 2
Hydrogen-bond geometry (Å, °) for (I).

| $D$—H⋯$A$ | $D$—H | H⋯$A$ | $D$⋯$A$ | $D$—H⋯$A$ |
|---|---|---|---|---|
| N6—H61⋯O77 | 0.86 | 2.10 | 2.937 (9) | 165 |
| N11—H111⋯O77 | 0.85 | 2.08 | 2.911 (9) | 164 |
| N21—H211⋯O62 | 0.85 | 2.21 | 3.038 (9) | 162 |
| N26—H261⋯O62 | 0.86 | 2.11 | 2.952 (9) | 166 |
| N33—H331⋯O17 | 0.85 | 2.10 | 2.943 (9) | 167 |
| N38—H381⋯O17 | 0.87 | 2.22 | 3.046 (9) | 159 |
| N48—H481⋯O2 | 0.86 | 2.16 | 2.981 (9) | 161 |
| N56—H561⋯O2 | 0.87 | 2.10 | 2.931 (9) | 158 |
| N63—H631⋯O32$^i$ | 0.86 | 2.17 | 2.994 (9) | 160 |
| N68—H681⋯O32$^i$ | 0.86 | 2.04 | 2.884 (9) | 168 |
| N81—H811⋯O47$^i$ | 0.86 | 2.09 | 2.927 (9) | 166 |
| N86—H861⋯O47$^i$ | 0.85 | 2.16 | 2.986 (9) | 163 |

Symmetry code: (i) $x + 1, y, z$.

## Table 3
Selected geometric parameters (Å, °) for (II).

| | | | |
|---|---|---|---|
| P1—O1 | 1.6194 (16) | P2—O1 | 1.6191 (17) |
| P1—O2 | 1.4791 (12) | P2—O3 | 1.4806 (12) |
| P1—N1 | 1.6341 (14) | P2—N3 | 1.6351 (13) |
| P1—N2 | 1.609 (2) | P2—N4 | 1.6075 (18) |
| | | | |
| P1—O1—P2 | 126.85 (8) | O1—P2—O3 | 110.79 (8) |
| O1—P1—O2 | 111.38 (8) | O1—P2—N3 | 99.81 (8) |
| O1—P1—N1 | 100.28 (8) | O1—P2—N4 | 107.09 (9) |
| O1—P1—N2 | 106.84 (8) | O3—P2—N3 | 117.26 (7) |
| O2—P1—N1 | 116.84 (7) | O3—P2—N4 | 110.13 (8) |
| O2—P1—N2 | 109.89 (8) | N3—P2—N4 | 110.93 (8) |
| N1—P1—N2 | 110.86 (9) | | |
| | | | |
| O2—P1—O1—P2 | 57.79 (11) | O3—P2—O1—P1 | 59.76 (11) |
| N1—P1—O1—P2 | −66.53 (11) | N3—P2—O1—P1 | −64.50 (11) |
| N2—P1—O1—P2 | 177.81 (10) | N4—P2—O1—P1 | 179.88 (10) |

## Table 4
Hydrogen-bond geometry (Å, °) for (II).

| $D$—H⋯$A$ | $D$—H | H⋯$A$ | $D$⋯$A$ | $D$—H⋯$A$ |
|---|---|---|---|---|
| N1—H1N⋯O3 | 0.87 (3) | 2.29 (3) | 3.046 (3) | 145 (2) |
| N2—H2N⋯O3$^i$ | 0.87 (1) | 1.99 (1) | 2.8531 (19) | 177 (2) |
| N3—H3N⋯O2 | 0.87 (3) | 2.24 (3) | 3.007 (3) | 147 (2) |
| N4—H4N⋯O2$^{ii}$ | 0.87 (1) | 2.02 (1) | 2.883 (2) | 175 (2) |

Symmetry codes: (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$.

### Data collection

| | |
|---|---|
| Gemini Ultra diffractometer with Atlas detector | 15622 measured reflections |
| Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2010) $T_{min} = 0.746$, $T_{max} = 1.000$ | 4265 independent reflections 3420 reflections with $I > 3\sigma(I)$ $R_{int} = 0.033$ |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.040$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.107$ | |
| $S = 1.60$ | |
| 4265 reflections | $\Delta\rho_{max} = 0.33$ e Å$^{-3}$ |
| 238 parameters | $\Delta\rho_{min} = -0.21$ e Å$^{-3}$ |
| 4 restraints | |

For (I), all H atoms belonging to nondisordered groups were located in a difference map, but those attached to C atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry [C—H = 0.93–0.98 Å and N—H = 0.86–0.89 Å, and with $U_{iso}$(H) = 1.5$U_{eq}$(C) or 1.2$U_{eq}$(N)], after which their positions were refined with riding constraints. Geometric similarity restraints were used between the two different *tert*-butyl groups of each of the five disordered assemblies. Displacement similarity restraints were used for a number of the disordered groups in the *tert*-butyl assemblies. The occupancies of the disordered groups were initially refined,

keeping the total occupancy fixed at 1 for each assembly, until the largest ratio of the final least-squares parameter shift to the final standard uncertainty was below 0.05. Then the occupancies were fixed, accelerating the final convergence. Despite the extensive modelling of the disorder in the *tert*-butyl assemblies, the final $R$ residuals remain fairly large [$R = 0.0961$ for all reflections with $I > -3\sigma(I)$ and $R = 0.0609$ for reflections with $I > 2\sigma(I)$]. This is most probably due to additional finer unresolved and unmodelled disorder, such as in the hitherto untreated *tert*-butyl assemblies, or splitting over more than two orientational sites for the five disordered *tert*-butyl assemblies.

For (II), all H atoms were discernible in difference Fourier maps and could be refined to reasonable geometries. In accord with common practice, H atoms attached to C atoms were kept in ideal positions during the refinement, with C—H = 0.96 Å. The methyl H atoms were allowed to rotate freely about the adjacent C—C bonds.

The positions of the N-bound H atoms were restrained to 0.87 (2) Å. All H atoms were refined with $U_{iso}(H) = 1.5U_{eq}(C)$ for the methyl groups or $1.2U_{eq}(N)$ for –NH– groups.

For both compounds, data collection: *CrysAlis PRO* (Agilent, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SUPERFLIP* (Palatinus & Chapuis, 2007). Program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003) for (I); *JANA2006* (Petříček *et al.*, 2006) for (II). For both compounds, molecular graphics: *Mercury* (Macrae *et al.*, 2008). Software used to prepare material for publication: *CRYSTALS* and *enCIFer* (Allen *et al.*, 2004) for (I); *JANA2006* and *enCIFer* for (II).

## References

Agilent (2010). *CrysAlis PRO*. Agilent Technologies, Yarnton, Oxfordshire, England.

Alcock, N. W., Wills, M. & Smith, A. (2005). Private communication.

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.

Bourne, S. A., Mbianda, X. Y., Modro, T. A., Nassimbeni, L. R. & Wan, H. (1998). *J. Chem. Soc. Perkin Trans. 2*, pp. 83–88.

Cameron, T. S., Cordes, R. E. & Jackman, F. A. (1978). *Z. Naturforsch. Teil B*, **33**, 728–730.

Chivers, T., Krahn, M., Schatte, G. & Parvez, M. (2003). *Inorg. Chem.* **42**, 3994–4005.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Gholivand, K., Della Védova, C. O., Erben, M. F., Mahzouni, H. R., Shariatinia, Z. & Amiri, S. (2008). *J. Mol. Struct.* **874**, 178–186.

Gholivand, K., Mostaanzadeh, H., Koval, T., Dusek, M., Erben, M. F. & Della Védova, C. O. (2009). *Acta Cryst.* B**65**, 502–508.

Gholivand, K., Mostaanzadeh, H., Shariatinia, Z. & Oroujzadeh, N. (2006). *Main Group Chem.* **5**, 95–109.

Gholivand, K., Pourayoubi, M., Shariatinia, Z. & Molani, S. (2005). *Z. Kristallogr. New Cryst. Struct.* **220**, 387–389.

Gholivand, K., Shariatinia, Z. & Pourayoubi, M. (2005). *Z. Anorg. Allg. Chem.* **631**, 961–967.

Gholivand, K., Tadjarodi, A. & Ng, S. W. (2002). *Acta Cryst.* E**58**, o200–o201.

Hempel, A., Camerman, N., Mastropaolo, D. & Camerman, A. (1999). *Acta Cryst.* C**55**, 1173–1175.

Hutton, A. T., Modro, T. A., Niven, M. L. & Scaillet, S. (1986). *J. Chem. Soc. Perkin Trans. 2*, pp. 17–24.

Kattuboina, A. & Li, G. (2008). *Tetrahedron Lett.* **49**, 1573–1577.

Ledger, J., Boomishankar, R. & Steiner, A. (2010). *Inorg. Chem.* **49**, 3896–3904.

Li, C., Dyer, D. J., Rath, N. P. & Robinson, P. D. (2005). *Acta Cryst.* C**61**, o654–o656.

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.

Palatinus, L. & Chapuis, G. (2007). *J. Appl. Cryst.* **40**, 786–790.

Petříček, V., Dušek, M. & Palatinus, L. (2006). *JANA2006*. Institute of Physics, Praha, Czech Republic.

Pourayoubi, M., Ghadimi, S. & Ebrahimi Valmoozi, A. A. (2010). *Acta Cryst.* E**66**, o450.

Pourayoubi, M., Nečas, M. & Negari, M. (2012). *Acta Cryst.* **68**, o51–o56.

Pourayoubi, M., Padělková, Z., Rostami Chaijan, M. & Růžička, A. (2011). *Acta Cryst.* E**67**, o450–o451.

Pourayoubi, M., Tarahhomi, A., Saneei, A., Rheingold, A. L. & Golen, J. A. (2011). *Acta Cryst.* C**67**, o265–o272.

Sabbaghi, F., Pourayoubi, M., Karimi Ahmadabad, F., Azarkamanzad, Z. & Ebrahimi Valmoozi, A. A. (2011). *Acta Cryst.* E**67**, o502.